The Tanzanian Minjingu Phosphate Rock

- possibilities and limitations for direct application

Ph.D. Thesis
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Abstract

The overall objective of this study is to investigate the possibilities and limitations for using the Tanzanian phosphate rock (PR) from Minjingu as a directly applied phosphorus (P) source in Tanzanian agriculture. The investigation includes literature review, mineralogical studies of both the soft and hard Minjingu PR materials, soil chemical and mineralogical analyses, field experiments and dissolution experiments.

Based on previous experimental work, the Minjingu PR (MPR) seems to be suitable for direct application to a number of annual crops on acid, P deficient soils in humid to sub-humid areas of Tanzania. However, the need of more information on the performance of MPR under a larger range of agro-ecological conditions have led to initiation of field experiments under the Phosphate Rock Utilization Project funded by the Danish International Development Agency (DANIDA). In connection with these field experiments, a number of additional studies were started with the aim of getting more information on the utilization of MPR in agriculture.

The soils at each experimental site were studied thoroughly with respect to physical, chemical and mineralogical properties and a model for the water balance at each site were used for the evaluation of moisture stress during the growing season. Both the effect on soil properties of dissolution of the three P sources in the field during the first two seasons and the effect of soil properties on PR dissolution were evaluated. In addition, laboratory dissolution studies were conducted in order to compare MPR with other well-known PRs and to evaluate the main soil properties controlling PR dissolution.

The mineralogical studies of the soft Minjingu PR presented here, show that it is a guano-derived, highly reactive PR consisting primarily of fluorine deficient carbonate apatite besides accessory minerals such as quartz, feldspars, calcite and dolomite. The neutral ammonium citrate (NAC) solubility of 2.7% P (6.2% P_2O_5) is higher than predicted from either the X-ray diffraction derived *a*-cell value of 9.36 Å or the fluorine content. The higher reactivity is probably caused by anomalously high crystal bound carbonate content and a fraction of the PR particles having a very small crystal size. The hard Minjingu PR consists of a fluorine deficient carbonate apatite with lower contents of crystal bound carbonate and fluorine in comparison with the soft ore. The solubility in NAC is slightly lower than the soft MPR, but conforms well to the general relations between crystallographic properties and NAC solubility. The difference between the two ore types has been attributed to different genetical histories. The deposit, which contains approximately 7 Mt of soft and hard, P containing rock of varying grade, is at the present and even increased application rates sufficiently large to supply the Tanzanian agriculture with P for several decades. A beneficiation plant, present at the mine, has been operating since 1983 and a ground powdery PR product containing 13.1% P (30% P_2O_5) is commercially available from the mine. Due to the difficulties of beneficiating the MPR ore into suitable material for production of soluble P fertilizers and the lack of processing facilities locally, it is recommended that the future use of MPR only involves its utilization as directly applied P source.

Both the soft ground beneficiated product as well as a beneficiated mini-granulated derivative (GPR) is currently being compared with triple superphosphate at three levels at ten different locations in the sub-humid to humid parts of Tanzania. The P levels, based on total P content, were 40, 80 and 120 kg P ha^{-1} respectively. The experiment runs for five seasons with P application done every year in the first four seasons. Maize is used as the test crop in all seasons. Nitrogen and other possibly deficient macro and micronutrients were added as basal applications. Results from the first three seasons show that at sites with significant P effect, both MPR materials are comparable with triple superphosphate (TSP) from the second season onwards. During the first season, PR products were generally inferior to TSP indicating a reduced effect of PR-P due to the delayed dissolution of the carbonate fluorapatite mineral in the soil. Mini-granulation generally reduces the relative agronomic effectiveness in comparison with the ground product due to the decreased specific surface area of the PR particles, but the difference is pronounced only in the first season. Hence, on sites with considerable dissolution of PR due to low soil pH, low exchangeable calcium and high P retention capacity, it seems that the pool of plant available P derived from MPR after one year, is comparable with P made available through soluble P fertilizers. On sites with significant P response, maize grain yield increases due to PR application ranged from 0.4 to 4.5 t ha^{-1} at simultaneous application of high rates of nitrogen (80-120 kg N ha^{-1}) and other macro and micronutrients, which based on soil and leaf analyses were expected to be deficient.

The lack of significant P response at the majority of the sites is either explained by sufficiently high levels of plant available soil P, climatical conditions or other soil fertility constraints including high subsoil acidity, which limited the effect of P and in some cases led to high residual experimental error. A number of nutrient deficiencies including both macro and micronutrients exist on the generally highly weathered and leached soils present at the ten experimental sites. Even the younger soils developed on volcanic ash, representing only slightly weathered soils, are having severe soil fertility problems including very high P retention capacity, low amounts of available micronutrients, low nutrient holding capacity and imbalanced proportions of exchangeable base cations leading to inefficient nutrient uptake and sub-optimum yields. It is suggested that increased and sustained yields are only to be expected in the future if fertilizer based recommendations incorporate the entire range of nutrient requirements on the basis of soil analyses, leaf analyses and agronomic evaluation of the agro-ecological conditions. For that, implementation of both national analytical and agronomic advisory services and availability of a selection of compound fertilizers containing macro and micronutrients are required. In addition to soil fertility strategies, improved water management strategies are essential in areas, which in some years experience erratic rainfall patterns. The water balance studies reveal that several sites experienced severe moisture stress during the critical grain filling period but at the same time was exposed to strong leaching and runoff of several hundreds of millimetres of rain emphasizing the need of implementing measures for a better water conservation.

Dissolution of MPR was monitored in the field during the first two years. The results show that between 6 and 65% of the added PR dissolves during the growing season where the soil is moist. More than 90% of the variation in the degree of PR dissolution could be explained by the PR type (mini-granulated or ground), soil pH and P retention capacity. The more acid and the more P retentive, the higher degree of dissolution. Apparently other possible soil characteristics such as exchangeable soil acidity and Ca, acid buffer capacity or available P content did not improve the regression coefficient significantly. This indicates that immediate proton supply to, and removal of P from the dissolving PR surface through diffusion are the main limiting processes controlling the degree of PR dissolution in these soils. The absolute difference in dissolution percentage of the mini-granulated MPR was as average over the two seasons approximately 9% lower than the ground product. This was most likely due to the decrease in specific surface area of the P containing particles when granulated. There are indications that high degree of PR dissolution also leads to high relative agronomic effectiveness.

MPR addition in the field had significant effects on soil properties such as soil pH, available P, total adsorbed P, exchangeable soil acidity and Al compared to TSP treated or non-treated soils. With PR application, soil pH and exchangeable acidity was generally maintained at the same level throughout the period whereas in non-treated soils it decreased and increased respectively. Exchangeable Ca increased significantly with PR application in contrast to a significant decrease in non-treated soils and a maintained level in TSP treated soils. Both fractions of available P and adsorbed P increased with P addition in contrast to no change for the control soils.

In the laboratory dissolution experiment, dissolution of MPR and GPR was compared with two well-known phosphate rocks with varying reactivity, i.e. North Carolina (NCPR) and Central Florida (CFPR). During 120 days, dissolution of the PR materials were in the order MPR~NCPR>CFPR>GPR. Hence, mineralogical properties and granule size have a profound effect on the degree of dissolution of PR materials in these soils. Dissolution of MPR was generally comparable with the highly reactive NCPR whereas mini-granulation reduced the dissolution with a magnitude similar to the reduction in dissolution due to the mineralogical differences between NCPR and CFPR. Both the results of the analyses of the effects of soil properties on the degree of dissolution and the effect of PR dissolution on soil properties were similar to the results obtained in the field.

The radioactive hazard from the Minjingu phosphate rock is considered mainly to be related to the ambient radiation exposure around the Minjingu hill and to inhalation of the dust during mining, beneficiation, handling, transport and application. Hence, measures should be taken in order to reduce the possibilities of inhalation through improved working conditions at the Minjingu mine. Although the dissolution experiments indicate a lower dissolution of GPR compared with MPR, the field experiments indicate that GPR after two years is as effective as MPR, indicating that granulation may be a possible option for reducing the dust problems during handling, transport and application. Granulation also opens the possibility for production of compound fertilizers, which are highly needed in Tanzania. Presently, there is need of more studies into the possible long-term effects of MPR mining and application on the pathways of radionuclides from rock to humans. Information on the relative potential influence of radionuclides derived from MPR on human health compared with other natural sources is also needed.

The results presented in this thesis support the previous findings that directly applied MPR can be used as an effective P source for maize on P deficient, acid soils in the sub-humid to humid areas of Tanzania and possibly also under similar conditions in neighbouring countries. However, as the P content is lower in MPR than in most soluble P fertilizers, transport is presently a serious constraint for its use far away from the mine. It is therefore, under the present infrastructural conditions, recommended to limit utilization to areas less than approximately 1000 km from the mine. Exactly where and how MPR and GPR will be an effective substitute for TSP must be based on detailed surveys of strategically selected areas where all soil productivity constraints including soil fertility, physical and climatical characteristics must be evaluated through soil and leaf analyses and field studies. In addition, socio-economic and local production economics must also be considered before final recommendations can be developed.

Through this work, new and additional knowledge has been obtained on the:

a) chemical and mineralogical properties of both the soft and hard ore phosphates
b) distribution of areas of Tanzania suitable for direct MPR application
c) effect of mini-granulation on the relative agronomic effectiveness of MPR
d) mineralogy and nutrient status of selected Tanzanian soils
e) effect of MPR application on soil properties and the effects of soil properties on MPR dissolution.

Keywords: Tanzania, Minjingu phosphate rock, direct application, dissolution, relative agronomic effectiveness, maize, granulation, mineralogy, reactivity, fluorine deficient carbonate apatite, guano, soil moisture balance, nutrient management, micronutrients, macronutrients, soil acidity, tropical soils

Preface

The Phosphate Rock Utilization Project (PRUP), initiated in May 1998, is forming one of the five components of the Agricultural Sector Programme Support (ASPS) to Tanzania funded by DANIDA. It is a collaborative project between the Department of Soil Science at Sokoine University of Agriculture in Morogoro, Tanzania (DSSSUA), Chemistry Department at the Royal Veterinary and Agricultural University in Copenhagen, Denmark (CDRVAU), and the Tanzanian Ministry of Agriculture (MAC).

The overall development objective of the component is to enhance the phosphorus supply for the Tanzanian agriculture using the indigenous sedimentary phosphate rock from the Minjingu mine as directly applied phosphorus source. The main activities of PRUP include field experiments, which are currently being carried out, under responsibility of Prof. J.M.R. Semoka (DSSSUA), over five seasons (1998-2003) at ten locations in the more humid parts of Tanzania. The specific objective is that results from these field experiments, together with information on the agro-ecological and the socio-economic conditions, form the basis for development of recommendations for the optimum use of the phosphate rock resources from Minjingu.

Two Ph.D. research studies were financially supported under PRUP during the initial three to four years of the project. The idea was that by linking their research activities closely to the main activities in Tanzania, a synergistic effect with bi-directional flow of information and manpower could occur, and more detailed information about the agro-geological and agro-ecological aspects could be achieved. As compensation for the project's financial support, the Ph.D. students have taken significant part in main field activities including preparation, supervision, data collection, processing, interpretation and presentation of the results. Overall this has been a successful arrangement and with some modifications it could form a model for research co-operation and build up of human resources in both countries in the future.

Most of the analytical data presented here have been carried out as part of this Ph.D. study at CDRVAU under supervision of Prof. O.K. Borggaard (CDRVAU). Although this thesis forms the output of the Danish Ph.D. student, it also draws upon data, including the maize yield data, from the main field experimental activities in Tanzania.

A number of persons, to whom I am very thankful, have contributed to my work including members of the research and technical staff at DSSSUA and CDRVAU, project partners around Tanzania as well as many others who I had contact with during the course of the work.

Special acknowledgements are given to Dr. Birgitte Rønn and Dr. Per Brockhoff (Department of Mathematics, RVAU) for valuable and highly appreciated help with the statistics and for the Ph.D. course in Mixed Linear Models. Dr. Christian B. Koch (CDRVAU) for his consistent support and encouragement including suggestions and help with the mineralogical techniques as well as for his teaching in two Ph.D. courses (Soil Mineral Determination and Soil Chemistry). Prof. Niels Erik Nielsen (Department of Agricultural Science, RVAU) for his advice and comments on the field experimental results and for his teaching in the Ph.D. course in Plant Nutrition. Torsten Mandal for his critical comments on parts of the manuscript. Dr. Tonci Balic-Zunic (Department of Geology, Copenhagen University) for highly appreciated comments on the chapter on the Minjingu mineralogy. Dr. John Bailey (Department of Geology, Copenhagen University) for carrying out X-ray fluorescence determination of microelements in several of the phosphate rock samples for free. Prof. Johnson M.R. Semoka (DSSSUA) for his co-operation and friendship during my two year stay in Tanzania. My fellow Ph.D. student Mbette M. Msolla (DSSSUA) for his company and friendship both at RVAU and SUA and for the co-operation on the Minjingu mineralogy. The drivers at SUA for taking us safely nearly 100,000 km around the roads of Tanzania. Dr. Jens Peter

Møberg for introducing me to Tanzania and for his indispensable advice during the progress of the work, drawing on his long experience on tropical soils. Prof. Ole K. Borggaard for valuable supervision and for his efforts in providing and allocating additional funds for finishing the work.

At last but not at least Ingrid, Linnea and Selma, my wife and children who bore the largest part of the brunt during the last four years.

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List of abbreviations

Å	Ångstrom = 10^{-10} m
AAS	Atomic Absorption Spectroscopy
AEZ	Agro-ecological Zone
ASPS	Agricultural Sector Programme Support
AWC	Available Water Content
BP	Before present
BSe	Effective base saturation
c.p.m.	Cycles per minute
CDRVAU	Chemistry Department, Royal Veterinary and Agricultural University, Copenhagen, Denmark
CEC	Cation Exchange Capacity
CFPR	Central Florida Phosphate Rock
DANIDA	Danish International Development Agency
DCB	Dithionite Citrate Bicarbonate
DSSSUA	Department of Soil Science, Sokoine University of Agriculture, Morogoro, Tanzania
E	Extraordinary wave refractive index
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray
FES	Flame Emission Spectroscopy
FIM	Finnish Marks
FINNIDA	Finnish International Development Agency
FTIR	Fourier Transform Infrared Spectroscopy
GEOMIN	Geological and Mineralogical Department, Ministry of Mines, Bucharest, Romania
GMPR	Granulated Minjingu Phosphate Rock
GPR	Granulated Minjingu Phosphate Rock
GSA	Goldfields of South Africa Ltd.
HIM	Hydroxy interlayered minerals
IFDC	International Fertilizer Development Centre
Ig	Igabiro
JCI	Japan Consulting Institute
LSD	Least Significant Difference
Ltd.	Limited
Lu	Lubonde
Ma	Magadu
MCG	Average moisture content as % of potential AWC in critical period after tasseling
MDG	Average moisture deficit at the critical grain filling stage (first half of the period between 50% tasseling and harvest)
MD_i	Moisture deficit on day *i* of the growing season
MIPCO	Minjingu Phosphate Company Ltd.
Ml	Mlingano
Mp	Mpangala
MPR	Minjingu Phosphate Rock
Ms	Msimba
Mt	Mega tons (10^6 tons)
NAC	Neutral Ammonium Citrate
NCPR	North Carolina Phosphate Rock
Nk	Nkundi
NMR	Nuclear Magnetic Resonance
NS	Non significant
O	Ordinary wave refractive index
PDF	Portable document format
PET	Potential evapotranspiration
pF	log(cm water column)
PPR	Positive Phosphorus Response
PR	Phosphate Rock
PRUP	Phosphate Rock Utilization Project
r.p.m.	Revolutions per minute
RAE	Relative Agronomic Effectiveness
RPR	Reactive Phosphate Rocks
RVAU	Royal Veterinary and Agricultural University, Denmark
SA	Sulphate of Ammonia
Sa	Sasanda
SEAMIC	Southern and Eastern African Mineral Centre
SEM	Scanning Electron Microscopy
STAMICO	State Mining Corporation, Dodoma, Tanzania
Su	Suluti
SUA	Sokoine University of Agriculture, Morogoro, Tanzania
TEA	Total Elemental Analysis
TEM	Transmission Electron Microscopy
TFC	Tanzania Fertilizer Company

TGA	Thermo Gravimetric Analysis
TRC	Tanzania Railway Corporation
TSh.	Tanzania Shilling
TSP	Triple superphosphate
Uk	Ukiriguru
USD	United States Dollars
UTM	Universal Transversal Mercator
WRBSR	World Reference Base for Soil Resources
XRD	X-ray Diffraction
XRF	X-ray Fluorescence Spectroscopy

1 Introduction

1.1 Justification and objectives

Tanzania has, like many other sub-Saharan countries, an urgent need for development and adaptation of technologies that can counteract the present downward spiral of soil fertility decline. The continued decline in the agricultural productivity have severe consequences not only for the national economies but also for the food security of the growing populations. Technologies for nitrogen (N) replenishment have readily been developed through biological practices such as improved fallows, N-fixing crops and combinations of organic materials and inorganic N fertilizers {69}. For phosphorus, non fertilizer based technologies are normally insufficient for the replenishment of P and the low use of inorganic P fertilizers has generally caused a decline in soil P fertility throughout most of sub-Saharan Africa {252}. Since 1961 a total amount of 115,400 tons of P has been applied in Tanzania, which compared to the area with arable land and permanent crops of approximately 45,000 km^2, corresponds to an annual application of 0.6 kg P ha^{-1} {62}. The gradual soil fertility decline has effectively reduced the soil productivity and several field experiments have already shown good response to both N, P and other plant nutrients suggesting that application of inorganic fertilizers are important components for increasing the productivity of the Tanzanian agriculture {152, 218}.

Among the reasons for the low use of P fertilizers are: low cash availability, low or uncertain value-cost ratio, delay in return of investment, little appreciation among farmers of P as an important plant nutrient, and to some degree supply {176, 208, 271}. Farmers may also be discouraged by the absence of immediate response to P compared to N. In some cases response to any fertilizer fails to appear, or large initial response to both N and P resumes after a few years to original, or even declining yield levels due to induction of other nutritional constraints, or as a result of bad land management practices. Unfortunately this leads to the widespread misconception among small-scale farmers that commercial fertilizers are degrading the soil fertility.

Generally, the characteristics of the well drained tropical soils in the sub-humid to humid areas, often old highly weathered and leached Ultisols or Oxisols, intensify the soil fertility problems as both the natural fertility and the resilience properties of these soils are poor {159, 216, 221, 251, 273}. Considering these factors together, P is often a major limiting macronutrient in tropical agriculture, and due to its geochemical nature an external input is strictly necessary in order to sustain the soil fertility {108, 220}.

The use of reactive phosphate rocks (RPR) has often been suggested as one of these technologies for alleviating phosphorus deficiency in tropical agricultural systems {36, 141, 216, 221}. Throughout the tropics, direct application of highly reactive phosphate rocks have often shown to be an agronomically comparable substitute for water-soluble P fertilizers {18, 37, 48, 77, 78, 126}. Whenever RPR deposits occur locally, the countries are able to supply the region around the deposit with a low cost P fertilizer with a minimum processing requirement, reducing the country's dependency on foreign exchange for importation of P fertilizers {207}. However, most phosphate rocks have lower P contents compared to water-soluble P fertilizers such as triple superphosphate, and the transportation cost is often a constraint for the use of RPR in areas far from the source, especially in countries with poor infrastructure such as in many sub-Saharan countries {143}. Hence the use of RPR should be based on a strategic implementation in the region close to the deposit so as to optimise the economical viability of the technology.

Difficulties with handling and application of the dusty powder product whereby most RPR is marketed have also contributed to the low acceptance and direct use of phosphate rocks in tropical agriculture and methods of mini-granulation and their effects on the agronomic effectiveness should therefore be considered {25, 78, 221}. Most limiting, however, for the possibilities of widespread use of phosphate rocks in agriculture is the reactivity, an inherent property of the rock, which is difficult to change without introducing relatively costly processing techniques such as partial acidulation, thermal treatment, compaction with soluble P sources or elemental S, or by co-application with organic or inorganic materials {14, 17, 28, 37, 47, 76, 149, 151, 155}. Only fluorapatites in, which appreciable amounts of carbonate substitute phosphate in the apatite crystal structure or the more rare fluorine deficient carbonate hydroxyapatites are soluble enough in acid soils to be effective substitutes for water-soluble P sources when applied directly {141, 266}. As these highly reactive phosphate rocks are not evenly distributed around the world, the possibility of introducing RPRs on a wide scale is not realistic, but for those countries, which possess or borders good resources this technology has great outlooks.

When RPRs substitute water-soluble P sources, the need of information about the agro-ecological conditions under which the rocks will be used increases as the range of conditions where the phosphate rocks are efficient decreases compared to water-soluble P sources. Among the most important criteria for a successful utilization of RPRs are acid soils, low levels of available P and exchangeable Ca and good soil moisture {27, 75, 78, 202, 216}. Hence if RPRs are to be used intensively in tropical agriculture, identification of the most important factors determining the agronomic effectiveness of RPR in agricultural systems becomes essential. In addition, other nutritional and productivity constraints must also be considered before response to RPRs can be expected and before recommendations can be developed. As will be seen in Chapter 6 the highly weathered soils of the tropics often possess multinutritional fertility problems in addition to those of N and P. Also soil water management is another key determinant, which needs to be addressed before any sustainable agricultural production can be achieved.

The Minjingu phosphate rock is ranking among the worlds most reactive phosphate rocks and the large number of pot and field experiments carried out during the past 35 years has clearly indicated that the Minjingu phosphate rock is suitable as a directly applied P source for tropical annual crops including maize, sorghum and cotton. The literature about the Minjingu phosphate is voluminous and preliminary agronomic recommendations based on the previous work have already been given {130, 236}. However, most fieldwork has been done on a limited number of soils in a limited number of agro-ecological zones and the need of an investigation of the agronomic effectiveness of MPR over a larger range of conditions in order to improve previous recommendations was among the main objectives for the initiation of the Phosphate Rock Utilization Project funded by DANIDA {157}.

The research activities of the two Ph.D. students who were funded by and attached to the project during the first years were closely related with the activities of the main project and hence they share a number of objectives with the main project. However, a few specific objectives are distinguishable.

The objectives of this Ph.D. study are to:
1) Introduce the reader to the subject of phosphate rocks with emphasis on the mineralogy, reactivity and dissolution of apatites (Chapter 2).
2) Review the previous information about Minjingu phosphate rock including origin, chemical and mineralogical characteristics, reserve exploration, mining and beneficiation (Chapter 3).
3) Present and discuss additional mineralogical and geochemical information about the phosphate bearing rocks found at the Minjingu deposit (Chapter 4).
4) Compile and derive key relations from early and recent MPR related agronomic experimental data and evaluate the suitability for direct application of MPR in Tanzania (Chapter 5).
5) Evaluate the physical, chemical and mineralogical properties of the soils used for field experiments in the project (Chapter 6).

6) Evaluate of the role of soil properties on the dissolution of MPR in Tanzanian soils under laboratory and field conditions and the effect of PR dissolution on soil properties (Chapter 7).

Some objectives shared with the Phosphate Rock Utilization Project are:

7) Evaluation of the short-term relative agronomic effectiveness of MPR for maize under field conditions on different soils from the sub-humid parts of Tanzania (Chapter 6).
8) Evaluation of the role of climatic factors and nutrients, other than N and P, at the selected experimental sites in Tanzania (Chapter 6).

It is the aim that the information database provided through the activities in the Phosphate Rock Utilization Project form the basis for further economical feasibility studies at farm level considering other parameters like crop price, transportation costs for crops and inputs, marketing facilities, availability of cash, local farming and cropping systems, farmers skills, availability of manure or other organic or inorganic nutrient sources, use of improved varieties, climatic variation etc.

2 Phosphate rocks

2.1 Origin

The term phosphate rock may apply to any material having high enough grade and quality of phosphorus to be of economical interest as raw material for the phosphate fertilizer industry or as a directly applied phosphorus source in agriculture {25, 38, 141}. Phosphate rocks are normally produced by mining and beneficiation of rocks or sediments with phosphate minerals as major constituents. Most phosphate deposits differ from one another with respect to P content, mineralogy of the dominant P bearing mineral, texture, and content, composition and physical arrangement of accessory minerals {111}. The actual composition of a phosphate deposit is typically a result of the geological or biogeochemical conditions during formation and the post-depositional alterations such as those caused by weathering. Phosphate deposits can roughly be divided into four categories: a) Igneous, b) marine sedimentary, c) guano, and d) deposits derived from weathering of the three first categories.

Igneous phosphate deposits occur mainly as masses or sheets of intrusive alkaline hard crystalline rocks such as nepheline syenites, pyroxenites or carbonatites, with apatite content of up to 10-15% for carbonatites and up to 75% for apatite-nepheline ore bodies {188}. The largest and commercially most important igneous deposits are those of the Kola Peninsula of Russia and Palabora in South Africa {38}. The P bearing mineral of the igneous intrusives is normally fluorapatite and accessory minerals typically include quartz, calcite, micas, K-feldspars, amphiboles, pyroxenes and feldspathoids depending on the parent rock.

Marine sedimentary phosphates, normally termed phosphorites, are forming in coastal areas where upwelling ocean currents driven by trade winds are bringing previously trapped phosphorus from deep ocean waters back to the surface waters where it re-enters the biogeochemical P cycle {241}. Some of it settles in shallow waters forming a phosphatic, organic-rich sediment from which pelletal apatite under suitable diagenetic conditions accumulates. Marine phosphorites vary in age from Precambrian to Neogene and accumulations of apatites on continental shelves are still taking place today {246}. Changes in the sea level and tectonic movements during geological time have exposed large deposits of phosphorites of marine origin such as those found in northern and western Africa and eastern and western USA, some of which contain up to 6 Gt of rock with at least 13% P {38}. The phosphates of these deposits typically consist of unconsolidated beds of pellets and nodules of carbonate fluorapatites (francolites) together with clastic minerals or chemical precipitates. The accessory minerals are often quartz, hydrated and less crystallized forms of quartz (chalcedony and opal), carbonates, as well as several kinds of phyllosilicates.

Guano deposits are localized accumulations of excreta primarily produced by birds or bats. Several bat guano deposits have been found around the world in caves inhabited by bats whereas bird guano deposits typically are found along coasts and on small oceanic or inland islands where upwelling of nutrient rich water or other factors provide favourable conditions for large colonies of sea birds {90}. Cormorants, boobies and some pelican species are important guano birds as they normally feed over a large trophophoric field and deposit the majority of their droppings on the colonized area. Deposits of bird guano are normally subdivided into nitrogenous (fresh) and phosphatic (old) guano depending on nitrogen content. Fresh guano bird excreta is a semi-solid highly aqueous mixture of inorganic and organic compounds. The phosphates of fresh bird guano typically consist of carbonate hydroxyapatites (dahllites) originating from the partly digested fish bones as well as more or less soluble phosphate precipitates formed after digestion and dissolution of the bone apatites {274}. In contrast to mammalian excreta in which most of the nitrogen is present as urea, fresh bird guano contains the relatively insoluble uric acid, which soon after excretion is decomposed by microorganisms to oxalic acid, ammonia and carbon dioxide. During this process a number of highly hydrated and readily soluble, ammoniacal and alkaline phosphate, sulphate and oxalate precipitates are formed, which, depending on the geochemical and environmental conditions, eventually are lost by leaching and volatilisation leaving behind a residual accumulation of various insoluble phosphates including carbonate apatites {66, 274}. With continuous weathering a gradual transformation into the next category of deposits is normally seen (see below). Commercially the guano deposits are insignificant due to their limited size but at local scale they may act as important sources of nutrients (N, P, K, S etc.). The nitrogenous "fossil" guano deposits of some of the desert islands off the coast of Chile and Peru were among the first phosphate rocks to be exploited commercially during the first half of the 19th century {274}. Today less than 2% of the world production of phosphate rocks derives from guano related deposits.

The last category comprises deposits, which are derived from the former categories either: a) as residual accumulation of phosphate minerals above weathered phosphatic rocks or sediments or b) as phosphatized rocks where dissolved phosphate from guano or phosphatic rocks has leached down into and precipitated in the underlying rock.

Residual deposits are found in connection with several of the carbonatites from around the world and in connection with some weathered limestones in North and South America. The phosphate minerals of these deposits are mainly fluorapatite or slightly carbonate substituted fluorapatite although Ca-Al-Fe phosphates such as crandallite and millisite and Al-Fe phosphates such as wavellite and variscite may also be associated with the apatites {141}. The content and type of accessory minerals are primarily determined by the original parent rock and the degree of weathering. Primary minerals as well as secondary minerals including phyllosilicates and sesquioxides are typically found in deposits developed on alkaline igneous rocks whereas secondary silicates and carbonates are common impurities in residual deposits developed on limestone or carbonatites. Although the size of these deposits is smaller compared to the igneous and marine sedimentary deposits their economic importance can be significant due to the normally thin overburden and loose structure. Also secondary enrichment of other valuable minerals such as pyrochlore (Nb), rare earths and titanium minerals associated with the alkaline rocks as minor accessory components makes these deposits valuable.

In phosphatized rocks, various phosphate precipitates are formed according to the geochemical conditions. High activity of calcium like when the underlying rock is composed of limestone favours the formation of calcium phosphates, mainly carbonate apatites, whereas volcanic or igneous rocks may result in the formation of Ca phosphates, Ca-Al-Fe or Al-Fe phosphates depending on the degree of weathering. The most important guano derived Ca phosphate deposits are those of the Pacific coral islands of Nauru, and Ocean Island and that of Christmas Island in the Indian Ocean. Here the soluble phosphates have leached through the coral limestones and precipitated mainly as carbonate apatites. Although being richer in fluorine compared with more recent guanos they all belong to the fluorine deficient francolites {90} (see Chapter 2.2). Important Fe and Al phosphate deposits derived from guano are those of the former islands off the northeastern coast of Brazil, which consist of circular plugs of weathered alkaline igneous rocks {38}. As for the deposits derived from igneous rocks or limestone, accessory minerals vary with the underlying rock and degree of weathering.

2.2 Mineralogy

Although more than 300 different phosphate minerals have been identified, the P bearing minerals in most commercial phosphate rocks belong to the apatite group.

The basic formula and structure of the apatites can be exemplified by the igneous apatites. These are normally found as well formed crystals with a composition forming a continuous series with fluorapatite

($Ca_{10}(PO_4)_6F_2$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH_2)$) and chlorapatite ($Ca_{10}(PO_4)_6Cl_2$) as end members. The fluorapatite crystal is hexagonal with lattice parameters a=9.367 and c=6.884 Å and with one formula unit of $Ca_{10}(PO_4)_6F_2$ per unit cell {53}. The crystal structure is composed of a three-dimensional network of PO_4^{3-} tetrahedra linked together by columns parallel to the c-axis of oxygen co-ordinated Ca^{2+} ions, the so called Ca(1). The corners of each unit cell coincide with channels parallel to the c-axis occupied by the F^- ions co-ordinated by another set of Ca^{2+} ions (Ca(2)), which again are linked to the main structure through oxygen atoms {53, 246} (Figure 1). The sites occupied by F^- is normally designated the hexad sites whereas sites occupied by the P atom, tetrahedrally coordinated with four oxygen atoms, are designated the tetrahedral sites.

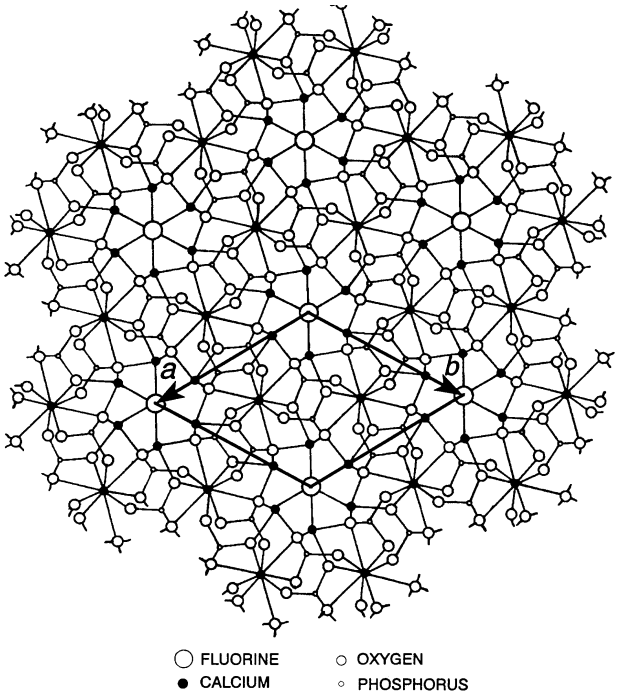


Figure 1. Projection of the fluorapatite structure on to the basal plane (0001). The c-axis is perpendicular to the plane of the paper and the a- and b-axes are as marked on the outline of a unit cell {53}.

Both igneous and sedimentary apatites generally contain various diadochic substitutions in the "open" apatite structure but in contrast to igneous apatites, the sedimentary apatites are characterized by having up to 25% of the phosphate in the so called tetrahedral sites substituted by carbonate in a 1:1 ratio (0-1.5 mol CO_3^{2-} per formula unit) {142, 179}. For carbonate fluorapatites, carbonate substitution is normally coupled with systematic substitutions of up to 6% of the Ca^{2+} by other cations such as Mg^{2+} and Na^+ and by accompanying excess fluorine in order to achieve electroneutrality {144}. If the carbonate substitution is accompanied by excess fluorine over that of fluorapatite (>2 mol F^- per formula unit) the apatite belongs to the excess fluorine francolites whereas carbonate apatites deficient in fluorine (<2 mol F^- per formula unit) belong to the fluorine deficient francolites. Dahllites are carbonate apatites poor in fluorine. Traditionally the distinction between francolites and dahllites were more or less than 1% fluorine respectively. However, a more appropriate nomenclature of carbonate apatites may relate to the ratio between the fluorine and hydroxyl content according to a 50% rule, i.e. francolites have more fluorine than hydroxyl and dahllites vice versa. The term collophane was originally thought to be a non-crystalline, amorphous phase of carbonate apatites but later it appeared from X-ray diffraction (XRD) and optical studies that they are merely sub-microscopic aggregates of cryptocrystalline apatites {66}. The isotropic nature is thought to be a result of indefenite amounts of non-structural water.

Dahllite is the principal phosphate mineral of bone material although fluorine contents up to 2% have been found in bone from cows grazing on F^- contaminated grass indicating that fluorine levels in the environment or food may influence the fluorine content of bones {53}. Under marine conditions, debris of skeletons of fish and other vertebrates have been found to undergo rapid diagenetic conversion from dahllite to francolite with fluorine contents increasing from about 0.3% to more than 3% F^- {246}. It is generally suggested that the fluorine content of most guano derived francolites has been acquired by post-depositional influence of F^- from the seawater replacing OH^- in the originally carbonate hydroxyapatitic structure {3}. Those guano deposits of avian origin, which have not been influenced by water containing F^- are generally low in F^- (<0.2%) {274}. Francolites formed under marine conditions almost exclusively include excess fluorine, which is also indicated by the dominance of excess fluorine francolites among the world marine phosphate deposits {246}.

Carbonate substitution in the tetrahedral sites in excess fluorine carbonate apatites has a significant and systematic influence on the crystallographic properties, which can be identified by changes in refractive indices and as slight lateral shifts in XRD peaks compared to fluorapatites. Crystallographic *a*-cell values calculated from XRD data range from 9.32 Å in highly substituted francolites to 9.37 Å in end member fluorapatites {49, 144, 247} (Figure 2). The corresponding negative birefringences are: O=1.634-1.613 and E=1.630-1.596 for 0% CO_2 to 8.5% CO_2 respectively {53}.

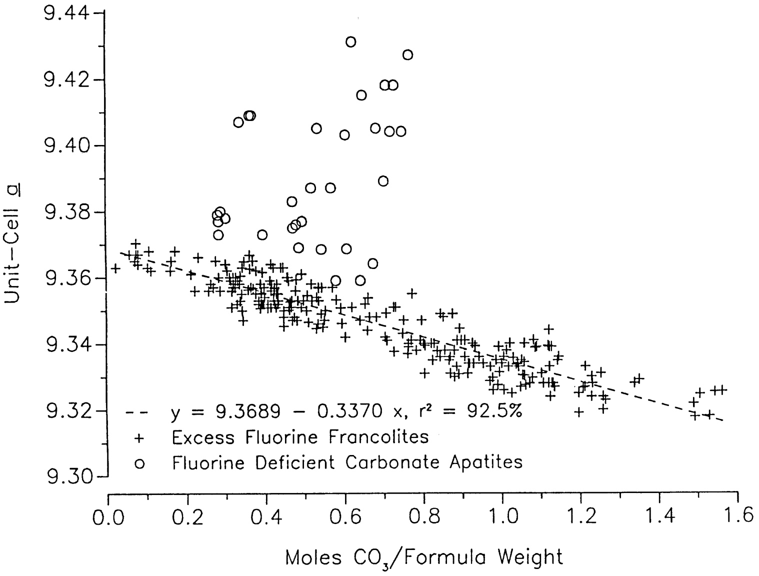


Figure 2. Correlation between crystallographic a-cell value and CO_3^{2-} in excess fluorine and fluorine deficient francolites {268}.

For the crystallographically more complex fluorine deficient carbonate apatites the relation between carbonate substitution and *a*-cell values is not clear (Figure 2) due to the possibility of simultaneous substitution by CO_3^{2-} both for PO_4^{3-} in the tetrahedral sites as well as for F^- and/or OH^- at the so called hexad sites in the channels {53, 268}. Lattice *a*-cell values typically range between 9.36 Å for the fluorine deficient carbonate apatites to 9.43 Å for carbonate hydroxyapatites (dahllites) and seem to be more correlated with fluorine than carbonate content {268} (Figure 3). In addition to the combined effect on lattice parameters of substitution with CO_3^{-2} at two different sites in the crystal structure, Ca vacancies, which have been found in biological apatites, may also influence *a*-cell dimensions and hence add another complication to the relation between *a*-cell values and carbonate substitution in fluorine deficient carbonate apatites {53}.

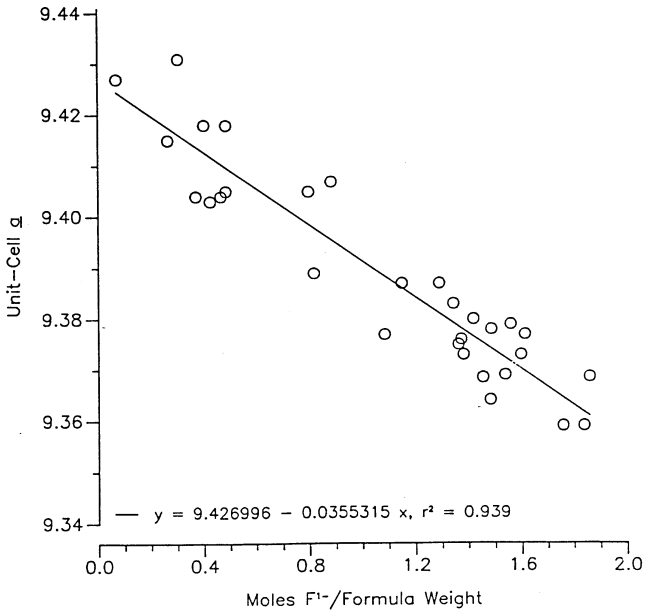


Figure 3. Correlation between crystallographic a-cell value and F^- *in fluorine deficient francolites {268}.*

The excess fluorine has been subject to much discussion since the first proposal of the linkage between CO_3^{2-} and F^- in the substitution for PO_4^{3-}. Neither the existence of a $(CO_3+F)^{-3}$ species nor the crystallographic residence of such a species has been proved yet but most studies indicate that CO_3^{2-} replaces PO_4^{3-} with the fourth oxygen site occupied by F^- or OH^- {53, 145}. From statistical analysis of a large number of sedimentary excess fluorine francolites it has been found that on average 18.5% of the CO_3^{2-} substituting for PO_4^{3-} is accompanied by F^- giving the following general formula for excess fluorine francolites {266}:

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-c}(CO_3)_cF_2F_{0.185c} \tag{1}$$

However, with Na^+ ranging on average up to 0.42 mol per unit cell for the highly carbonate substituted francolites ($a=1.25*c/(6-c)$ and $b=0.46*(c/(6-c)$ for $c=0$ -> 1.51) it seems that Na^+ together with excess F^- are not able to compensate entirely for the decrease in negative charge caused by CO_3^{2-} for PO_4^{3-} substitution, and according to model (1) above, the surplus positive charge increases with increasing carbonate substitution. Based on data from unaltered francolites such as those found on the sea floor, McArthur {140} conclude that PO_4^{3-} is substituted by $(CO_3^{2-}+F^-)$ in a 1:1 ratio and argues that this substitution must be coupled with substitution of hexad F^- with OH^- or else the 1:1 ratio would not be seen. The presence of OH^- has been proved by IR spectroscopy in fluorine deficient francolites but McArthur suggests that this may also be the case for at least the unaltered francolites from the sea floor. He suggests that formula (1) is reformulated to:

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-c}(CO_3)_cF_cF.OH. \tag{2}$$

where F. and OH. signify structural F^- and OH^- in the hexad sites and F_c excess F^- accompanying CO_3^{2-} in the tetrahedral sites. How exactly the $(CO_3^{2-}+F^-)$ is configured in the crystal remains unknown.

Increased carbonate substitution is also considered responsible for the generally smaller crystal sizes of sedimentary apatites compared with the crystalline fluorapatites of igneous origin. Substitution of the tetrahedral PO_4^{3-} with the planar CO_3^{2-} or the suggested distorted $(CO_3+F)^{-3}$ tetrahedra is likely to develop structural incompabilities, which limit the number of unit-cell repetitions that are possible before the structural misfit prevents further growth of the individual crystallites {49, 142, 144}. The combination of small crystallites and the destabilization of the apatite structure has a very important practical implication as the solubility of excess fluorine francolites in dilute acids (e.g. neutral ammonium citrate, NAC) and soils, increases with increasing carbonate substitution (Figure 4) {4, 25, 141, 268}. As carbonate substitution in excess fluorine francolites as shown in Figure 2 is negatively correlated with *a*-cell dimensions, simple XRD analyses are normally very valuable as preliminary indicators on mineralogy and solubility and hence suitability of unknown phosphate rocks for direct application to soils {111, 268}.

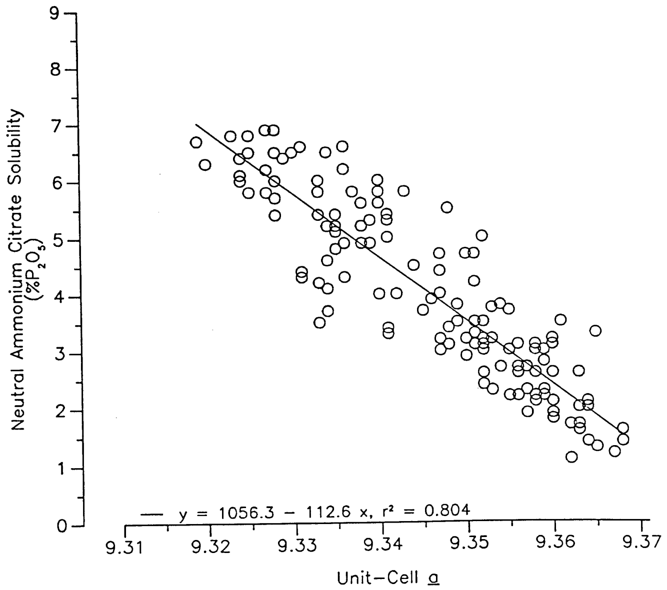


Figure 4. Correlation between solubility in neutral ammonium citrate and a-cell value for excess fluorine francolites {268}.

In contrast to the excess fluorine francolites it seems that the solubility of the fluorine deficient francolites in NAC irrespectively of carbonate substitution increases with increasing *a*-cell dimensions and decreasing fluorine content corresponding to a higher OH^- content {266, 268} (Figure 5 and Figure 6).

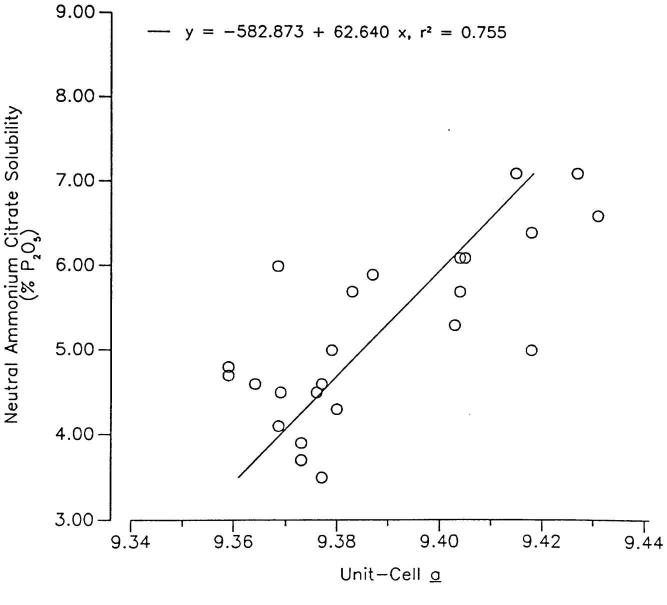


Figure 5. Correlation between solubility in neutral ammonium citrate and a-cell value for fluorine deficient francolites {268}.

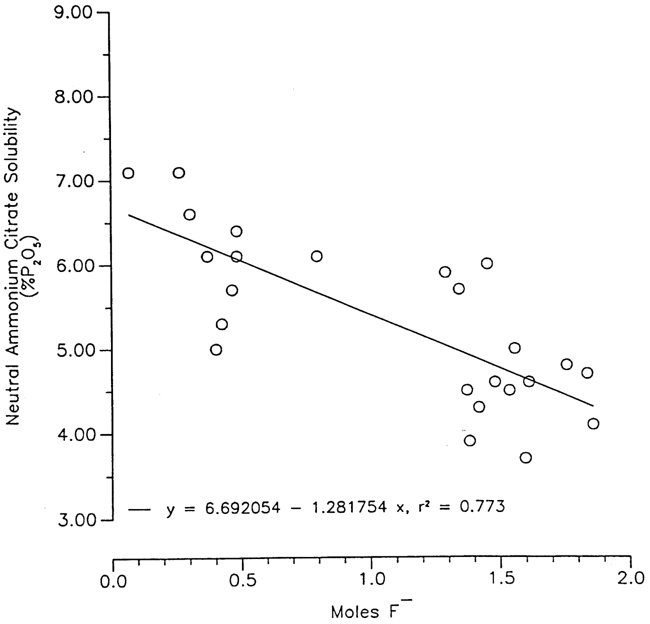


Figure 6. Correlation between solubility in neutral ammonium citrate and F^- content for fluorine deficient francolites {268}.

Based on thermodynamic calculations, Chien {41} found that the free energy of reaction for the dissolution of francolites in dilute acids increases as the CO_3^{2-} for PO_4^{3-} or OH^- for F^- substitution increases. Hence, this may also help explaining the increased solubility of excess fluorine francolites with increasing carbonate substitution and the increased solubility of fluorine deficient francolites and dahllites with decreasing fluorine content.

Other common isomorphic substitutions in francolites include Ba^{2+}, Sr^{2+}, K^+ and U^{4+} for Ca^{2+} and SO_4^{2-} and SiO_4^{4-} for PO_4^{3-} {246}. If any of these substitutions are significant components of the carbonate apatites one would expect deviations from the general relationships developed for the francolites due to differences in ionic radii and/or charge of the substituting ions.

The degree of carbonate substitution in apatites has traditionally been determined by wet chemical procedures after selective removal of free calcite with triammonium citrate at pH 8.1 (Silvermann's solution) {244}. However, the method is not applicable for phosphorites containing less soluble carbonates such as dolomite, and Schuffert et al. {231} developed on the basis of a suite of synthetic carbonate substituted francolites an empirical equation relating the carbonate substitution with XRD derived peak pair differences ($\Delta 2\theta$ for the (004) and (410) or (300) and (002) reflections respectively). Data from natural non-dolomitic francolites in which carbonate content were determined traditionally agreed closely with the equation indicating that carbonate substitution in natural francolites can be estimated fairly well from high resolution XRD diagrams independently of accessory minerals. Estimation of carbonate substitution using infrared spectroscopy suffer from the same problems as direct chemical determination but for non-dolomitic phosphate rocks empirical correlations between *a*-cell values and the CO_2-index have been derived from IR spectra {141}.

2.3 Reactivity and solubility of phosphate rocks

Rajan et al. {202} defined PR reactivity as the combination of PR properties that determines the rate of dissolution of the PR in a given soil under given field conditions. According to this definition reactivity is a kinetic property of the PR and does not include effects of soils, plants and management practices although they may have a profound and sometimes interacting effect on the rate of dissolution. PR reactivity is preferably determined from the amount of PR, which has dissolved during a given time in a soil where equilibrium conditions have not yet been met. However, as the measurement of the rate and degree of dissolution of a PR in a given soil under field conditions is laborious, several alternative methods have been proposed and used to estimate PR reactivity including laboratory and pot dissolution experiments, empirical methods such as dissolution in dilute acid solutions {42, 44} and measurement of crystal unit cell dimensions {268} (Chapter 2.2).

The definition of PR reactivity is useful when comparing the relative reactivity of a number of PRs added to a given soil suitable for using PRs. Hence, screening PRs this way enables identification and selection of the most suitable PRs for direct application and quite often good correlation has been found between the agronomic performance of a range of PRs and their reactivity determined either as the amount dissolved during a specific period of time or estimated from empirical equations {4, 44, 46, 126, 134, 201}.

After selection of the most suitable PR, next step is to evaluate how a particular PR performs under different soil-plant conditions and correlations between factors that influence PR dissolution and the agronomic performance such as soil properties are often important components in the process of making fertilizer recommendations based on PRs.

2.3.1 Determination of PR dissolution

Several analytical methods have been developed to determine the dissolution of PR, mainly in non-calcareous soils {78, 202}. Dissolution is normally measured either:

a) indirectly by determination of the amounts of reaction products released during dissolution or
b) by direct determination of the residual non-dissolved PR.

Both methods require a non-treated control soil to which the increase in reaction products or residual PR is related. If PR dissolution is determined under field conditions and not in closed systems, difficulties may arise from estimation of the amount of PR added to the soil and from the removal of reaction products through uptake, leaching or erosion. Hence, exact estimates of depth of incorporation, bulk density, removal of reaction products, evenness of application as well as representative sampling becomes important when collecting soil samples in the field and converting the amount applied per hectare to corresponding amounts in the surface horizon.

Reaction products

The indirect method involves measurement of the increase in extractable P or exchangeable Ca over that of the non-treated control and its relation to the amount of PR-P or PR-Ca added, i.e. ΔP or ΔCa divided by the total P or Ca added through the PR. Both methods assume that:

a) all P and Ca respectively, released by the dissolution is retained by the soil and is subsequently extracted from the soil by the selected extraction method and
b) only negligible amounts of non-dissolved PR will dissolve during extraction.

The first assumption that reaction products are retained may be fulfilled in most situations as the P adsorption capacity and Ca exchange capacity in most soils is higher than the amounts normally applied. Whether the reaction products are entirely removed during extraction without additional PR dissolution has been investigated in detail {202}. The main suggestions are that PR dissolution based on the increase in sorbed P is best estimated by a two step sequential extraction involving an initial removal of exchangeable Ca by a buffered solution of NaCl, $BaCl_2$ or EDTA followed by extraction with dilute NaOH removing all adsorbed phosphate {202}. Removal of exchangeable Ca is considered necessary in order to avoid precipitation of Ca-phosphates during the following alkaline extraction step and buffering have been found to reduce dissolution of non-dissolved PR during extraction in acid soils containing significant amounts of exchangeable acidity, which otherwise could cause additional PR dissolution when released to the extracting solution {23, 88, 197, 253}. NaOH have been found to extract negligible amounts of non-dissolved PR but most NaOH extracts are highly coloured by dissolved organic matter, which may interfere with the molybdenum blue method when measuring phosphorus {39}. Hence, acidification of the extract in order to precipitate the organic acids followed by centrifugation or complete oxidation of the dissolved organic matter may be required before phosphorus measurement.

The ΔCa method assumes in addition to those of the ΔP method:

a) congruent dissolution of the PR material releasing both P and Ca at similar rates and
b) no preferential dissolution of other accessory Ca minerals such as free carbonates.

Estimation of exchangeable Ca can be achieved using standard techniques such as neutral 1 M NH_4-acetate {88, 202}. The assumption about congruent dissolution seems most likely in case of carbonate fluorapatites as the entire apatite structure breaks down during dissolution. For less reactive carbonate fluorapatites containing significant free carbonates the second assumption may not be fulfilled due to the differences in solubility between the apatite and the free carbonates {22, 244}. Hence the ΔCa method should be restricted to highly reactive non-calcareous PRs.

Residual PR

The method of direct estimation of residual P requires sequential P extraction where the final step typically involves a strong dilute acid in order to dissolve any remaining non-dissolved P compound. The increase in residual P compared to the non-treated control divided by the total amount of P added estimates the amount of non-dissolved PR. The assumptions are that:

a) all reaction products released during dissolution have been removed before the final acid extraction and
b) only negligible amounts of non-dissolved PR will dissolve before the final step and
c) the final acid extraction is able to extract all the non-dissolved P bearing minerals.

This method is similar to the indirect method except that one or two additional extraction steps are included, e.g. a dithionite-citrate-bicarbonate (DCB) extraction and a final extraction with a strong dilute acid. The increase in DCB extractable P has generally been found to be insignificant in most short time dissolution studies and the step can normally be omitted. However, as DCB extractable P represent strongly adsorbed P within the interior of sesquioxides (occluded P), inclusion of this step may be relevant in long term dissolution studies where occlusion of released P may occur. The assumptions that all reaction products are removed prior to the final step and that negligible amounts of non-dissolved PR dissolves during extraction follows the same argumentation as with the indirect method. Dissolution of non-dissolved PR during DCB extraction is normally considered insignificant due to the bicarbonate buffered pH of the extracting solution {148}. The assumption that the final acid extraction removes all non-dissolved PR were found to hold for 0.5 M H_2SO_4 whereas HCl up to 4 M seemed to be insufficient in some soils {255}. However, if the DCB step is omitted, the final acid step may not represent total extractable P, as only a part of the occluded P will be released in highly weathered soils containing significant amounts of sesquioxides {39}.

2.3.2 Empirical methods

Most empirical estimates of PR reactivity are based on dissolution in dilute acid solutions. For the carbonate apatites the most widespread are neutral ammonium citrate, 2% citric acid and 2% formic acid, but other methods such as absolute citrate solubility or acid or alkaline ammonium citrate have also been used {25, 42, 43}. However, a number of factors influence the measurements including mineralogical and physical characteristics of the PR and the PR solubility expression.

The influence of PR mineralogy on solubility were outlined in Chapter 2.2 where especially the degree of carbonate substitution, fluorine content and crystallite size of are the main factors influencing the reactivity of the francolites. Igneous PRs normally having larger non-porous crystals are expected to have lower solubility than sedimentary apatites irrespective of fluorine content. Accessory minerals such as free carbonates may suppress the solubility especially in NAC and dilute citric acid as a result of excess neutralisation of the extracting reagent and it is often recommended to determine P in a second extract rather than in the first {44}. Cementing minerals such as accessory silica and clays may also reduce PR solubility as the area of acid attack is reduced. In addition, particle size distribution of the PR may influence the solubility due to the increased specific surface area so that decreasing particle size normally increases solubility {42, 117, 118}. It has been found that the PR solubility is more or less constant irrespective of PR grade and solubility should preferably be expressed as % of rock and not as % of total P as the latter normally increases with decreasing grade giving misleading impression of PR reactivity {42}. Solubility of non-apatitic minerals such as Fe and Al phosphates or modified PRs such as calcined carbonate apatites or partial acidulated PRs should normally be interpreted differently than for the francolites despite using the same extractants {43}.

2.3.3 Factors affecting PR dissolution in soil

PR dissolution in soils is influenced by a number of reactions as illustrated in Figure 7. Basically PR dissolution is a question of sufficient proton supply to the PR mineral surface and a correspondingly sufficient removal of reaction products away from the same surface {78, 216}. One can think of a push or pull effect according to the law of mass balance where a sufficient source of acidity and a sufficient sink of reaction products enhance dissolution. However, the two actions must occur coincidently or else the general thermodynamic laws will prevent further dissolution. As all soluble reactants and products must enter the soil solution on the way to and from the PR mineral surface, PR dissolution is strongly governed by the processes controlling solute movement in the soil, i.e. diffusion and mass flow and processes controlling the exchange of elements between the soil solution and soil solids, organic matter or plants, i.e. sorption, ion exchange, precipitation, or interaction with soil organic matter or plants. An understanding of the rate limiting or rate determining reactions in Figure 7 is essential, as they will determine the overall rate of PR dissolution.

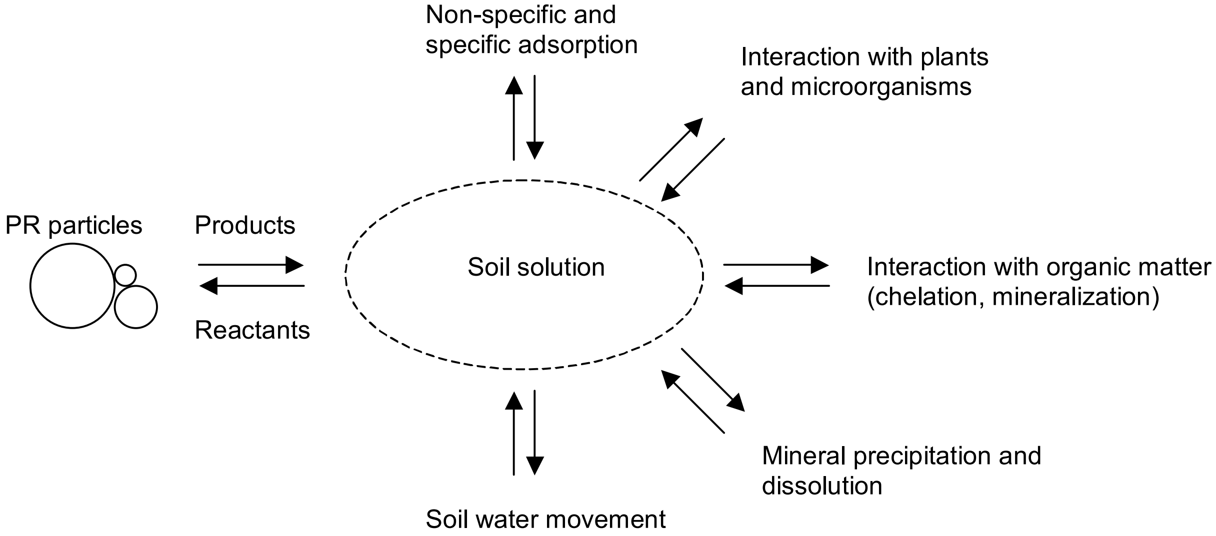


Figure 7. Illustration of the reactions influencing PR dissolution.

Among the factors influencing the PR-solution interphase is apatite crystal size and PR particle size, which were discussed above. The larger the contact between the PR mineral and the soil solution, the larger the area available for solute movement will be. Hence, soil moisture becomes a very significant determinant for PR dissolution due to its effect on the flux of ions across the solid-solution interphase by diffusion. Diffusion is the net movement of an element or gas from a region of high chemical potential to a region with lower chemical potential with the gradient in the chemical potential acting as the driving force and so differences in concentration between the film surrounding the PR particle and the soil solution becomes important. As soil moisture decreases, the pathway through water filled soil pores increases and hence solute movement by diffusion decreases dramatically {258}. As the rate of most of the reactions between solutes present in the bulk soil solution and the various sinks are high compared with diffusion, the rate limiting step for PR dissolution seems to be diffusion of reactants and products to and from the mineral surface {258}. However, in some situations, such as in the field, mass flow, induced by rain or water uptake by plants, may also contribute to solute movement and hence increase PR dissolution {216}.

Exchangeable acidity and Ca^{2+}

Soil solution acidity in the short term and exchangeable acidity in the long term are the primary sources of protons required for PR dissolution. Hence, the more acid the soil solution is and the more exchangeable acidity is present in the soil the higher potential PR dissolution. The role of soil pH and exchangeable acidity has been confirmed by numerous dissolution experiments {105-107, 123, 202, 203} and among the various soil and plant factors evaluated by Kirk and Nye {118} soil pH seems to play a dominant role for PR dissolution. The effect of high soil acidity may also have an indirect effect on PR dissolution through an increased P sorption capacity and normally low exchangeable Ca^{2+} levels {24, 133}. The H^+ buffer capacity, defined as the amount of base required to increase the soil pH by one unit, has often been used as an estimate of the capacity of a particular soil to release acidity or to buffer the released alkalinity during dissolution {205}. The influence of H^+ buffer capacity or exchangeable acidity on PR dissolution may depend on the type and amount of PR applied and on the content of accessory minerals such as calcite. If the amount of exchangeable acidity exceeds the amount required to obtain complete PR dissolution the effect of increasing amounts of exchangeable acidity may not be seen {205}. At higher pH, PR dissolution increases with increasing levels of exchangeable acidity.

Soil solution concentration of Ca^{2+} have been found to be of major importance for PR dissolution through the effect on Ca^{2+} diffusion from the mineral surface to the soil solution {118}. As the Ca^{2+} soil solution concentration is largely controlled by cation exchange reactions with the soil solids, Ca^{2+} saturation, i.e. the amount of CEC available for Ca^{2+}, has in many studies proved to be determining for PR dissolution {133, 135, 203, 204}. In analogy with H^+ buffer capacity, the use of Ca^{2+} buffer capacity, i.e. the slope of the curve relating exchangeable Ca^{2+} to Ca^{2+} in the soil solution has been proposed as a suitable measure for the size of the Ca^{2+} sink in the soil {202}.

P sorption

The soil solution concentration of P is generally much lower than Ca^{2+} leading to a high concentration gradient between the mineral surface and the soil solution. Hence, compared with Ca^{2+}, diffusion of P into the soil solution does normally not limit the rate of PR dissolution, which was also indicated by the sensitivity analysis by Kirk and Nye {118}. However, several analyses have shown that increasing P sorption capacity is positively correlated with PR dissolution {105, 107, 135, 203, 248}. It may not be P sorption capacity per se, which influence dissolution but rather the P buffer capacity, or P affinity, which is normally correlated with the P sorption capacity. The P buffer capacity has been estimated as the slope of the linear part of the curve relating sorbed P to equilibrium P concentration.

Mineral precipitation

Depending on the solubility product constants of soil minerals and on the concentration of the various elements in the soil solution, mineral precipitation reactions may also contribute to the removal of reactions products from the soil solution during PR dissolution. For instance, at low soil pH, F^- released during PR dissolution could partly be sorbed to sesquioxides like P and partly precipitate as AlF_3. At higher pH the concentration of F^- in the soil solution may be controlled by fluorite (CaF_2) {54}. Hence, the influence of soil solution concentration of F^- is generally considered insignificant compared to those of Ca^{2+} and P {205}.

Leaching and interaction with plants

Depending on rate of PR application, type of plant species, removal of plant products and surplus precipitation, plant uptake and leaching will more or less effectively remove reaction products from the soil and soil solution {79}. However, leaching of P will probably be insignificant compared to Ca^{2+}. Plants may also contribute significantly to the PR dissolution by rhizosphere processes including acidification and chelation or by taking up large amounts of Ca^{2+} {16, 48, 64, 85}. Depending on the cation and anion balance during nutrient uptake, plants species such as many legumes or plants feeding primarily on NH_4^+ may exudate protons, which acidify the rhizosphere and thereby supply protons for further PR dissolution {1}. Hence, at more neutral soils with little proton supply, rhizosphere processes may become determining for PR dissolution and agronomic effectiveness. Also mycorrhizal fungi may provide more effective removal of P from the soil and thereby enhance dissolution.

Organic matter

Microbial decomposition of soil organic matter may have significant effect on PR dissolution through the effect of proton supply and chelation by organic acids released during mineralization {14, 26, 92}. It may also indirectly increase PR dissolution by increasing the CEC and Ca-buffer capacity of the soils {202}. On the other hand, application of manure may due to the relatively high Ca contents, high pH and high proton buffering capacity reduce PR dissolution {136}.

3 The Minjingu phosphate rock

3.1 Background

The Minjingu phosphate deposit situated in the northern Tanzania was discovered by Goldfields of South Africa Ltd. (GSA) in July 1956 when an aerial geophysical and scintillometric survey showed a radioactive anomaly at the small Minjingu Hill, which rises above the plains of the Eastern Rift Valley (Figure 8) {264}.

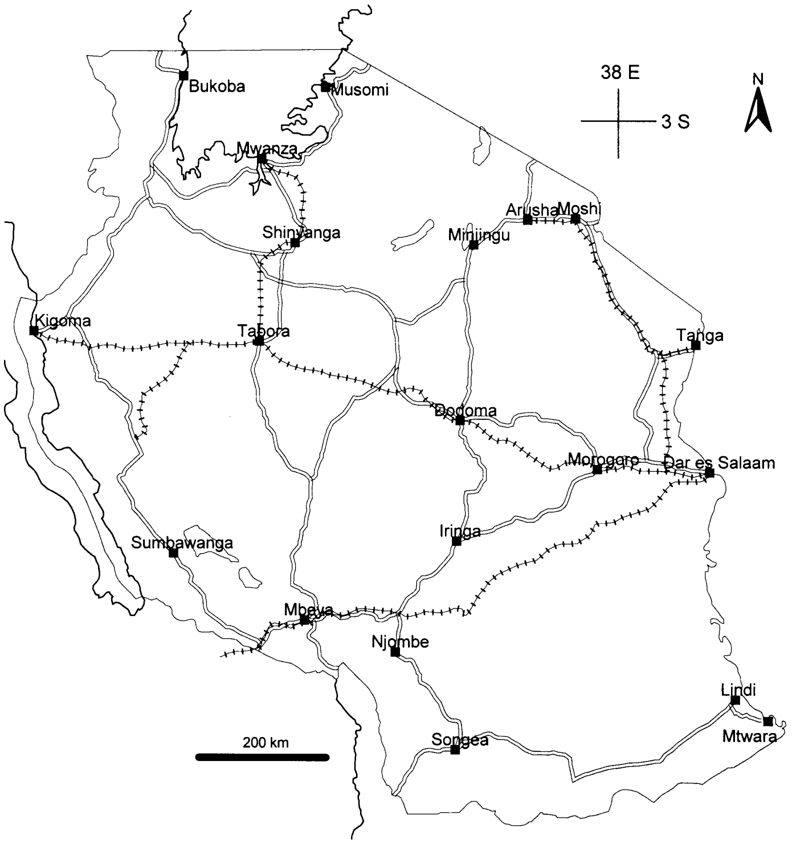


Figure 8. Map of Tanzania with major roads and railway system.

Field surveys carried out soon after revealed that the deposit consisted of guano-derived phosphorus bearing rocks and sediments of varying consistency and fabric. After detailed pitting, drilling and trenching surveys during the period from 1957 to 1959 the total ore reserve was estimated to 4.4 Mt of porous, friable, fine grained phosphate ore, and 4.5 Mt of hard and semi-hard, conglomeratic phosphate ore, totally averaging 8.7% P (20% P_2O_5) {185} (see also Chapter 3.3). Material from the soft ore was collected for preliminary agronomic tests, which indicated that directly applied phosphate rock was as effective as superphosphate produced from the same material, and that it performed better than a directly applied Moroccan phosphate rock {71}. Despite these early indications of the high agronomic effectiveness of directly applied Minjingu phosphate rock, the geological and economical appraisals in the following years exclusively considered the utilization of the Minjingu phosphates as raw material for the production of soluble phosphate fertilizers. In the early seventies the supply of phosphate rock for the newly build fertilizer factory in Tanga in northeastern Tanzania was the main objective for the development of a phosphate mine.

3.1.1 The Finnish Minjingu Phosphate Project

A number of international consulting firms and local authorities including the State Mining Corporation (STAMICO), reassessed during the 1960's and 1970's the first survey carried out by GSA, and conducted further geological ore reserve appraisals, technological and mineral dressing tests and identified mining and processing input requirements in order to evaluate the feasibility of a phosphate mine {68, 97, 120, 146, 162, 175, 264}. Exploitation of natural indigenous resources for national agricultural needs, saving of foreign currency through import substitution and employment opportunities were among the most important national objectives for the phosphate mining project. As both Klöckner Ltd. and Kemira Ltd. who carried out feasibility studies emphasized a high capital:output ratio and a low profitability, several international donor organizations were approached in order to reduce loan costs. In 1979, after negotiations with various contractors, the Finnish KONE Ltd. was selected to deliver the mining and beneficiation plant on a turn-key basis using financial aid from the Finnish International Development Assistance (FINNIDA) {32, 200}. A new parastatal Minjingu Phosphate Company (MIPCO) functioning under STAMICO was established. MIPCO was responsible for the mining operations, the beneficiation process, and the transport and loading of the material into railway wagons in Arusha. The material was then transported by Tanzania Railway Corporation (TRC) to Tanga and used for domestic production of soluble superphosphates by the Tanzania Fertilizer Company (TFC) at the fertilizer factory in Tanga. A five-year training and technical assistance programme was included for the management and transfer of operational know-how from KONE to MIPCO. The initial Finnish aid was 63 mill. FIM for the mine and plant and 17 mill. FIM for the five-year technical assistance programme. Later the Finnish aid continued through four phases of technical assistance up to 1991 with another 33 mill. FIM giving a total grant of 113 mill. FIM (approx. 25 mill. USD) for the Minjingu Phosphate Project {200}. During the period from 1983 to 1991 a total of 133,900 tons of concentrate was produced of which 87% was used by TFC for production of inorganic phosphate fertilizers in Tanga (Table 1).

Table 1. Stripping, mining, production and sales of Minjingu phosphates (1983-2001).

Year	Stripping (tons)	Mining (tons)	Production (tons)	Sales (tons)			
				TFC	Direct application	Export	Total
1983	62,000	39,000	20,000	18,100	-	-	18,100
1984	105,000	22,000	14,000	14,500	-	-	14,500
1985	103,000	56,000	21,000	21,200	-	-	21,200
1986	55,000	8,000	10,000	11,300	-	-	11,300
1987	15,000	41,000	18,400	17,500	660	-	18,160
1988	31,000	30,000	14,700	10,700	200	2,000	12,900
1989	3,000	13,000	8,300	4,400	200	2,900	7,500
1990	17,000	48,000	25,000	19,200	560	3,700	23,460
1991	6,000	2,000	2,500	-	960	640	1,600
1992	NE	700	4,500	-	3,900	500	4,400
1993	NE	-	2,200	-	4,100	100	4,200
1994	NE	400	1,100	-	500	600	1,100
1995	NE	2,200	960	-	500	600	1,100
1996	NE	1,400	730	-	480	300	780
1997	NE	3,300	1,800	-	1,000	1,300	2,300
1998	NE	3,100	1,400	-	500	1,300	1,800
1999	NE	10,800	6,100	-	300	5,800	6,100
2000	NE	15,200	6,900	-	100	6,600	6,700
2001	NE	NE	900	-	100	500	600
Totals							
1983-1991	397,000	259,000	133,900	116,900	2,580	9,240	128,720
1992-2001	NE	37,100	26,590	-	11,480	17,600	29,080
1983-2001	NE	NE	160,490	116,900	NE	26,840	157,800

NE: Not estimated. Source: Mwambete, I., personal communication (2000) and {130, 200}.
TFC: Tanzanian Fertilizer Company (used for production of phosphate fertilizers at the factory in Tanga).

The figures indicate that the potential production capacity of 100,000 tons of concentrate per year from the annual mining of 165,000 tons of ore was never met. The reasons for the low performance were multiple but mainly external to the mine and plant. Largest constraints were that the assumptions concerning the demand from TFC never came true mainly due to technical processing problems and lack of inputs at the fertilizer factory in Tanga {8, 32, 200}. The factory was constructed in 1971-72 but by the early 1980's the plant was already in poor condition and needed rehabilitation in order to produce fertilizers. Apparently the Minjingu concentrate was both economically and technically inferior to Moroccan and Jordanian phosphate rocks, which had previously been used by TFC and the recovery rate and quality of the fertilizer was low {112}. Phosphate rock consumption by the Tanga factory never exceeded 20-30% of the designed capacity of 100,000 tons per year throughout the entire operational life. As TFC was MIPCO's largest and almost only customer the performance of MIPCO was obviously very sensitive to the performance of TFC.

The transport of the material first 105 km by truck to Arusha and later 435 km by rail to Tanga also proved to be much more problematic than originally assumed mainly due to bad roads causing technical failure and a railway line, which was not capable of hauling the volumes planned. In some cases entire wagons disappeared on the way to Tanga. Ironically, very costly improvements such as construction of the present Minjingu-Arusha bitumen road and importation of new wagons by TRC for the haulage of the phosphate were implemented the same year as the fertilizer production in Tanga came to an end and production of phosphate concentrate also almost stopped (Table 1). In 1990, the acid tower of the fertilizer factory collapsed causing an indefinitely termination of the production of soluble phosphates in Tanga. As MIPCO failed to find major alternative channels for the product only few hundred to few thousand tons of concentrate were produced annually by MIPCO and sold primarily to Tanzanian and Kenyan large and small scale customers (Table 1).

During the evaluation of the Finnish Minjingu Phosphate Project in 1994, the evaluation team emphasized the question of ore reserves and indicated that the reserves are much smaller than originally assumed. The beneficiation plant was originally designed on the basis of the three main upper layers (<15-20 m) of the soft ore located on the northern slope of the Minjingu Hill. Those layers were specifically surveyed by the Japan Consulting Institute (JCI) in 1967 and their corrected reserve estimate was 668,000 tons of workable material (Chapter 3.3) {97}. Based on the figures in Table 1 the average phosphate recovery rate during 1983-1991 was 52% (133,900/259,000 tons) resulting in an initial and remaining production potential of 345,000 tons and 211,100 tons of concentrate respectively. These figures agree well with the calculations made by van Kauwenbergh {265}. Put in another way, almost twice the amount of concentrate, which has been produced so far, should still be present in the remaining part of the three layers. However, even a quick look at the three layers, which today are almost mined out indicates that the ore reserves or the recovery rate have been overestimated as indicated by the Finnish evaluation team. On the other hand, a reserve of 668,000 tons of ore could probably not have justified the construction of the present beneficiation plant and the Finnish Minjingu Phosphate Project apparently assumed that more of the proved reserves could be used after the three upper layers were mined {265} (see also discussion in Chapter 3.3).

If the beneficiation requirements were reduced, for instance if the material primarily was meant for direct application, a large reserve of the hard and semi-hard ore could be included in the potential workable reserve giving much better prospects for future mining.

The Finnish evaluation team was quite critical about the feasibility studies leading up to the project, which they claim did not seriously consider the potential economic viability of the mine, the risks involved in the production, the quality of the concentrate, the long haulage distance and the marketing of the product {200}. They concluded that it would have been better if the project never had taken off. Looking back on the economic merits from MIPCO also indicate that the economic performance of the mine throughout has been disastrous (Table 2).

Table 2. Production costs and product sales prices.

TSh. per ton	1983	1984	1985	1986	1987	1988	1989	1990	1991
Cost	2,070	2,840	2,400	4,430	11,002	4,974	9,804	7,894	48,666
Price	750	925	1,203	1,665	1,998	2,400	5,785	7,250	5,000

TSh. per ton	1992	1993	1994	1995	1996	1997	1998	Average 1983-1998
Cost	28,255	65,900	22,000	97,600	146,900	60,300	73,900	36,808
Price	15,000	22,000	50,000	50,000	50,000	50,000	50,000	19,624

Source: Mwambete, I., personal communication (2000).

It seems that the project from the beginning suffered from a number of intrinsic technical and infrastructural problems some of which had been foreseen by the various consulting companies. The fact that the production never met the planned volumes only made things worse.

Political reasons rather than technical, such as the wish to exploit national resources thereby creating development and independence of foreign import, must therefore have played a dominant role for the initiation of the Finnish Minjingu Phosphate Project.

The sight at Minjingu during the late 1990's and the early 2000 was not very encouraging as only few trucks and machinery were in working condition. Mildly said the whole place looked rather run down as many other similar parastatal companies from the postcolonial era. However, the mine was still operating under highly reduced capacity and produced small volumes of concentrate throughout the period following the dramatic decrease in production in 1991 (Table 1).

In January 2000 MIPCO Ltd. was put under liquidation by the Tanzanian government and in July 2000 interested investors were urged to bid on the company assets and mining area, which were sold as a package. By July 2001 a private national investor had been found and the entire Minjingu mine including remaining ore reserves, beneficiation plant, mining equipment, office buildings and residential houses were sold for the sum of TSh. 720 mill. (USD 900,000). The strategy of the new management is presumably to market the Minjingu concentrates for direct application in Tanzania and Kenya.

3.2 Geological setting

The Minjingu phosphate deposit is located at 35°54.6' E and 3°42.5' S in the Eastern Rift Valley, six kilometres east of Lake Manyara (960 m) around the footslopes of the small Minjingu Hill (1071 m), an inselberg of Neoproterozoic rocks composed of light coloured granular granite-like peracidites and alkali granites with amphibolitic inclusions (Photo 1) {120, 192}. Schlüter {226} suggested the hill to consist of massive quartzites with banded gneiss in the centre. The deposit has a width of 800 m in WNW-ESE direction and a length of 700 m in ENE-WSW direction.

Occurrences of shore marks, algal stromatolites and beach deposits in the area surrounding the lake indicate that the present Lake Manyara is a remnant of a much larger paleolake, which some time during Pleistocene covered an area 3-4 times larger than the present lake {223, 224, 229, 250, 261}. Four paleolake stages have been identified from the paleoshorelines with the first and second stage reaching a level of 1036 and 997-1006 m above sea level respectively, and the following two stages being outside the reach of the Minjingu hill (Figure 9) {250}. It is generally assumed that the lake has shrunk gradually from the largest extension to the present level, although occasional intermittent transgressions may have occurred as well {250, 261}.

Photo 1. The Minjingu hill (arrows indicate where soft and hard ore samples were collected for analysis, Chapter 4).

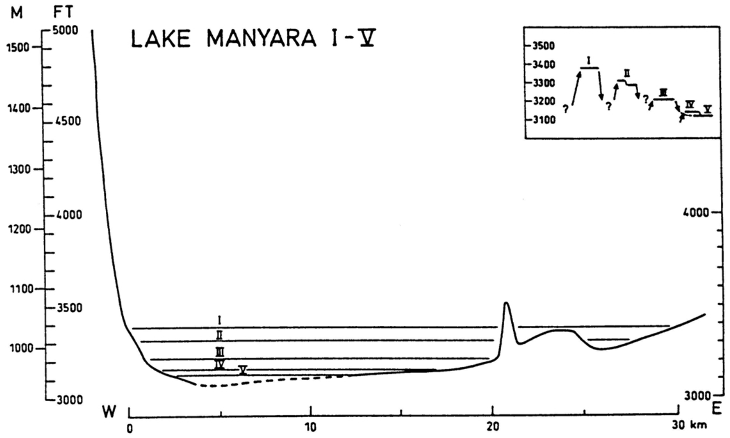


Figure 9. East-west profile across the Lake Manyara basin from the Manyara Escarpment in the west to the Minjingu Inselberg and slowly rising coast in the east. Four paleolake levels (I-IV) are indicated with respect to the present Lake Manyara (V) {250}.

During the first stage the Minjingu hill became an isolated paleoisland, which presumably acted as a resting and/or nesting place for a large monospecific colony of an extinct cormorant species identified as Phalacrocorax kuehneanus {223, 261}. From the first stage the lake gradually regressed to the second stage during which the hill in the later phase became connected to the mainland and acted as a cliff on the edge of the lake {250}. Due to the easy access to the Minjingu Hill by predators at this stage, it seems most likely that the birds shifted to other nearby islands to the south (The Pyramids, Besi and Frutia Hills) restricting the deposition of phosphates at Minjingu to the period from the largest extension of the first stage to the beginning of the second lake stage.

Various fossil materials have been identified including stromatolites and oncolites, gastropods, large three dimensional trace fossils of unknown biological origin, and isolated fish and bird remains suggesting that guano and associated bones, feathers and skeletal fragments are the main sources of the phosphates {223, 226, 228, 229, 261}. The majority of the deposit seems to derive from the guano residues although several larger bone fragments originating from dead individuals of the birds and fish living around and in the lake are prolific in certain layers (so-called "samaki" (fish) beds) indicating that some kind of catastrophic events may have occurred from time to time.

The stratigraphic age of the phosphates is still uncertain although absolute dating using radioactive disequilibrium methods have estimated the upper soft layers to 260,000 years +/- 10% {223}. Carbon dating of stromatolites representing the third lake stage gave maximum age estimates of 92,000 years suggesting that the second lake stage should be older than that but younger than 130,000-140,000 years, which was assigned to the first stage corresponding to the high lake levels reported from Lake Natron-Magadi in the north {250}. The transgression within the Manyara basin was suggested to occur around 140,000 years ago {250} (Figure 10).

Based on the chronology presented by Somi {250} and with the assumptions that the deposition occurred from the first lake stage up to the first phase of the second lake stage, the Minjingu phosphates were deposited in the period from 135,000 BP to 110,000 BP. In agreement with this estimate, Schlüter {226} suggested on the basis of comparative studies of guano deposits off the Peruvian coast that the Minjingu deposit may have formed during a period of a few thousand years.

Other studies, including geomorphic interpretations have led to late Pliocene or early Pleistocene age estimates indicating that the phosphatic sediments should be much older (1-1.6 mill. years) {261}. Hence, although Pleistocene age at present seems most probable exact dating awaits more studies.

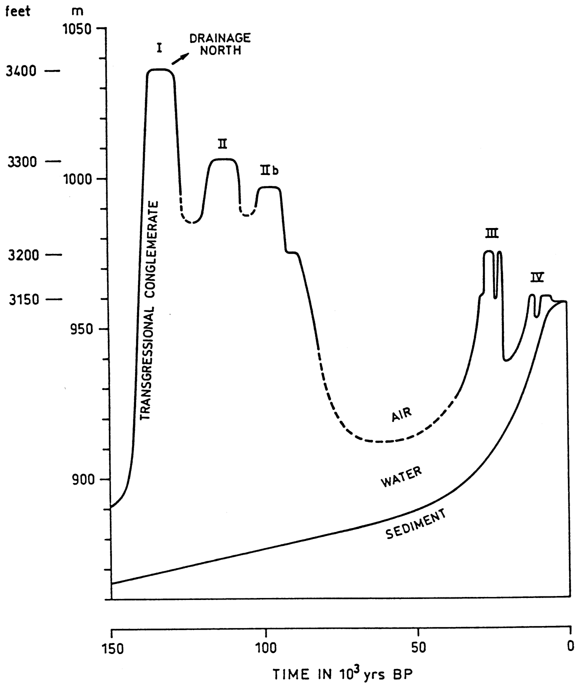


Figure 10. Changes in lake level with time {250}.

The presence of stromatolites and other trace fossils in the Pleistocene lake sediments suggests that the lake at least during periods had an alkaline hydrochemical composition, presumably owing to weathering of the widespread Plio-Pleistocene and recent alkaline extrusive rocks to the north and west of the lake, and the fact that the lake is located in a warm tropical climate in a closed basin with no outlet {227-229}. It is possible that the chemical composition gradually became more concentrated as the lake regressed {224, 250}. The present hydrochemical composition of the lake indicates a highly alkaline soda lake with high levels of Na^+, Mg^{2+}, Cl^-, SO_4^{-2} and HCO_3^- and a pH of 9.8 {225, 227}. The paleobiological fossil assemblage at Minjingu shows only few species but partially in great individual number supporting the idea of extreme hydrochemical conditions during deposition giving rise to mono and oligospecific communities {229}.

The deposit contains two distinct ore types (Photo 2):

1) The soft ore, which is present as white, porous, friable phosphate beds (<995-1000 m above sea level) interlayered with sandy, clayey and marly lake sediments. The phosphates are mainly composed of particles of biogenic origin mixed with detrital mineral grains from the crystalline basement rocks (Chapter 3.5 and 4). The soft phosphate beds are primarily found north of the hill where the individual layers are up to 7 m thick and extend out from the hill in a circular direction with a downward dip of 4-6° and thin away at a distance of approximately 250 m from the hill. The soft phosphates are found to a maximum depth of approximately 950 m above sea level {120}.

2) The indurated hard ore, which on the northern side is only present above the soft ore (>995-1000 m above sea level) around the fringe of the basement rock and on the southern side of the hill consists of more weathered particles of biogenic origin and secondary phosphatic minerals together with detrital mineral grains from the crystalline basement rocks (Chapter 3.5 and 4). The particles are generally cemented in a matrix of cryptocrystalline quartz (colloidal silica), clays and other secondary minerals and appear often conglomeratic with an opal and chert-like grey cement. On the southern side of the hill the surf action apparently was larger due to the prevailing wind direction and shallower depth resulting in a more mixed clay-phosphate deposit with less stratification at least close to the surface. Beneath the mixed ore on the southern side soft phosphate layers similar to those found on northern side have also been identified {120}. The cementation of the hard ore has also influenced the bulk density (2.56-2.78 t m^{-3}) compared with the soft ore (1.64-1.88 t m^{-3}) {97}. The hard phosphates are found to a maximum height of approximately 1030 m above sea level {120}.

Photo 2. Typical soft (S6) and hard (H7) ore fragments.

3.3 Surveys and reserve estimates

New Consolidated Goldfields Ltd., formerly Goldfields of South Africa Ltd. (GSA) were the first to survey the area through their concession known as Minjingu S.E.P.L. 150 and 154 Mbulu District, Tanganyika Territory {185}. In the period 1957-1959 information from a total of 125 pits and 23 boreholes were carefully evaluated and resources down to 61 m were fully proved to 4.4 Mt (4.8 mill. short tons) of soft, fine grained phosphate beds (8% P (18.5% P_2O_5)), interbedded with montmorillonitic clays, and 4.5 Mt (5.0 mill. short tons) of hard and semi-hard siliceous-rich phosphatized rock (9.3% P (21.4% P_2O_5)) (Figure 11). This survey represents the most comprehensive work done on the reserve estimation and the figures are basically still valid as estimates of total ore reserve. Most citations on reserve estimates are based on these figures {7, 19, 38, 80, 83, 94, 139, 169, 194}.

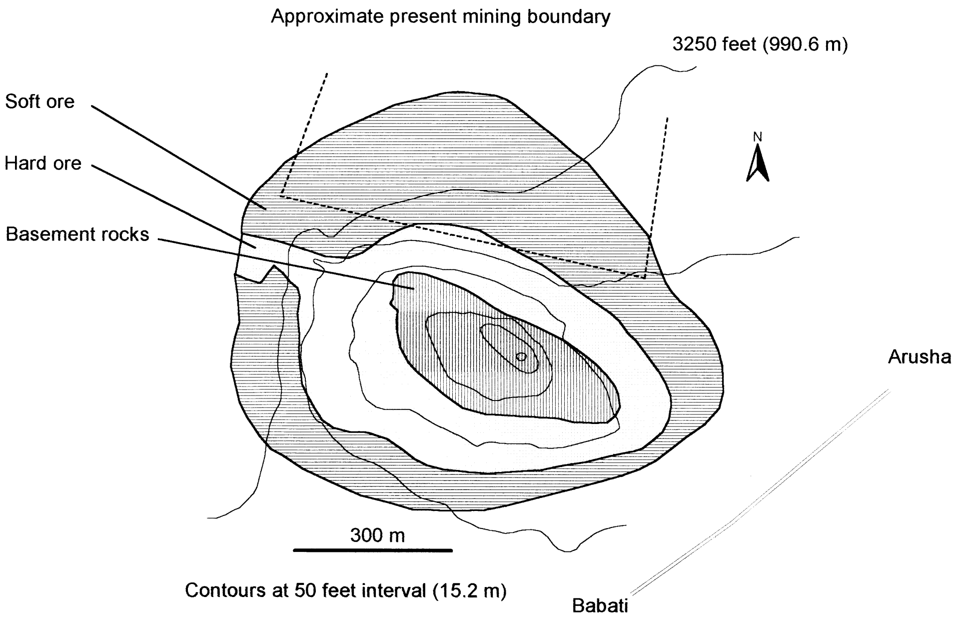


Figure 11. The delineation of the deposit based on the first survey made by Goldfields Ltd.

During the first survey they mined approximately 20 tons of material form zone B3, which includes the upper soft layers on the northern side close to the hill just below the hard type A ore where the different soft layers tend to join and form a thick bed. Various samples were dispatched to phosphate authorities in Germany, UK and USA for advice on beneficiation and suitability for manufacture of superphosphates and elemental P, and for agronomic experimentation in Kenya and Tanzania.

During 1961 GSA also surveyed around The Pyramids located 12 km to the southwest of Minjingu. A total of 63 pits down to the groundwater at 9-15 m depth around Mwembe Hill (the northern Pyramid) revealed at least two layers of slightly radioactive collophanic phosphate sands containing 8.7% P (20% P_2O_5) interbedded with green clays. Phosphate layers were also identified around the perimeter of the southern Pyramid. The Pyramids are larger than Minjingu and bird life could have been more disperse resulting in a smaller and less concentrated deposit. The geologic map of the area also indicates phosphates around Besi and Frutia Hills further to the southwest but apparently no further investigations have been made so far {192}.

Later in 1967 the Japan Consulting Institute (JCI) {97} reassessed and improved the previous survey in terms of geologic potential and correlation, distribution, quality and properties of the three main phosphate layers on the northern side of the hill (layer C, D and F, 2-15 m below the surface). Additional three pits and three trenches were excavated and correlated with the survey by GSA. The minable reserve estimate of these three layers was 668,000 tons of ore with a weighted average of 9.3% P (21.2% P_2O_5). With an expected average recovery rate of 68% the mine would yield 454,000 tons of concentrate with an average of 13.7% P (31.3% P_2O_5). As mentioned in Chapter 3.1 the actual recovery rate was 52% yielding a slightly lower output than expected. In addition to the reserve estimation JCI also assessed the local conditions for mining and beneficiation and proposed a detailed production plan on the basis of the three main beds in the northern section of the deposit.

In 1970 Klöckner Industrie Anlagen Gmbh. {120} carried out a detailed feasibility study concerning the utilization of Minjingu phosphate rock as raw material for the production of soluble phosphates at the factory in Tanga. As the factory was already under construction the objective of the investigation was to determine whether the mine would be able to supply the factory with 120,000 tons of concentrate (13.1% P (30% P_2O_5)) annually for at least 10 years corresponding to a minimum economically minable ore reserve of 2.2 Mt. Reassessing the two previous surveys and carrying out additional field studies considering the thickness of overburden and pit waste, and the thickness and P content of the individual phosphate beds they estimated the total economically minable reserve to 4,338,180 tons (7.9-8.7% P (18-20% P_2O_5)) (Table 3). Apparently they used a bulk density of 2 t m^{-3} irrespective of ore type, which is quite different from the figures given by JCI {97}, and the tonnages may therefore vary accordingly.

Table 3. Total economically minable resources (tons) as evaluated by Klöckner Industrie Anlagen Gmbh. {120}.

Material	North	South	Total
Hard ore	188,350	1,093,690	1,282,040
Soft ore	1,730,060	1,326,080	3,056,140
Overburden and pit waste	968,800	98,300	1,067,100
Total P ore	1,918,410	2,419,770	4,338,180

Irrespective of bulk density it can be seen from Table 3 that substantial resources are present close to the surface in the southern section, which so far has been left untouched. The mixed ore type in the south may however lead to lower grade of the concentrate, as the selected beneficiation method is less capable of separating the phosphates from the accessory minerals. Also the possible presence of saline groundwater in the deeper layers could impose problems with the current mining technique or at least increase the ore drying requirements. Apparently a large part of the total phosphate ore as estimated by GSA have been excluded by Klöckner Ltd. as being not economically minable due to the lower P content and thick overburden. Although Klöckner Ltd. estimated the minable reserves being sufficient to supply the factory in Tanga for at least 10 years they stressed the marginal feasibility of the mine primarily due to the long transport of the concentrate from the mine to Tanga. During their survey they also reassessed the survey around Mwembe Hill but found it insignificant for economic mining.

In 1975 J.L. Weaver made a re-interpretation of the previous reports and estimated the total reserves of the soft ore to 2.88 Mt (8.3% P (19% P_2O_5)) whereas A.P. Shah in 1976 after an additional drilling campaign estimated the soft ore to 1.97 Mt (10.5% P (24% P_2O_5)). Just before mining had started, KONE Ltd. also made an estimate of 1 Mt (10.3% P (23.6% P_2O_5)) of the soft ore for which the mine was designed. After mining had begun, STAMICO apparently made another drilling campaign, which must be considered the most recent estimation of both the soft and hard ore {130}. The estimates, which take into account the previously mined ore, are presented in Table 4. Hence, over 7 Mt of P ore is supposedly present at Minjingu today.

Table 4. Most recent estimates of Minjingu resources.

Total soft ore reserves (North, South, West) before mining	3.29 Mt (8.9% P (20.4% P_2O_5))
Soft ore mined up to 1999	0.89 Mt
Total soft ore reserves by 1999	2.40 Mt
Hard ore reserves (not mined up to now)	4.84 Mt (10.5% P (24.1% P_2O_5))

3.4 Mining and beneficiation

Mining

The present opencast pit located at the northern side of the Minjingu hill is designed to mine the first three beds of soft phosphate down to a maximum depth of 15-20 m {80}. The pit is sloping parallel to the phosphate layers towards north were the drainage occurs (Photo 3).

Photo 3. Present mining pit with the lake and rift escarpment in the background.

Mining operations include stripping off surface and interlayers of clay and sand, and excavation of the phosphates using bulldozers and hydraulic excavators. According to Table 1 the stripping:mining ratio is about 1.5. The clays are dumped in large heaps to the west and north of the pit whereas the phosphate material is transported using front-end dump trucks to the pre-drying area where it is spread out, crushed and mixed by bulldozers.

Large blocks of impurities such as lumps of clays and quartzite are removed by hand from the drying area. Sun drying effectively reduces the cost of drying the material during the beneficiation process although it is possible only if the mine is working below the potential production capacity. Mining operations continue throughout the year except during the rain season from December to April where the work is carried out intermittently.

Beneficiation

Several mineral dressing studies including both dry, wet and calcination processes were carried out on both the hard and soft ore in the period up to the construction of the beneficiation plant {68, 70, 71, 97, 120, 160-162}. Generally the dressing studies showed that beneficiation of the soft ore by drying and size classification yielded an acceptable concentrate and P recovery rate primarily due to different mechanical behaviour and granulometric composition of the phosphates and accessory minerals. Studies on the hard ore showed in contrast to the soft ore that size classification was not effective for the upgrading of the hard ore as the granulometric analyses showed almost the same phosphate content irrespective of size class {68, 234}. For the hard ore, GEOMIN proposed a dressing method, which in addition to size classification and grinding included wet attrition and flotation using various flotation reagents. They also carried out the flotation tests with positive results using alkaline water with similar composition to that of Lake Manyara. In some cases the flotation method yielded acceptable concentrates but the recovery rate was very sensitive to ore quality and grade, which apparently was very variable and difficult to control.

Eventually, a dry beneficiation process was chosen designed primarily for the soft ore. It consists of ore pre-drying, comminution, hand picking, artificial drying and size classification (Figure 12).

From the pre-drying area the soft ore is conveyed directly to a pre-screening station with an 8x8 mm single deck vibrating screen. Phosphate lumps from the overflow is recovered by hand picking whereas non-phosphatic materials goes to waste (Photo 4). The hand picked lumps and the underflow is temporarily stored in a 230 m^3 bin from which the ore is discharged into a rapid dryer reducing the moisture content at 800-1000 °C from approximately 15% to 3-5%. The dried ore passes a 2x12 mm single deck vibrating screen where the oversize, consisting mainly of quartz and feldspar grains, goes to waste. The undersize is conveyed to a gravity classifier from where the coarse material passes a 0.4x8 mm electro-magnetic screen, which separates oversize magnetic minerals to waste and the undersize to the final storage silos. The fines from the gravity classifier are brought together with dust from other sources of the beneficiation process to the de-dusting system and finally to the storage silos.

Photo 4. Hand picking platform.

Especially accessory minerals such as dolomite and quartz, which are known to occur in the Minjingu concentrate, are undesired impurities in the wet process production of phosphoric acid {263}. The selected method of dry beneficiation only removes about half of the feldspar and dolomite whereas the quartz content remained the same leading to a relatively low quality concentrate {207, 264}.

In case the hard ore is processed a few more steps are included. From the feeding station it passes an impact crusher, which reduces the size to less than 50 mm before conveyed to the pre-screening station and rapid drying.

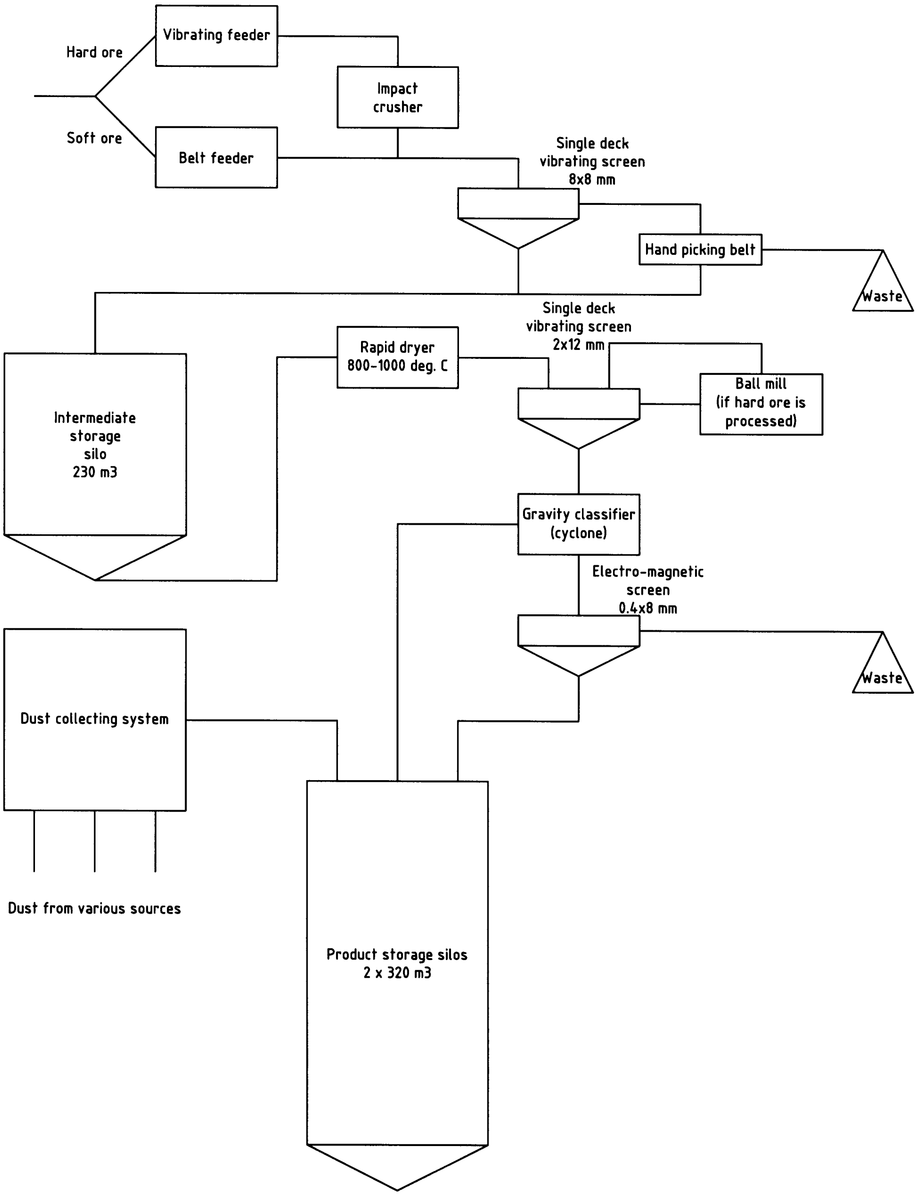


Figure 12. Flow sheet of the beneficiation process at Minjingu (modified from Hangi {80} and Brinkman & Kantor {32}).

After the second screening the oversize is ground using a ball mill after which it returns to the second screen and the electro-magnetic screen. It is not clear how well the designed beneficiation process works with the hard ore although there are indications that the silica content is high (I. Mwambete, personal communication, 2000). An indication of the difficulties can be derived from the study carried out by the Southern and Eastern African Mineral Centre {234}. They proposed a beneficiation method similar to the dry method used at Minjingu and obtained at 50% P recovery a concentrate (<0.106 mm) having 12.4% P (28.4% P_2O_5) and 21.5% SiO_2 from raw material originally having 10.7% P (24.4% P_2O_5) and 27.8% SiO_2. Thus production of an acceptable concentrate from the hard ore using the present beneficiation method seems to be difficult primarily due to the intimate association between the minerals and their granulometric composition.

3.5 Petrography, mineralogy and geochemistry – review of previous work

Information on the mineralogical characteristics of the Minjingu phosphate rock is fragmented and not readily available. The first detailed petrographical, chemical and mineralogical characterization of both the hard and soft ore was carried out by GEOMIN {68} in 1969-70. Before that GSA {185} had suggested that the phosphate in the soft ore was collophane originating from the reaction between soluble phosphates from bird guano and the alkaline lake water. The Japanese Consulting Institute {97} found that the main minerals in the soft ore were hydroxyapatite, carbonate hydroxyapatite (dahllite), quartz, clays (montmorillonite and illite) and minor contents of analcime. Actual kind of samples analysed or methods used were not given. Parallel to the study of GEOMIN, Klöckner Ltd. also carried out relatively detailed petrographical and mineralogical studies of both the basement rocks, the lacustrine marly deposits and the phosphates {120}. In 1978 Tennessee Valley Authority (TVA) examined a soft ore sample, and found it to consist of approximately 60% microcrystalline fluorhydroxyapatite with the remaining part consisting primarily of quartz, feldspars, calcite, dolomite, clays and goethite {112}. Van Kauwenbergh {264} made a relatively detailed characterization of the soft ore and the beneficiated concentrate in terms of apatite type and content of accessory minerals. The results of the crystallographic analysis based on X-ray diffraction (XRD) indicated a carbonate fluorapatite (francolite) with low carbonate substitution predicting low reactivity and low suitability for direct application. Mineralogical analysis of the hard ore carried out by SEAMIC {234} in connection with an upgrading experiment assessed the rock to be composed of mainly quartz and apatite grains cemented by clay minerals. On the basis of XRD analysis and X-ray fluorescence (XRF) analyses it was suggested that the apatite mineral was mainly carbonate hydroxyapatite and hydroxyapatite. Most of these findings are discussed further in Chapter 3.5.1 and Chapter 4.3.

3.5.1 Petrography and mineralogy

As the analyses carried out by GEOMIN {68}, Klöckner Ltd. {120} and van Kauwenbergh {263, 264} represent the most comprehensive of the previous studies of the petrography and mineralogy of the Minjingu deposit and as the information is not readily available a brief summary and discussion of the results is given below. The first description of the soft and hard ore fragments is based on the microscopic analysis of raw samples and thin sections carried out by GEOMIN {68}.

The soft ore

1. Samples from the soft ore (zone B) appeared to be non-homogenous, consisting mainly of two types of rock fragments:
    a) Friable fragments in a proportion of 70-80%, light coloured, with rounded edges and aspect of weakly consolidated sandstone consisting primarily of phosphatized fossil rests with fibrous aspect and generally elongated habitus cemented by clayey minerals and carbonates. In reduced proportion were crystals and aggregates of quartz, feldspars, mica, amphibole and pyroxene as well as micronic inclusions of zircon, apatite, garnet, orthite, and fluorite.
    b) Rock fragments in a proportion of 20-30%, greenish-grey, here and there with yellowish hue formed by 0.2-3 mm thick bands of schistous clays consisting of fossil rests (35%) directed parallel to the stratification and embedded in a cement (65%) formed by a mixture of clayey minerals, carbonates, organic substances and glauconite. White coloured fragments (0.5-5 mm) consisting of quartzite with feldspar inclusions were also present in reduced proportion (5%).
2. Carbonate hydroxyfluorapatite was identified as being the prevalent mineral in the soft ore (70%) being mainly francolite and subordinately collophane (Table 5). The distinction between francolite and collophane was primarily made on the basis of micromorphology and isotropy. The francolite appeared as colomorphous, anisotropic, fibrous deposits, embedded in a cement of clayey minerals and carbonates. Various shapes of phosphatic fragments such as fibres, prismatic crystals, arcs and radial

deposits ranging from 0.02-3 mm could be identified when observed with crossed nicols. The collophane was isotropic and occurred as pockets and nodules (coprolites) with sizes between 0.1-0.6 mm. In contrast to the smooth surface of the francolite it appeared slightly rugged when observed with parallel nicols. The chemical analysis indicated isomorphous substitution or micromixture with SiO_2, Al_2O_3, Fe_2O_3, MgO and Na_2O in the francolite/collophane phase. The maximum P content of the pure apatite was estimated to 15.9% P (36.5% P_2O_5).

Table 5. Mineralogical composition of the soft ore (zone B) and distribution of Si, Al and Ca to main minerals {68}.

Mineral	Distribution (%)	SiO_2	Al_2O_3	CaO
Francolite/collophane	70	-	-	90-92
Dolomite/calcite	10	-	-	8-10
Quartz/colloidal silica	5-7	44-46	-	-
Feldspar	3-5	20-26	32-34	<0.2
Montmorillonite/illite	7	24-26	50	-
Biotite/muscovite/amphibole/pyroxene	2-3	8-10	16-18	-
Fe-oxides/hydroxides	0.5	-	-	-
Apatite/garnet/zircon/orthite/glauconite	Trace	-	-	-

3. The carbonates appeared in a proportion of about 10% being mainly dolomite and subordinately calcite closely mingled with the clayey minerals forming the cement of the soft ore. The carbonate structure was from cryptocrystalline up to microcrystalline. The clay minerals were primarily montmorillonite and subordinately illite.
4. Several primary and secondary minerals were present in the phosphate mass. The silica appeared both as free quartz and as colloidal silica deposits. The free quartz as well as feldspars represented by plagioclase and microcline were present as irregular grains with sizes between 0.1-3 mm, the majority being over 0.2-0.3 mm. Mica, pyroxene and amphibole appeared as lamellar or prismatic crystals (0.1-0.2 mm thick and 0.5-0.8 mm long), and limonite as fine impregnation and dentritical deposits. Accessory minerals occurred sporadically and were extremely fine sized (<0.03 mm).
5. The granulometric analysis on dried and disintegrated samples where the >25 mm fraction had been removed showed the highest concentration of phosphate is found in the size classes larger than 0.1 mm. Below 0.1 mm especially the clay content increases. The highest recovery of phosphate was found in the 0.16-0.2 mm size class (>40%).

The hard ore

Seven hard ore samples (zone A) were subjected to microscopic examination of thin sections prepared from raw materials, which had been crushed to less than 3 mm. Unfortunately the sample locations could not be determined exactly as the denominations did not relate directly to any of the previous surveys. However, all samples were definitely of the hard ore type. The samples included four samples from shaft no. 3 (sample no. 1, 2, 3, 4), one sample of clayey sandstone (SG1), one sample of phosphatized clay (SG2) and a mixed average sample of five of the six raw samples (Table 6). Sample no. 2 from shaft no. 3 was left out from the mixed average sample due to a very high P content (16.4% P (37.45% P_2O_5)) indicating a not very representative and almost pure phosphate sample. A summary of the description by GEOMIN {68} is given below.

1. Phosphate minerals are the dominating constituents of the hard samples (50-99%). They are represented by hydroxyfluorapatites primarily as collophane and subordinately as francolite. The brown or greyish phosphate fragments have a compact or spongy aspect reaching 3-4 mm in the samples no. 1-4 and generally smaller sizes in the SG samples (<0.5 mm). Due to the crushing of the ore samples before shipment from the mine it was not possible to assess the original grain sizes and macro-morphological composition of the raw ore. However for samples no. 1-4 it appeared that the phosphate constituted the mass of the rock in which other mineral grains were embedded. For SG1 the phosphates were also

constituting the mass of the rock but with a larger fraction of quartz, feldspars and clayey minerals. In contrast the phosphate minerals were primarily found as veins and pockets in the cracked masses of clay minerals in the SG2 sample. In all samples the collophane appeared as a slightly rugged isotropic mass whereas the francolite was seen as anisotropic fibrous crystals or as fine grained and colomorphous deposits. From the morphological examination and the chemical analyses it was stated that the phosphate was entirely bound to calcium phosphates (francolite, collophane and apatite).

2. The free silica appeared primarily as free quartz grains except in SG2, which was dominated by fine impregnation with colloidal silica in the clay and collophane mass. Quartz grain sizes ranged from 0.02 mm up to the crushing size (3-4 mm) with the majority being below 0.2-0.5 mm.
3. Feldspars were the second most common accessory mineral and were found in all samples except sample no. 2 in a proportion of 2-7%. Size and aspect were as for the quartz.
4. The clay minerals were dominated by montmorillonite and subordinately by illite. Samples no. 1-4 had very low contents of clays in contrast to the SG samples. In SG2 the clays appeared as a compact mass, in SG1 as pockets (0.05-1 mm) and in samples no. 1-4 as fine impregnations. In general the clays were closely associated with iron oxides and hydroxides, colloidal silica and collophane.
5. Needle like crystals with lengths up to 0.15 mm and thickness of 0.01 mm inferred as apatite crystals were found in all samples. Especially in sample SG1 they were observed at the microscope as fine crystals, disseminated in the phosphate mass or in crystal pockets.
6. In contrast to the soft ore in which carbonates were identified it was concluded that all Ca was bound to calcium phosphates except for a minor fraction of Ca associated with the clays in the SG samples. The petrographic analysis and the total chemical analysis suggested that some of the Mg^{2+}, K^{+}, Na^{+} and all the SO_4^{-2} were entering the phosphates as isomorphic substitutions for Ca^{2+} and PO_4^{3-} respectively. Quite interestingly GEOMIN {68} also suggested that 75-80% of the silica in sample no. 2 was present as isomorphous substitution for PO_4^{3-} in the phosphates whereas for the remaining samples it appeared to be between 3-9%. They also suggested that some of the aluminium were associated with the phosphates as substitution although association with the primary minerals and the clays were also indicated. Iron was found to appear both in association with clays and the phosphate mass and as free secondary iron oxides and hydroxides.
7. Other accessory minerals included hornblende, chlorite, glauconite, garnets, zircon, pyrite and organic substances. They were all found in amounts less than 0.5-1%.

The analyses by GEOMIN {68} were carried out with great care and may currently represent the best petrographical description of the phosphates. Comparing with other studies it also appears that their descriptions were based on representative samples of both the soft and hard ore. However, crystallographic properties of the phosphates were not investigated and the suggestion that Si, Al and Fe may substitute PO_4^{3-} in the soft and hard ore phosphates are not supported by other studies (Chapter 4.2). In addition, the needle-like crystals identified in the hard ore samples and interpreted as apatites may probably more correctly be associated with the unknown platy minerals, which were identified during the mineralogical investigations in this project (Chapter 4.2).

Table 6. Petrographical, mineralogical and chemical characterization of the hard ore samples {68}.

	Shaft samples				SG1	SG2	Average
	1	2	3	4			(1, 3, 4, 5, SG1, SG2)
Macro-morphology	Grey-brown coloured samples containing 1) brown hard fragments of calciumphosphate and 2) a grey-yellow matrix of friable phosphate fragments with grey-white coloured quartz and feldspar mineral grains and clays				Light greenish to grey samples containing 1) hard fragments of a clay-phosphate mixture with colloidal silica, and free quartz, feldspar and apatite grains and 2) friable fragments with similar mineral composition but with higher clay content		
Mineralogy				%			
Francolite/collophane	78-80	98-99	80-82	75	50-52	50-51	65
Quartz/colloidal silica	15-20	<1	15	15-17	15-20	15	15-16
Feldspar	2-3	0	1-3	5-10	5-10	2-3	5-10
Montmorillonite/Illite	<1	<1	<1	0.5	15	25-30	7-10
Mica and other 2:1 silicates	tr.	tr.	tr.	tr.	2-4	<0.5	<0.5
Fe-oxides/hydroxides	<0.5	<0.5	1	1	3-4	3-4	1-2
Apatite/hornblende and other	<0.5	<0.5	<0.5	<0.5	2-5	<1	<1
Chemistry				%			
P_2O_5	30.46	37.45	30.88	28.40	20.85	19.55	24.55
CaO	33.60	43.20	34.59	31.88	22.48	21.93	28.91
SiO_2	21.20	3.03	18.60	21.98	31.76	32.45	25.98
Al_2O_3	3.31	4.66	3.33	6.10	7.07	7.86	6.25
Fe_2O_3	0.99	1.16	1.70	1.66	4.10	4.35	2.47
MgO	0.60	0.36	0.52	0.27	1.32	1.15	0.63
K_2O	0.96	0.48	0.58	1.01	3.61	4.33	2.59
Na_2O	0.65	0.55	0.75	0.70	0.70	0.49	0.70
SO_3	0.17	0.12	0.14	0.15	0.16	0.24	0.10
CO_2	1.68	1.87	1.48	1.41	1.21	0.93	n.d.
F^-	2.23	1.83	1.24	1.47	0.92	0.92	1.10
Cl^-	0.10	0.12	0.14	0.12	0.16	0.12	0.28
Ignition loss	5.71	7.90	7.79	6.62	7.07	7.49	6.56

The independent study by Klöckner Ltd. {120}, although not being as detailed, supported and supplemented the study made by GEOMIN. Thin sections of the soft ore revealed a greenish-white, soft, porous and layered material consisting of closely packed and partly oriented biogenic phosphate particles (0.1-0.8 mm) surrounded by a thin film of an extremely fine-scaled illitic mineral or palygorskite and in rare cases some calcite. Clastic mineral grains of quartz, feldspar and hornblende were also present in the matrix. Without naming the phosphate minerals explicitly the phosphate phases were divided between collophane and a very finely fibered apatite, which in majority were remains of bird bones. The collophane appeared as coprolites as well as darker cores of the fibrous apatite particles.

The hard ore appeared as a green-yellowish conglomerate with white-grey cement. The foreign rock debris primarily consisting of quartz and quartz-rich rocks varied between several mm and several dm in size. Thin sections revealed an isotropic matrix of gel phosphate and colloidal silica in which angular mineral grains of quartz, feldspar, hornblende, mica and biogenic phosphate particles were embedded. Again the phosphate particles were divided into a cryptocrystalline apatite phase (bone fragments) and a collophane phase (coprolites and gel phosphate).

Thin sections of the basement rocks showed a granular fabric of quartz in which closely intergrown inclusions of alkali feldspars and few occurrences of oligoclase and mica appeared. The friable, olive green to grey interlayering clays of the deposit were found to consist of relatively pure clays of sericite-illite in a mixed cement of calcite, analcime and the finely fibered foliaceous clay mineral palygorskite. Lime pebbles of 0.05-0.1 mm in size were more or less evenly distributed.

This study confirms many of the findings of GEOMIN and adds more information on the clay mineralogy and basement rocks. Klöckner also identified the colloidal silica, which may contribute to the cementing of the hard ore. Colloidal silica was not identified by van Kauwenbergh (see next) nor during our investigations (Chapter 4.2) but based on the two former descriptions it seems likely that it is present at least in the hard ore.

The mineralogical and chemical study by van Kauwenbergh {263, 264} of a soft ore sample, a bird bone concentrate and the beneficiated product using XRD and scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) revealed a quite complex nature of the phosphates. The X-ray diffraction pattern of a powder sample closely resembled that of a carbonate hydroxyapatite supporting the previous suggestions by various authors that the soft ore phosphates were of the fluorine deficient francolites or hydroxyapatite types (see Chapter 2.2). However, the total chemical analysis showing relatively high fluorine content (see Table 7) as well as the X-ray determined *a*-cell dimension (9.353 Å) indicated an excess fluorine francolite. Based on previous regression models between *a*-cell values and apatite composition the stoichiometric formula of the soft Minjingu phosphate was suggested to be:

$$Ca_{9.84}Na_{0.11}Mg_{0.04}(PO_4)_{5.52}(CO_3)_{0.48}F_{2.19} \qquad (3)$$

indicating a francolite with low carbonate substitution and hence low reactivity {144, 263} (Figure 4, Chapter 2.2). The predicted solubility in neutral ammonium citrate (NAC) based on the *a*-cell value is 1.3-1.5% P (2.9-3.4% P_2O_5) indicating a low to medium reactive phosphate rock {126, 268}. The actual measured solubility in NAC have ranged between 1.8-4% P (4.1-9.4% P_2O_5) indicating a medium to highly reactive PR (see Table 7), which has also been confirmed by pot and field experiments (Chapter 5). These high solubilities can only occur if the apatite is of the highly carbonate substituted francolite type or of the fluorine deficient francolites {268}. Van Kauwenbergh suggested the discrepancy between the measured and predicted solubilities as the ore being composed of a mixture of apatites with varying solubilities, which apparently XRD was not able to resolve. Based on the SEM analyses three different apatite phases were identified: a) clear, angular fragments of apatite resembling igneous-derived fluorapatite, b) bone fragments of biogenic origin (fish and birds) and c) microcrystalline apatite aggregates. The bone fragments, which he found to have a very high NAC solubility of 5.6% P (12.9% P_2O_5) (Table 7) was therefore suggested to have a dominant influence on the NAC solubility of the concentrate {264}.

The analyses of van Kauwenbergh represent the first characterization of the crystallographic properties of the soft phosphates. However, the results of the analyses described in Chapter 4.2 do not support the suggestion that the soft ore phosphates are excess fluorine francolites and it appears that the general relations between *a*-cell values and elemental composition or reactivity cannot be used. Even the figures presented by van Kauwenbergh {263, 264} do indicate fluorine deficiency in the soft ore despite F/P_2O_5 being larger than 0.089 (see discussion in Chapter 4.3). The suggestion on the presence of fluorapatites of igneous origin are also not supported by the findings of GEOMIN, Klöckner or the data in Chapter 4.2. However, the suggestion of different solubilities of the various phosphate fragments seems quite plausible.

3.5.2 Chemical composition and solubility

Total chemical composition of the Minjingu phosphate rock has been published by various sources (Table 7). However, most figures originate from a limited number of analyses. The figures of the non-beneficiated ore represent material from the hard ore and soft upper layers, which typically range between 8.7-13.1% P (20-30% P_2O_5) indicating a low to medium grade ore. The P content of the deeper layers is generally below 8.7%P (20% P_2O_5) {120, 185}. The F/P_2O_5 ratio is above and below or close to the ratio for pure fluorapatite (F/P_2O_5=0.089) for the soft and hard ore samples respectively indicating that the soft ore samples may belong to the excess fluorine francolites whereas the hard ore samples belong to the fluorine deficient francolites or carbonate hydroxyapatite series {268} (see also the discussion in Chapter 4.3).

The hard ore contains a significantly higher silica content compared to the soft ore primarily due to a higher content of accessory feldspars, quartz and colloidal silica and in some cases clays as also indicated by the study of GEOMIN (Table 5 and Table 6). From the few mineral dressing tests of the hard ore it is seen that the silica content of the beneficiated material although being significantly reduced still remains too high for further wet processing.

Beneficiation of the soft ore generally increases the P content from 8.7-13.1% P (20-30% P_2O_5) in the raw material to more than 13.1% P (30% P_2O_5) in the concentrate. Although the $CaO:P_2O_5$ ratio of the soft concentrate is generally within acceptable limits for further processing other impurities such as soluble chlorides leading to corrosion of plant equipment and dolomite leading to a higher acid consumption, difficulties in filtering and increased viscosity of the acid, indicate a relatively low quality ore. Aluminium and silica are mainly present in feldspars and other inert primary minerals as well as in the clays, which normally require some kind of wet beneficiation process. The iron content, which is generally low, is present both as free oxides and in the clay minerals.

The neutral ammonium citrate solubility averages 2.6% (6% P_2O_5) and 1.8% P (4.2% P_2O_5) corresponding to approximately 23% and 17% of total P for the soft and hard ore samples respectively, indicating a slightly lower reactivity of the hard ore, which can possibly be attributed to the high degree of cementation of the phosphate particles. Based on the NAC solubility values both the soft and hard Minjingu phosphate rock can be considered highly soluble and comparable with the best phosphates found worldwide for direct application to soils {49, 126}.

The content of radionuclides and trace elements are listed in Table 8 and in addition a few others have been reported (in mg kg^{-1}): Nb (14), Nd (25) {11}, and As (8), Se (3), Hg (40) {267}. When comparing with other sedimentary phosphorites it is seen that levels of Cd, Hg, Pb, Se, Cr, V, Ni, Y, Zr and Ce are low, As, Co, Cu, Mn and Zn are medium and U, Th, Li, Rd, Sr, Rb, Ba and Ti are high {84, 122, 179, 267}. La is showing both low and high values. It should be emphasized that levels of potentially hazardous elements such as Cd, Hg, Pb and Cr are low.

Table 7. Total chemical composition[1] of soft and hard Minjingu (primary reference in bold).

Sample[2]	P_2O_5	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	CO_2	F^-	Free H_2O	Ign. loss	Cl	NAC	Citr. acid	Source
							%							mg kg^{-1}	% P_2O_5		
NBHO	24.55	28.91	25.98	6.25	2.47	0.63	2.59	0.70	0.10		1.10		6.56	2800			**{68} (average sample)**
BHO	34.10	40.75	8.70	3.37	1.72	0.60	1.07	0.90	0.32	1.85	1.93		6.63	1100			**{68}**
BHO	28.7	44.3	11.8	2.54	1.93	0.41	0.91	0.88	0.18		1.53		6.26	610			**{234}**
NBHO	24.19	32.22	28.15	3.84	1.01	0.29	0.85	1.15		2.03	1.94	0.87	3.57		4.3		**H10 (see Chapter 4)**
BHO	27.70	34.03	19.23	4.29	1.75	0.43	0.94	0.94		2.77	1.77	0.88	5.49		4.6		**H11 (see Chapter 4)**
NBHO	22.69	29.24	30.75	5.16	1.24	0.23	0.86	1.42		1.93	1.72	0.84	4.01		3.6		**H3 (see Chapter 4)**
NBHO	27.55	35.9	21.65	3.18	0.97	0.17	0.55	0.93			2.18		4.12				**H7 (see Chapter 4)**
NBSO	31.13	40.85	14.64	2.44	1.00	1.64	0.72	0.52	0.26	1.83	2.10		2.43	2400	4.1	10.3	**{19}**
BSO	32.98	42.80	10.18	3.04	1.74	tr.	0.57	0.75	0.33	3.28	1.30		1.55	10900	4.4	10.4	**{19}**
NBSO	26.33	37.15	13.89	2.89	0.51	4.05	1.55	1.31	0.14	3.50	2.57		6.98	1100			**{68}**
NBSO	25.0	38.8	12.5	2.2	1.3	2.6	1.2	1.4	0.28	6.9	2.6	5.8	13.7	145	6.1		**{263}**
BSO	29.0	41.7	9.4	1.2	0.89	3.2	0.78	1.3	0.23	3.1	3.1	4.1	10.7	127	5.6		{34, 150, 166, 207, **263**}
Bone	32.6	48.5	1.1	0.2	0.1	2.5	0.1	1.0	<0.13	9.1	3.0	1.6	11.9	46	12.9		**{264}**
BSO	34.4	40.85		1.70	1.00	2.80	1.31	3.07		3.12							**{122}**
BSO	28.6	41.80		0.94	1.57	2.32	0.72	0.54	0.25	4.3	3.1	4.4	11.0	150		5.27	**{129}**
BSO	29.34	38.98		2.62	1.59	1.72	0.52								9.4		**{260}**
BSO	30.25	46.17			0.83	2.42	0.31	1.51		3.08							**{215}**
BSO	28.1														6.0		**{217}**
BSO															6.7		**{212}**
BSO	34.8	46.4	10.4	2.3	1.0	3.4	1.4	0.84			2.8				2.86[3]		{**40**, 102}
BSO	34.01	46.39	10.40	2.33	1.02	3.40	1.43	0.84									{153, 177, 235}
BSO	33.9	46.5	10.40	2.32	1.02	3.4	1.43	0.84									{155}
BSO	28.8	46.3	10.4	2.3	1.0	3.4	1.4	0.84					8.7		5.6		{12, 156, 238}
BSO	30.63	50.72	11.17	1.28	0.58	1.64	0.62	0.54									{**91**, 92}
NBSO	29.23	42.03	9.50	1.56	1.02	2.22	1.14	0.85		3.60	3.29	1.59	5.87		6.1		**S6 (see Chapter 4)**
BSO	30.33	44.29	6.77	1.11	0.69	1.77	0.68	1.20		4.02	3.51	1.91	6.41		6.1		**S8 (see Chapter 4)**
BSO	30.35	44.34	6.92	1.10	0.58	1.85	0.63	1.12		4.14	3.51	1.60	6.49		6.3		**S10 (see Chapter 4)**
BSO	30.52	43.25			0.49	2.73	0.31	0.86	0.26	4.40	2.46	2.49	7.44				**{274}**
BSO	29.26	43.39			0.15	1.15	0.05	0.66	0.21	8.46	2.47	2.00	10.90				**{274}**
North Carolina[4]	30.5	49.2	2.0	0.4	0.6	0.5	0.1	1.1	2.5	6.0	3.7	1.0	11.6	114	6.2		**R1 (see Chapter 4)**
Central Florida[4]	32.7	47.3	5.0	1.6	1.2	0.4	0.1	0.6	1.3	3.5	3.9	0.9	7.8	80	4.5		**R2 (see Chapter 4)**
Araxa[4]	36.1	48.2	1.1	0.47	3.0	0.11	0.07	0.33	0.93	1.6	2.2	0.39	1.6	326	1.4		**R3 (see Chapter 4)**

[1] Values are based on 110 °C dry weight. Free H_2O should not be included in totals. Ignition loss may include some CO_2 and F^-.

[2] NBSO = Non-beneficiated soft ore, BSO = Beneficiated soft ore, NBHO = Non-beneficiated hard ore, BHO= beneficiated hard ore, NAC = Solubility in neutral ammonium citrate (second extraction), Citr. acid = Solubility in 1% citric acid, Free H_2O = Weight loss, 105 °C, 1 hour, Ignition loss = weight loss, 1000 °C, 1 hour, tr. = trace, blank cells = not determined.

[3] Presumably P (6.6% P_2O_5) and not P_2O_5 as the authors rank it among the most reactive phosphate rocks such as North Carolina PR.

[4] Source: IFDC

Table 8. Trace elements and radionuclides.

Sample	Li	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Cd	Ba	La	Ce	Pb	U	Th	Source
											mg kg^{-1}										
NBHO			30	48				32	270	19	3646		29		1040	5	132	7	103	16	H3 (see Chapter 4)
NBHO			53	16				39	245	12	3571		29		1139	50	15	4	244	12	H7 (see Chapter 4)
NBHO			68	49				36	226		2956		5		908						H10 (see Chapter 4)
NBHO			74	63				50	364		5276				1277						H11 (see Chapter 4)
NBSO			111	31				29	509	15	5470	5	16		3415	91	129	3	202	56	S6 (see Chapter 4)
BSO			36	29				25	348	6	6703	38			2107	78	146	2	310	126	S8 (see Chapter 4)
BSO			32	3				23	343	7	6535	47			2044	8	112	<1	303	107	S10 (see Chapter 4)
BSO					470		11	17	248					0.1				5			{239}
BSO	9			18	523	23	6	17	299	16	6700			9	4400			16			{122}
BSO		1500			348			61	220	20	4405	27							42	21	{84}
NS			42	16										1				2	390		{267}
NBSO		1080									8800				2240						{263}
BSO		800									11800				1790						{34, 150, 263}
Bone											7010				1790						{263}
BHO		1380							280		4740				2110				310		{234}
BSO		840			310																{153, 177, 235}
BSO					390																{155}
BSO					310																{12, 156, 238}
BSO		120			230																{91, 109}
BSO					470				172					0.1							{274}
BSO					230				201					0.1							{274}

NBSO = Non-beneficiated soft ore, BSO = Beneficiated soft ore, NBHO = Non-beneficiated hard ore, NS = not stated

3.6 The issue of radiation

Early analyses of the soft ore estimated the uranium content to be in the range of 110-370 mg U kg^{-1} {71}, and later GEOMIN {68} cited the content to be 210-850 mg U kg^{-1} averaging 380 mg U kg^{-1}. Other studies gave similar values for both the soft and hard Minjingu phosphates {11, 15, 84, 137, 234}. These levels are considered high when compared with 103 phosphate rock samples from 25 sedimentary phosphorites from around the world {267}.

The natural radioactivity of MPR is mainly originating from ^{238}U and its decay products. ^{232}Th and ^{235}U and their progenies occur only in small concentrations and their contribution to the natural radioactivity is relatively low (less than 20%) {137}. The radionuclides are assumed to be directly related to the apatite phase in the MPR as substitution for Ca (Chapter 4). From radiochemical and radiometric analyses of MPR raw material and fertilizer end and by-products it was found that during production of soluble phosphate fertilizers at the fertilizer factory in Tanga most of the radionuclides were transferred from the MPR raw material to the soluble fertilizer end product (SSP, TSP) {137}. Apparently some of the ^{226}Ra was lost along with the phosphogypsum by-product rendering it unsuitable as building material due to the risk of increased indoor ^{222}Rn levels. Instead it was discharged directly into the Indian Ocean {32}. Modern production of high analysis P fertilizers normally removes almost all radioactive contaminants making the radiation hazard from P fertilization minimal {240}. When MPR is used as directly applied phosphorus source, dissolution of the apatites continues several years after application and it may be assumed that all radionuclides eventually will be released to the soil. Depending on soil properties including organic matter content, clay mineralogy, redox conditions, pH and presence of complexing ligands, most of the radionuclides will be more or less strongly retained by adsorption to inorganic and organic soil constituents leading to a gradual build up of radionuclides in the soil {163}. The long-term consequences for such a build up, including the effects of climate changes and changes in management, are not well known. For instance, an increase in soil pH above 6 after liming increases the potential mobility of U^{6+} species due to complexation with carbonate. Chelation by organic compounds released by plant roots and microorganisms may increase the mobility of radionuclides in the root zone {121}, whereas erosion of soil particles adsorbing radionuclides or MPR application to soils with low organic matter contents may lead to dispersal of radioactivity in the environment.

Makweba and Holm {137} made a theoretical estimation of the effect of several years of application of MPR, SSP or TSP to soils and found that it would only increase the levels of external radiation over the natural background by 2%. Hence, direct radiation exposure due to MPR application is probably insignificant. More important are the pathways of radionuclides from the soil to plants, animals and humans {127}. Radioactive decay products originating from trace amounts of ^{238}U in phosphate fertilizers used in tobacco fields are known to appear in cigarette smoke indicating that such pathways may exist {199}. Pot studies with wheat and beans have been conducted in order to assess the plant uptake of radionuclides in various plant parts but so far the results have not been published (M.M. Makweba, personal communication, 2000). Rothbaum et al. {206} estimated on the basis of uranium recovery in soil samples after addition of a total of 1,300 g U ha^{-1} through P fertilizers during 88 years that the uptake of uranium by wheat grain and straw was less than 10 g U ha^{-1} corresponding to less than 1% uptake during the entire period. The results showed that virtually all the uranium remained in the surface horizon, which was ascribed to absorption by organic matter. Studies of nine long-term fertilization experiments (>50 years) from the USA with TSP application at 30 kg P ha^{-1} yr^{-1} did not show any increase in uptake of U, Ra or Th in various plant parts {163}. However, the average content of uranium in MPR indicates that continued or large single application of MPR would result in a larger addition of U than in the above-mentioned experiments. For instance if 50 kg P ha^{-1} was applied as MPR during 10 years, a total of 1,460 g U ha^{-1} would be applied exceeding the amount applied during 88 years at Rothamsted. Hence, continuous application of MPR through many years may lead to larger accumulation of radionuclides in the soil compared with values normally seen for P fertilized soils.

During the Phosphate Rock Utilization Project (Chapter 6), the activity of ^{226}Ra, ^{232}Th and ^{238}U in soft (S8) and hard (H11) MPR samples (see sample designations in Chapter 4.1) as well as in selected grain and soil samples were determined using a High Purity Germanium detector measuring the gamma radiation in the energy range of 20-2000 keV during 2-4 days. The gammalines at 609 keV, 911 keV and 63 keV were used for determination of ^{226}Ra, ^{232}Th and ^{238}U respectively. The measurements were carried out at the Radiation Research Department at Risø National Laboratory in Denmark. Prior to measurement, the samples were homogenized manually, dried at 100 ºC overnight and weighed into 200 cm^3 plastic beakers placed directly on the detector. The measured activities were related to standard reference samples (NBL 103, New Brunswick Laboratory) containing known activities of U, Th and Ra and the activities of the samples were calculated after correction for self-absorption due to differences in density among the measured samples. The results are presented in Table 9. High activities of ^{226}Ra and ^{238}U are found in the PR samples whereas soil samples show significantly lower activities. With the methods used, activity levels in grain samples were below the detection limit despite measuring times of 4 days. The radionuclide activity of the PR samples are generally comparable with previous figures and indicate that both the soft and hard ore samples contain significant amounts of radionuclides primarily belonging to the ^{238}U decay series {15, 137, 171}. The soil samples from the high rate MPR treatments from Nkundi indicate increased activities of ^{226}Ra and ^{238}U compared with the control or TSP treatment whereas samples from Sasanda only show an increase in ^{226}Ra levels. It seems that the data do not allow for certain conclusions on the effects of MPR application on radionuclide activity in soils probably due to the relatively small amounts applied (2x120 kg ha^{-1} MPR-P corresponding to 1832 kg ha^{-1} MPR or approximately 0.7 kg U ha^{-1}). From the analyses of the grain samples, uptake of radionuclides in maize grains after three consecutive MPR applications (3x120 kg ha^{-1} MPR-P) seems to be very limited.

Table 9. Radionuclide activity of PR, soil and grain samples.

Type of sample	ID/Treatment	^{226}Ra Bq kg^{-1}	^{232}Th Bq kg^{-1}	^{238}U Bq kg^{-1}
MPR				
Soft ore	S8	3444±207	560±38	4367±272
Hard ore	H11	2167±128	943±60	1653±105
Soil (after second season)				
Sasanda	P control	57±4	192±13	98±7
	120 TSP	63±4	197±14	110±9
	120 MPR	64±5	178±12	71±10
Nkundi	P control	21±2	46±4	19±2
	120 TSP	22±2	50±4	19±3
	120 MPR	28±3	50±4	34±5
Grain, (from third season)				
Sasanda	120 TSP	<0.6	<1.1	<2.2
	120 MPR	<0.5	<0.9	<1.8
Nkundi	120 TSP	<0.8	<5.5	<2.9

In a recent study {15}, the activity levels of ^{226}Ra in leaf vegetation harvested near the Minjingu mine showed a very large increase (150-250 times) compared with control samples collected from an area not influenced by the Minjingu phosphates. Also surface water from the mine pit showed increased ^{226}Ra activity levels whereas cattle meat from Minjingu apparently did not show any increase compared with control samples. In contrast to the measurements done by Mustonen and Annanmäki {171}, dosimeter measurements carried out by Banzi et al. {15} near the office buildings at Minjingu over a five year period, revealed that the average ambient radiation dose rate in air was 28 times larger than the average terrestrial dose rate worldwide and about 14 times higher than average dose rates for nearby control sites. The ambient radiation levels found at Minjingu were considered outstandingly high and exceeded the allowed dose limit more than 12 times. Apparently, the Minjingu area rank among sites with the highest known background levels of radiation worldwide. Hence, it seems that the ambient radiation doses received by the mineworkers at Minjingu is imposing a serious health problem, which is not easy to remove by protective measures.

In addition, significant health risks due to the excessive radiation levels are likely to exist in connection with the mining and processing of the ore {11, 15, 137, 171}. High alpha dose to human tracheo-bronchial lymph nodes could result from inhalation and retention, in the nodes, of the highly insoluble Th isotopes, which are present in the mining dust {127}. Inhalation of the dusty product by the mine and factory workers has been of great concern throughout the mine life at Minjingu, Arusha and Tanga and some additional de-dusting equipment have been installed at Minjingu after measurement of radiation doses many times higher than the maximum values stipulated by international norms {171, 200}. However, dusting is still significant during many of the mining and processing operations and only few and inefficient protective measures are used.

Concerns about uptake and retention of radionuclides in the human body are normally related to irradiation of specific internal organs and tissues. As bones normally serve as the major site for long-term retention of radionuclides and as osteoprogenitor cells (stem cells) are lining the bone surfaces and the bone marrow an increased exposure to radionuclides increases the risk of bone sarcomas and leukemias {127}.

Hence, the content of radionuclides in the Minjingu phosphate impose a significant hygienic health problem, which must be thoroughly considered before further use of the phosphates can be recommended. Especially the health problems linked with the mining and processing the phosphates must be improved significantly and the public living around the Minjingu mine must be correctly informed about the precautions to be taken. A number of recommendations on improved safety measures have already been given {171}. Also farmers applying the phosphate rock in the field should be instructed about safety in a similar fashion as with the use of pesticides. For the direct application of the phosphates to soils more investigations should estimate the long-term environmental effects and the pathway from rock to soil, plants, animals and humans. The calculations should also take into account the various age and occupational factors, which characterize the various steps in the utilization of the phosphates and which may influence the effective dose rates.

4 Mineralogical investigations carried out during the Phosphate Rock Utilization Project

The previous studies of the Minjingu deposit indicated some important differences between the hard and soft ore types in terms of petrographical, chemical and mineralogical composition (Chapter 3.5). They also indicated that the geochemistry and phosphate mineralogy of the Minjingu deposit is different from most other guano derived or marine sedimentary phosphate deposits. Although the very detailed descriptions of the thin sections of the soft and hard ore samples provide representative and highly valuable information on the petrography of the Minjingu ore there is still need of more detailed mineralogical analyses as the exact phosphate mineralogy is still not fully understood. Especially clarification of the previous discrepancies between the apatite mineralogy and chemical solubility is important in order to understand the relation between phosphate mineralogy and suitability for direct application. Considering the wish to exploit the large resources of the hard ore at Minjingu in the future and the previous difficulties in beneficiating the raw material, more information on the petrographical and mineralogical composition of the hard ore is also needed.

The objectives of the mineralogical study presented here are to:

Characterize ore samples taken from various layers of the soft and hard ore type with respect to:

a) mineralogy of the main P bearing minerals
b) apatite stoichiometry (apatite unit cell formula based on Ca^{2+}, Na^{+}, Mg^{2+}, Sr^{2+}, PO_4^{3-}, CO_3^{2-}, F^- and OH^-)
c) *a* and *c*-cell dimensions and crystal size
d) qualitative characterization of accessory minerals and cementing agents (colloidal silica, dolomite, lime, feldspars, micas, quartz, clay minerals and organic matter)
e) content of radionuclides, trace elements and heavy metals (U, Ra, Th, Sr, Se, V, As, Cd, Pb, Cr, Hg, Cu, Zn)
f) solubility in neutral ammonium citrate
g) possibilities for beneficiation on the basis of the mineralogical composition and arrangement of the P bearing minerals.

4.1 Materials and methods

Ore samples

Several rock samples were collected from various parts of the deposit (Figure 11, Table 10 and Photo 1). Five samples (S1-S5) originate from the profile wall from the southeastern corner of the mining pit in the northern section where several of the main soft phosphate layers, representing a significant time span in the deposition, are visible (Photo 1 and Photo 5). Seven samples (H1-H5, H7, H8) were collected from the hard ore on the northern side (Photo 1 and Photo 6), one soft sample (S6) from the current mining area (Photo 3) and one sample entirely consisting of large non-guano fossil bones (S7). A number of reference samples were included for comparison including: a) beneficiated samples of both the hard (H10, H11) and soft (S8, S10) Minjingu, b) beneficiated carbonate fluorapatites (francolites) from North Carolina (R1) (IFDC stock no. R232,48), Central Florida (R2) (IFDC stock no. R231,77) and a beneficiated weathering product (R3) (francolite) originating from the Brazilian igneous deposit of Araxa, and c) two igneous fluorapatites (R4, R5) from Kola (Russia) and from the Gardiner Complex in East Greenland respectively.

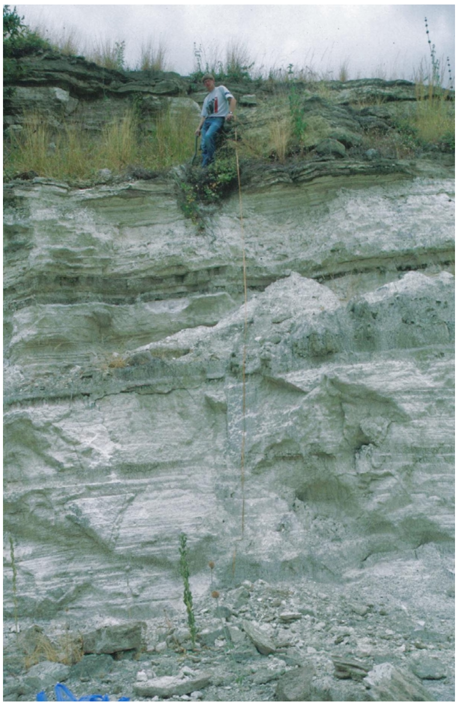


Photo 5. The vertical profile of the soft ore.

Photo 6. Hard ore type.

Beneficiation of the Minjingu samples were done at the factory at Minjingu and at The Southern and Eastern Mineral Development Centre (SEAMIC) in Tanzania {234} for the soft and hard ore samples respectively. The two North American and the Brazilian phosphate rocks were provided by the International Fertilizer Development Centre (IFDC), and the two igneous rocks from the mineralogical collection of Copenhagen University.

Also ground samples of the soft and hard Minjingu respectively compacted with triple superphosphate (TSP) at a ratio of 1:1 total P, and a sample of the interlayering clay from the current mining area were included.

Representative sub-samples of the raw ore materials were obtained by crushing and random picking among coarse gravel sized (2-6 cm) lumps of each sample followed by further crushing and grinding to less than 250 µm.

X-ray diffraction

Unoriented powder diffraction patterns were obtained using a Siemens 5000 diffractometer and CoK_{α} radiation (average wavelength of $K_{\alpha 1}$ and $K_{\alpha 2}$, λ=1.791 Å) from a tube operated at 40 kV and 40 mA. CoK_{β} radiation and interfering background scatter were removed with monochromator. Divergence, antiscatter and receiving slits were 1 mm, 0.6 mm and 0.1 mm wide respectively. Medium resolution diffractograms (0.6° 2θ min^{-1} at 0.05° 2θ increments, 10-90° 2θ) were made from all samples for qualitative assessment of the major accessory minerals and for preliminary evaluation of the apatite variability. High-resolution diffractograms (0.05° 2θ min^{-1} at 0.05° 2θ increments, 29-67° 2θ) were prepared from selected samples where the goniometer alignment was monitored using silicon in 1-2% concentration as internal standard. Interplanar *d*-spacings was calculated using Bragg's equation and the lattice constants were then calculated using a least squares method solving the general expression for hexagonal crystals according to the following equation {142}:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}}} \tag{4}$$

where the Miller indices used were 002, 300, 202, 310, 222, 312, 213, 321, 410, 402 and 004. The calculations were made using the freeware UnitCell with *d*-spacings as input variable and minimizing the sums of squares of the residuals in 2θ {86}. Unit cell refinement was done by excluding potential deleterious observations as suggested by Holland and Redfern {87}. Average *a* and *c* values and the 95% confidence interval were calculated for each sample. Estimates of the apatite crystal size of the samples were calculated using the Scherrer line broadening technique from the 002 reflections of the apatite obtained from the high resolution scans. Instrumental broadening was estimated from the 111 reflection of the internal silicon standard. Structurally bound CO_3^{2-} was estimated from the high-resolution scans using the peak pair difference of both $\Delta 2\theta_{(004)-(410)}$ and $\Delta 2\theta_{(300)-(002)}$ according to Schuffert et al. {231}.

Infrared absorption (FTIR)
Fourier Transform Infrared absorption spectra were obtained using the KBr pellet method with 0.35 mg of sample in 300 mg KBr compressed at 150 MPa in an evacuated die. Spectra were recorded over the range 4000 to 400 cm^{-1} on a Perkin Elmer FTIR 2000 spectrometer. Absorption spectra were used for qualitative assessment of the accessory minerals present, and for the carbonate apatites for calculation of the CO_2-index based on the ratio of intensities of the C-O and P-O absorptions, which is found to be directly proportional to the weight ratio CO_3/PO_4 {141}. The C-O absorption is the average intensities of the 1455 and 1428 cm^{-1} bands measured from the background base at 1800 cm^{-1}, and the P-O absorption is based on the intensity of the 602 cm^{-1} band measured from the background base at 700 cm^{-1}. Presence of hydroxyl was also determined from FTIR spectra of samples dried at 110 °C for 16 hours.

Chemical characterization
Some selected samples were subjected to total chemical analysis using X-ray fluorescence (XRF) {125}. The following elements were measured: Si, Al, Fe, Ca, Mg, K, Na, Mn, Ti, P, V, Cr, Cu, Zn, Sr, Y, Zr, Ba, La, Ce. Total C and S were determined by measurement of the infrared absorption by CO_2 and SO_3 respectively, evolved from combustion of a powder sample at 1350 °C in an oxygen flow {55}.

Determination of F^- was done by dissolving a sub-sample with dilute perchloric acid (2.5 M $HClO_3$) for 16 hours followed by measurement of F^- using a F^- specific electrode {56}.

Solubility in neutral ammonium citrate (NAC) was done by extracting 0.5 g of ground PR (<50 µm) under continuous shaking on a hot water bath with 50 cm^3 of hot (65 °C) 1 M neutral ammonium citrate during 1 hour followed by centrifugation and repeating the treatment with ammonium citrate. NAC extractable P was measured in both extracts using the molybdenum blue method.

Petrographic examination
Undisturbed samples of both the hard and soft ore were impregnated in a polyester resin according to Murphy {170} with a more detailed description of specific methods by Msolla {167}. After cutting, polishing and carbon coating, the embedded samples were subjected to scanning electron microscopy (SEM) in order to describe the type, texture, size, shape and arrangement of the mineral constituents and their mode of agglomeration. SEM analysis using a microprobe technique with energy dispersive X-ray (EDX) provided compositional information about the various mineral components. SEM analysis was also carried out on non-

impregnated platinum-coated samples of H7 and S6 in order to get three-dimensional photographs of the sample constituents.

Other methods
A dispersed sample of S8 was examined by transmission electron microscopy (TEM) and S4 and H7 by nuclear magnetic resonance (NMR) for ^{31}P and ^{29}Si.

4.2 Results

The XRD analysis showed that apatite was the dominating mineral phase in all samples except for H1, which contained large amounts of quartz (Table 10). Quartz, K-feldspars, calcite and dolomite were identified in some of the soft ore samples whereas only quartz, K-feldspars and Na-Ca feldspars were found in the hard ore. Clay minerals were not identified by XRD in any of the phosphate samples presumably due to the low amount and the fact that only unoriented specimens were scanned. Airdry and glycerol treated oriented scans of the interlayering green clays treated with 0.2 M EDTA at pH 11 for 5 hours at 100 °C in order to remove calcite and some dolomite/apatite {22} indicated an expanding 2:1 layer silicate mineral (smectite) with a shift of the main peak from 14 Å of the air dry sample to 18 Å of the glycerol treated sample.

Examples of high resolution X-ray diffractograms of a soft and hard ore sample and two reference samples are given in Figure 13. The crystalline fluorapatite of igneous origin (R5) is showing high intensity reflections with narrow, well separated peaks resolving both $K_{\alpha1}$ and $K_{\alpha2}$ at higher angles and the 211 and 112 peaks around 37.4 °2θ. In contrast to the igneous fluorapatite the microcrystalline to cryptocrystalline carbonate apatites (S4, H2, R2) generally show broader peaks due to the smaller crystal size, which is also demonstrated by the data in Table 10. Average crystallographic *a*-cell dimension of the soft and hard samples of 9.356±0.006 Å and 9.370±0.004 Å respectively, indicate that the soft Minjingu phosphates are of the low to medium carbonate substituted excess fluorine francolites whereas the hard Minjingu phosphates are of the fluorine deficient francolites or very low carbonate substituted excess francolites (Chapter 2.2).

Figure 14 show examples of FTIR spectra of two reference samples as well as soft and hard Minjingu samples. Compared with the crystalline fluorapatite (R5) the characteristic CO_2 absorption doublet at 1455 and 1428 cm^{-1} and the C-O band at 865 cm^{-1} is a strong evidence of the presence of CO_3^{2-} substituting for PO_4^{3-} in the carbonate apatites {141, 209}. The increased absorption and the shift of the P-O stretch at 573 cm^{-1} of the fluorapatite towards 566 cm^{-1} for the carbonate apatites is also regarded diagnostic for the increased CO_3^{2-} substitution {141}. A similar shift in the 601 cm^{-1} band in the fluorapatite to 605 cm^{-1} for the carbonate apatites is also seen. The fact that the 566 cm^{-1} P-O band for all samples equals or is less intense than the 605 cm^{-1} P-O band as well as the missing O-H stretching and bending bands at 3560 and 632 cm^{-1} for dried samples respectively, suggest that none of the samples belong to the hydroxyapatite series. However, as the OH stretching mode around 3550 cm^{-1} is highly sensitive to the polarisation direction, i.e. it's expression changes dramatically with the orientation of the crystals, it could be possible to overlook it. A small absorption band at 3535 cm^{-1} for the fluorapatite (R5) suggests that minor amounts of F^- have been replaced by OH^- {209}. Molecular water adsorbed to the apatites and which is seen as broad absorption bands around 1624 and 3460 cm^{-1} for the non-heated samples virtually vanishes after heating.

Among accessory minerals quartz were identified in most of the hard samples (H1, H2, H5, H7, H8, H10, H11) by strong absorption bands at 799, 777, 694, 502 and 470 cm^{-1} and dolomite in S2 and S7 at 877 and 727 cm^{-1}.

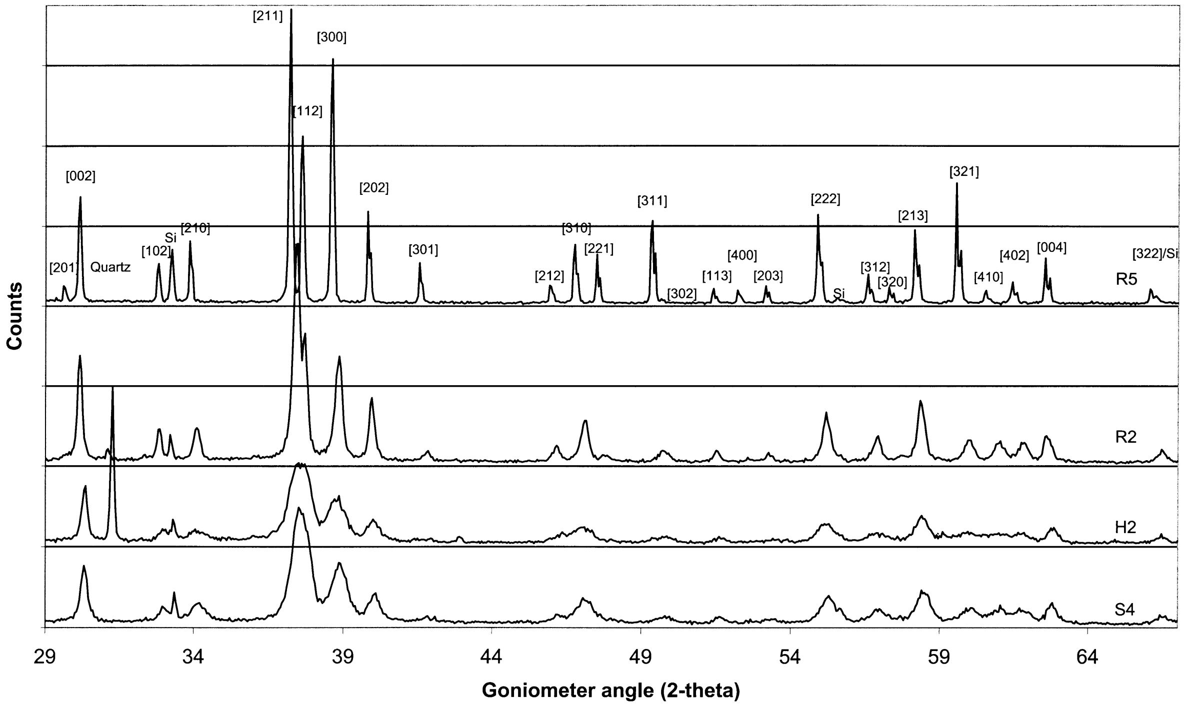


Figure 13. X-ray diffractograms of S4, H2, R2 and R5.

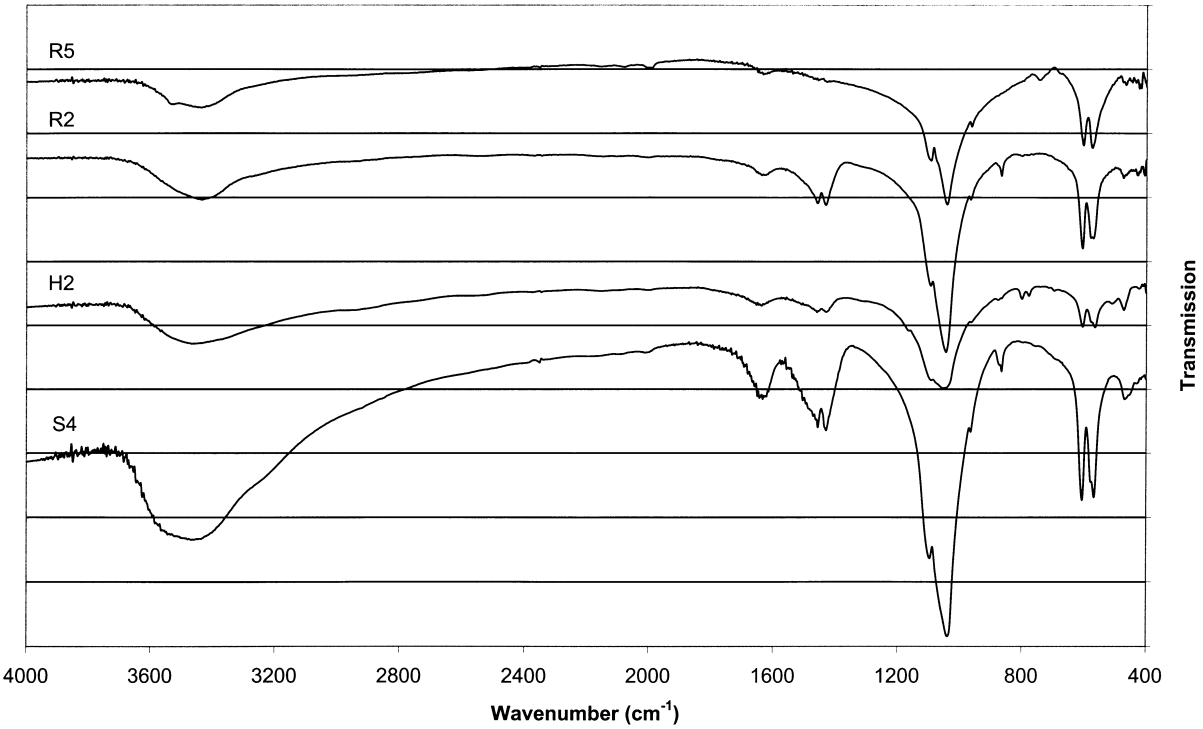


Figure 14. FTIR spectra of S4, H2, R2 and R5 (air dry).

Table 10. Crystallographic properties and estimation of carbonate content in soft and hard Minjingu and reference phosphate rocks.

Sample Id.	Description	Identified minerals[a]	*a*-cell dimension (Å)[b]	*c*-cell dimension (Å)	Crystallite size (nm)	CO_2 $\Delta 2\theta$[c] (300)-(002) (%)	CO_2 $\Delta 2\theta$ (004)-(410) (%)	CO_2-index	CO_2 (%)
		XRD	XRD	XRD	XRD	XRD	XRD	IR	Ignition
S1	Bottom of profile + 12 m	A, F	9.348±0.004	6.891±0.004	100	4.6	3.0	0.63	-
S2	Bottom of profile + 6 m	A, D, C, (F, Q)	9.342±0.005	6.892±0.008	120	4.7	2.2	0.77	-
S3	Bottom of profile + 4 m	A	9.355±0.005	6.891±0.006	110	3.6	2.2	0.66	-
S4	Bottom of profile + 2 m	A	9.359±0.011	6.893±0.012	120	2.2	2.5	0.59	-
S5	Bottom	A, F	9.361±0.002	6.891±0.002	100	3.0	1.7	0.59	-
S6	Mining area, June 99	A, F	9.364±0.007	6.893±0.007	80	3.7	2.0	0.59	3.6
S7	Fossil bone fragments	A, D	9.362±0.006	6.888±0.006	180	4.2	3.1	0.85	-
S8	Commercial concentrate	A, D	9.362±0.006	6.899±0.007	80	2.0	3.0	0.73	4.0
S10	Commercial concentrate	A, F	9.355±0.006	6.890±0.007	80	2.5	3.0	0.64	4.1
	Average soft rock		9.356±0.006	6.892±0.002	108±24	3.4±0.8	2.5±0.4	0.62[d]±0.03	-
H1	Hard clay-chert conglomerate	Q, A (F)	9.373±0.007	6.898±0.008	150	2.1	1.8	-	-
H2	Grey porous sample	A, Q	9.375±0.005	6.890±0.006	170	0.2	0.5	0.61	-
H3	White-grey porous conglomerate	A, F, Q	9.364±0.004	6.884±0.004	100	2.3	0.7	0.61	1.9
H4	Hard clay-like sample	A, Q	9.370±0.004	6.892±0.005	160	0.6	1.2	0.52	-
H5	Grey-white porous conglomerate	A, Q, F	9.362±0.006	6.888±0.006	220	1.4	1.3	0.68	-
H7	Grey-white porous conglomerate	A, Q, F	9.371±0.008	6.886±0.007	170	1.2	2.1	0.50	-
H8	Chert-like	A, Q	9.361±0.008	6.892±0.008	130	1.4	2.1	0.57	-
H10	Ground non-beneficiated hard rock	A, Q, F	9.375±0.003	6.892±0.004	140	0.6	0.4	0.58	2.0
H11	Ground beneficiated hard rock	A, Q, F	9.375±0.006	6.888±0.007	240	0.1	0.4	0.53	2.8
H	Average hard rock		9.370±0.004	6.890±0.003	164±33	1.1±0.6	1.2±0.5	0.58±0.05	-
R1	North Carolina (sedimentary francolite)	A, Q	9.328±0.005	6.888±0.005	250	5.2	4.6	0.59	10.7
R2	Central Florida (sedimentary francolite)	A, Q	9.356±0.003	6.908±0.003	150	4.5	4.5	0.47	4.4
R3	Araxa (weathered igneous fluorapatite)	A	9.359±0.010	6.915±0.016	100	-	-	0.28	-
R4	Kola (igneous fluorapatite)	A	9.383±0.004	6.892±0.004	640	-	-	-	-
R5	Greenland (igneous fluorapatite)	A	9.386±0.009	6.898±0.014	680	-	-	-	-

[a] Identified minerals listed in decreasing quantity as inferred from X-ray diffractograms. A=apatite, C=calcite, D=dolomite, F=feldspar, Q=quartz (brackets indicate trace amounts).

[b] With 95% confidence interval.

[c] Based on the method of Schuffert et al. {231}.

[d] S2, S7 and S8 are left out of average as carbonates were identified by XRD.

Dash = not determined.

Figure 15 shows scanning electron micrographs of the soft ore samples S6 and S1 at different degrees of magnification. In agreement with the previous observations (Chapter 3.5.1) the soft ore consists of a very porous matrix of biogenic fragments (skeletal remains), which in places are surrounded by or embedded in a mass of clays and/or collophane particles. The bone fragments, which in S6 range between 0.01 to 0.25 mm in size generally have a compact aspect and an elongated habitus and preserve much of the original bone morphology. Most of the bone fragments are broken into smaller pieces lying close to each other like a jigsaw puzzle indicating slight post-depositional stress presumably caused by slumping of the sloping sediments close to the hill {226, 261}. The collophane and collophane-clay mixtures differ morphologically from the bone fragments and occur both as heterogeneous porous masses surrounding the compact fragments (Figure 15 bottom) and as mixtures of clay particles and microcrystalline apatite crystals (Figure 15 top). The silicate clays are in parts forming the matrix in which the phosphate particles are embedded (Figure 15 middle). Only few accessory minerals were identified by the SEM analysis indicating that they occur only sporadically. Transmission electron microscopical analysis confirms the presence of extremely small apatite crystals (20-60 nm) (Figure 16).

An example of the hard ore is presented in Figure 17. It consists of a porous matrix of various primary mineral grains and skeletal fragments as well as a secondary platy mineral, which tends to fill the spaces between the larger fragments (seen as needle like features in Figure 17). In contrast to the soft ore, the bone fragments are sub-angular to rounded with more porous and fibrous aspect preserving only little of the original bone morphology indicating a more advanced weathering stage. Silica is primarily present as free quartz and in feldspar grains. Neither clays, calcite, dolomite nor colloidal silica were identified indicating that other substances such as the platy minerals may also contribute to the cementing of the hard ore.

Microprobe analyses were categorized into five classes depending on sample morphology, probing area and elemental composition (Figure 18, Table 11). Observations high in Ca and P and low in Si typically showed fluorapatite composition whereas observations high in Si and without any significant Ca and P represent the pure silicate clays. In between these two extremes were a number of observations showing intermediate levels of Ca, P and Si indicating that the probing area included varying amounts of both apatites and clays. An arbitrary limit of 1.7% SiO_2 based on a visual distribution of the observations was used to distinguish between apatite and apatite-clay mixtures (Table 11). In the hard ore samples, the microprobe analyses did not indicate measurements on pure clays but the figures indicate the presence of a clay-apatite mixture as both Si, Al, Fe, K and Mg increases with decreasing P and Ca content (Figure 19). The composition of the silicate clays in the soft and hard ore samples, estimated from the intercept with the y-axis corresponding to the apatite-free silicate clay, indicated that the clays were potassium saturated dioctahedral montmorillonite and beidellite respectively. The following average formula units were calculated from the data in Table 11:

Montmorillonite in the soft ore samples : $K_{0.8}(Al_{0.7}Fe(III)_{0.3}Mg_{1.1})[Si]_4O_{10}(OH)_2$
Beidellite in the hard ore samples: $K_{0.4}(Al_{1.5}Fe(III)_{0.4}Mg_{0.2})[Si_{3.5}Al_{0.5}]O_{10}(OH)_2$

The platy mineral observed in the hard ore sample (Figure 20) did not show apatitic composition and was therefore classified separately (Table 11). As the composition of the plates with significant amounts of Ca, Mg, Al, Fe, Sr and P is quite unusual it is assumed that the probing area included other phases than just the platy mineral giving average composition of at least two minerals. High resolution XRD diagram of the <50 µm fraction of H7 indicated presence of montgomeryite ($Ca_4MgAl_4(PO_4)_6(OH)_4 \cdot 12H_2O$), which partially agree with the composition of the platy mineral (Figure 21).

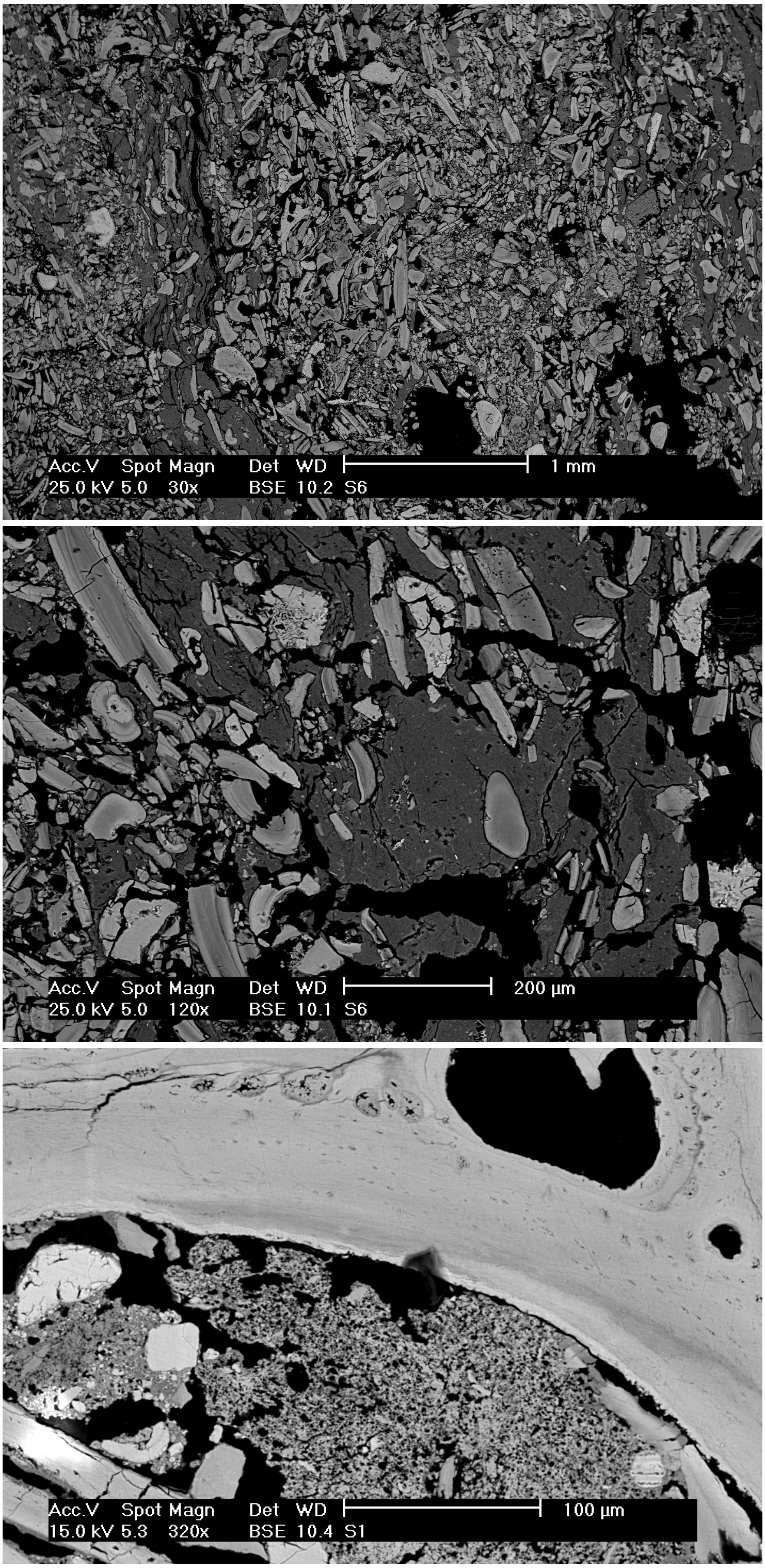


Figure 15. Scanning electron micrographs of soft ore samples S6 (top and middle), and S1 (bottom).

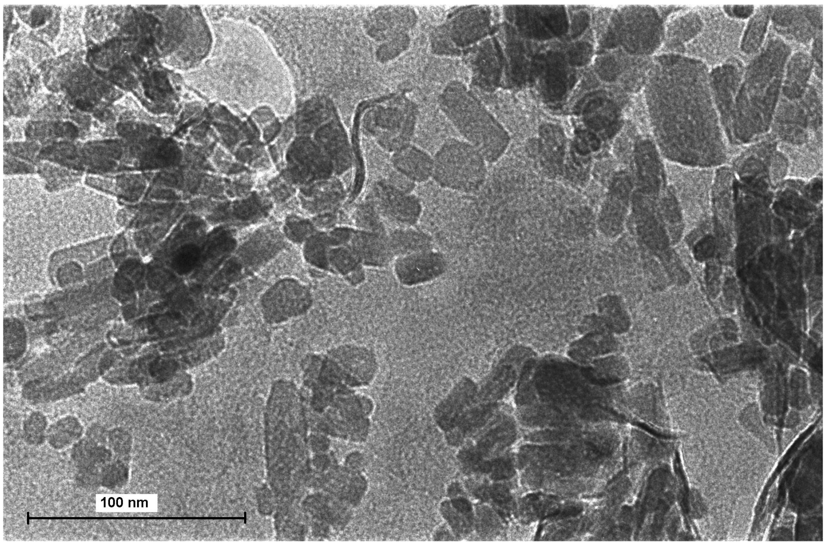


Figure 16. Transmission electron micrographs of the soft ore sample S8.

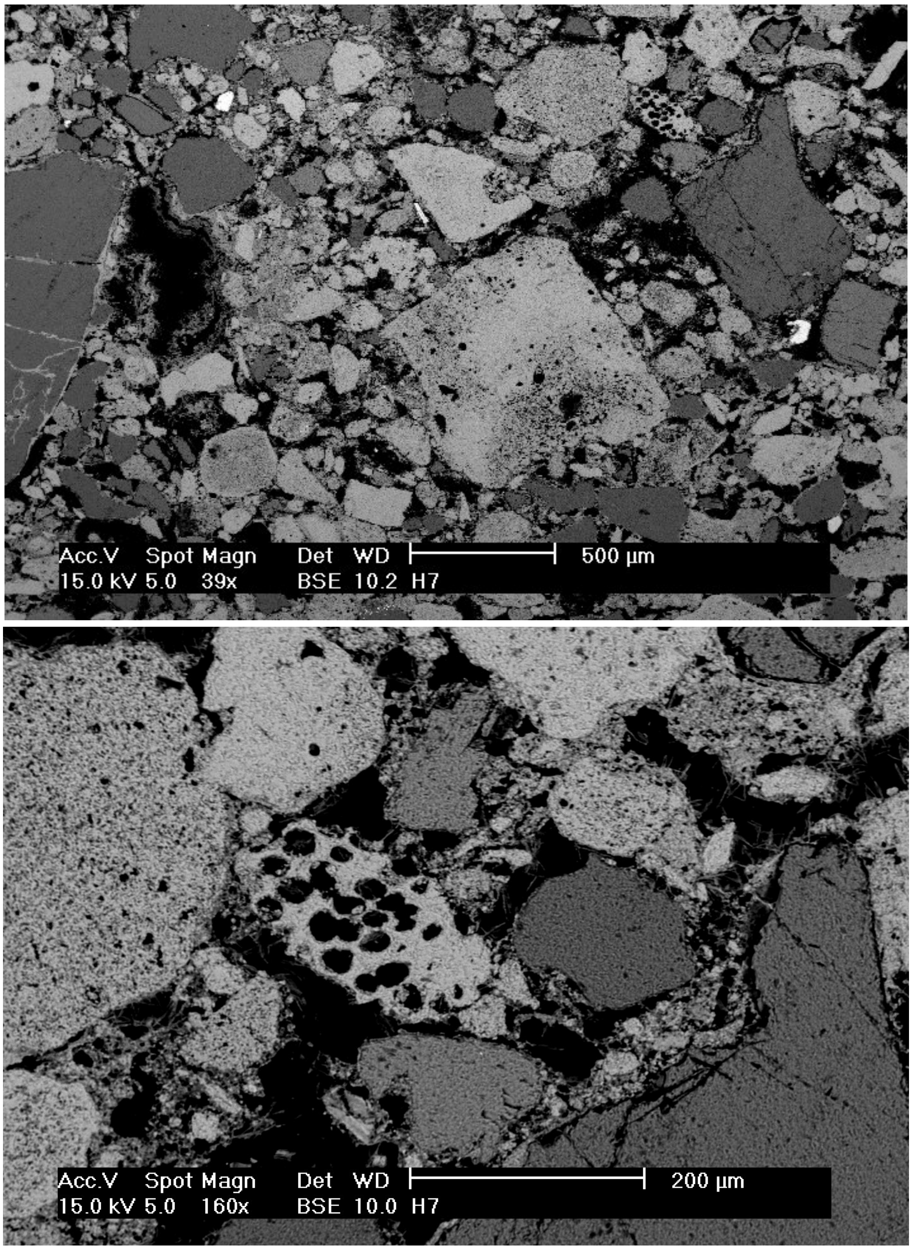


Figure 17. Scanning electron micrographs of the hard ore sample H7.

The NMR studies indicated that P present in the soft and hard ore samples entirely belonged to the alkaline earth orthophosphates {72}. However, different intensities of the sidebands between the two sample types indicated a higher crystallinity of the hard ore samples compared to the soft ore samples. A slight chemical shift for Si in the PR samples compared with a quartz standard was probably a result of the presence of clay minerals in the PR samples.

Table 11. Average elemental composition of the SEM-microprobe analysis of the various components of the soft and hard ore.

	Soft ore fragments			Hard ore fragments				
	Bone	Collophane	Clay	Bone	Clay	Plates	K-feldspar	Ca-Na-feldspar
Subset	SiO_2<1.7	SiO_2<1.7	SiO_2>1.7	SiO_2<1.7	SiO_2>1.7	SiO_2<4.3	-	-
No. of obs.	n=27	n=40	n=96	n=53	n=26	n=21	n=2	n=6
Chemistry								
P_2O_5	37.01	36.78	-	38.73	-	41.47	0.30	0.39
CaO	56.39	56.35	-	54.08	-	23.62	0.31	5.68
SiO_2	0.14	0.26	62.3	0.38	56.5	2.02	64.60	61.93
Al_2O_3	0.01	0.00	9.7	0.84	26.9	9.17	18.18	23.07
Fe_2O_3	0.07	0.09	5.9	1.13	8.4	16.08	0.16	0.13
MgO	0.46	0.46	11.2	0.12	2.4	3.79	0.00	0.02
K_2O	0.04	0.06	7.4	0.06	5.6	0.14	15.47	0.23
Na_2O	0.91	0.90	-	0.78	-	0.19	0.78	8.29
TiO_2	0.14	0.17	-	0.14	-	0.55	0.02	0.03
SrO	0.88	0.92	-	0.56	-	2.78	0.00	0.07
SO_3	0.03	0.07	-	0.01	-	0.00	0.03	0.07
CO_2	n.d.	n.d.	-	n.d.	-	n.d.	n.d.	n.d.
F^-	3.8	3.8	-	3.0	-	0.00	0.00	0.00
Cl (mg kg^{-1})	760	380	-	950	-	500	70	150
Cd (mg kg^{-1})	790	730	-	710	-	520	0.58	370
U (mg kg^{-1})	330	110	-	250	-	470	1240	170

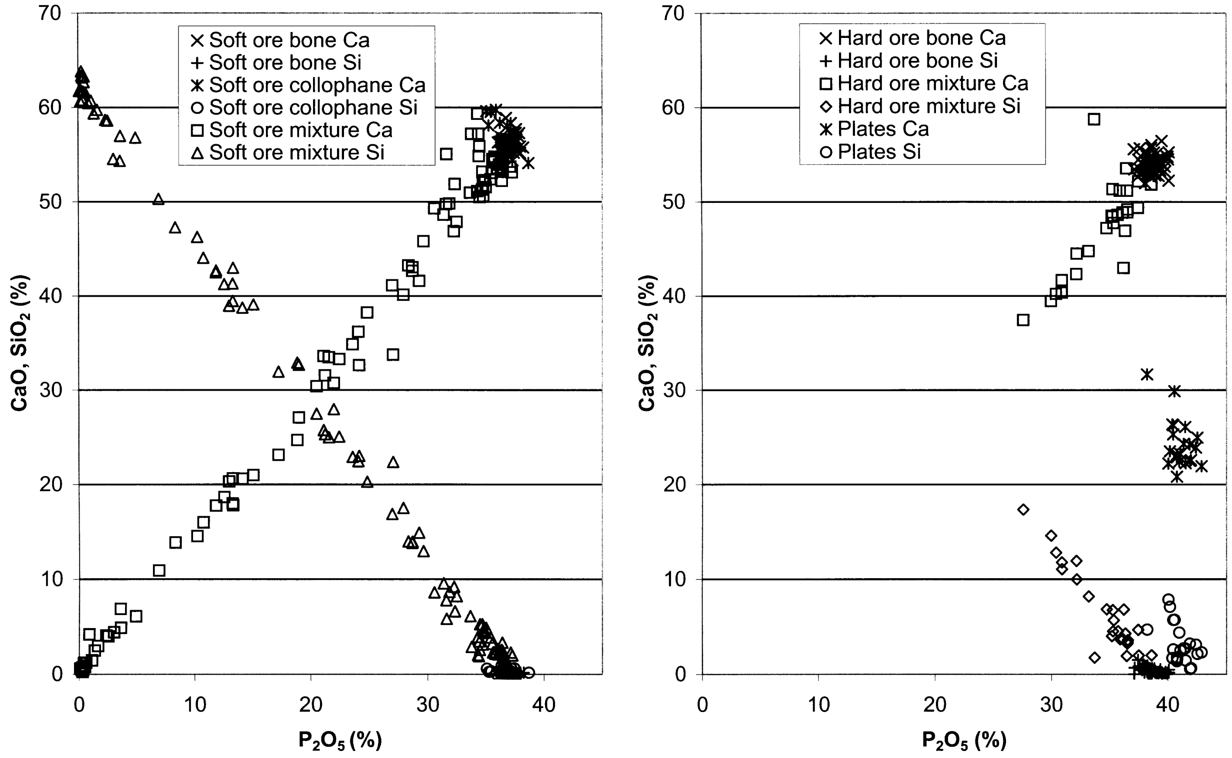


Figure 18. Microprobe based CaO and SiO_2 versus P_2O_5 content of the various fragments found in the soft (left) and hard (right) ore samples.

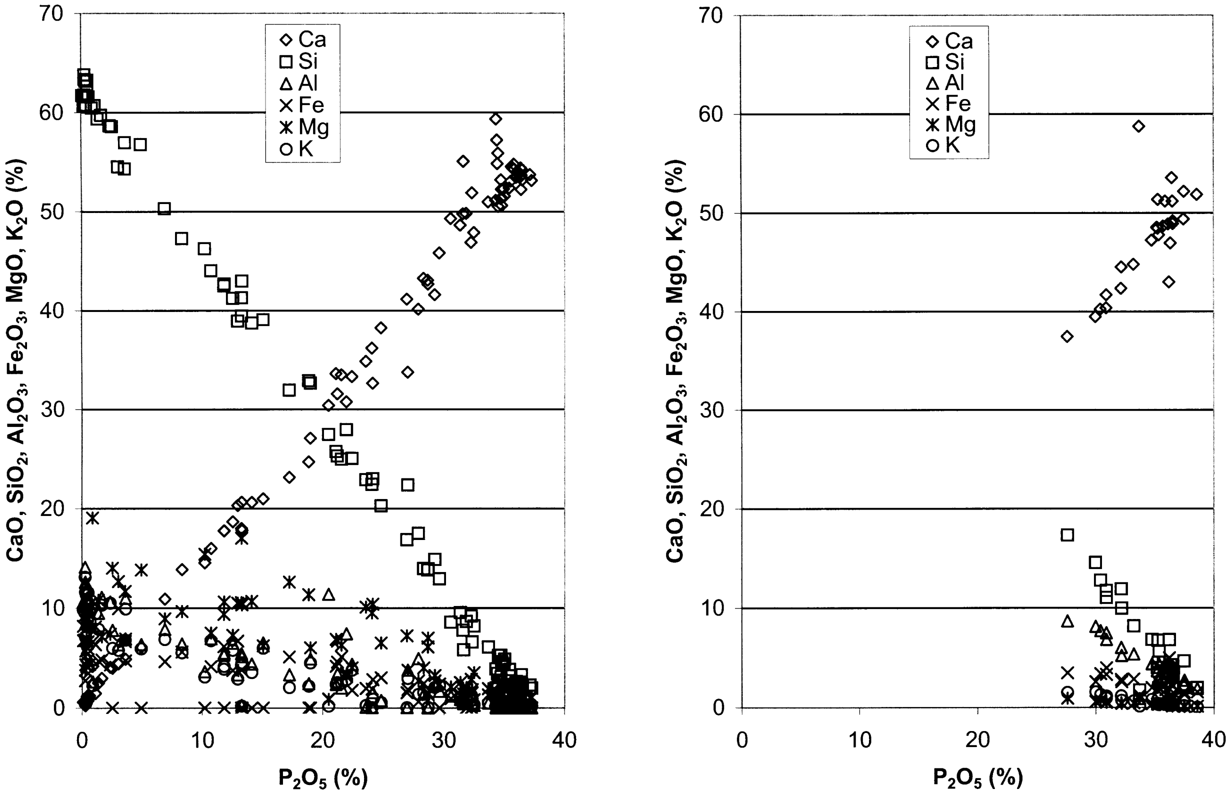


Figure 19. Microprobe based CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO and K_2O content versus P_2O_5 of the apatite-clay mixtures from the soft (left) and hard (right) ore. Intercept with y-axis corresponds to apatite-free clays.

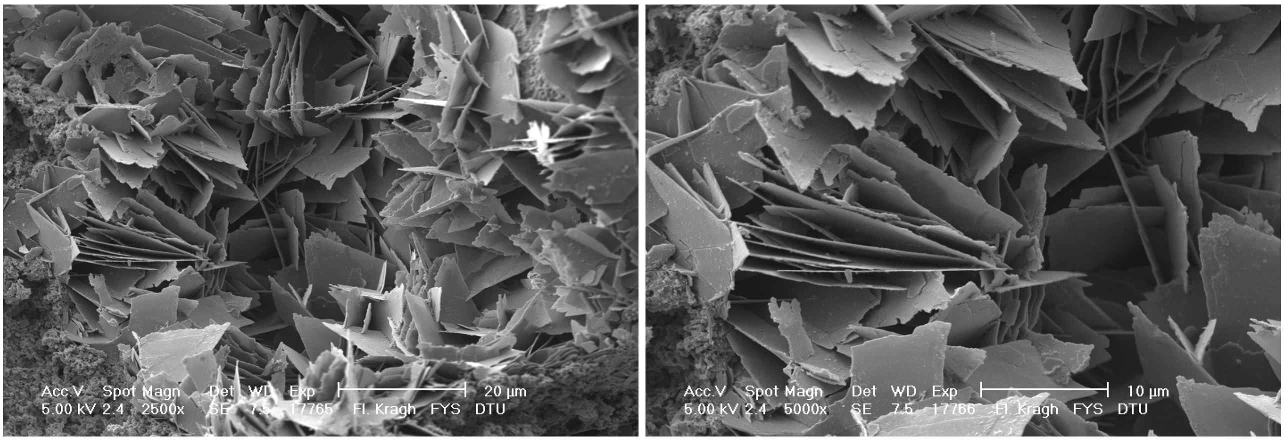


Figure 20. Scanning electron micrographs of the unknown platy mineral.

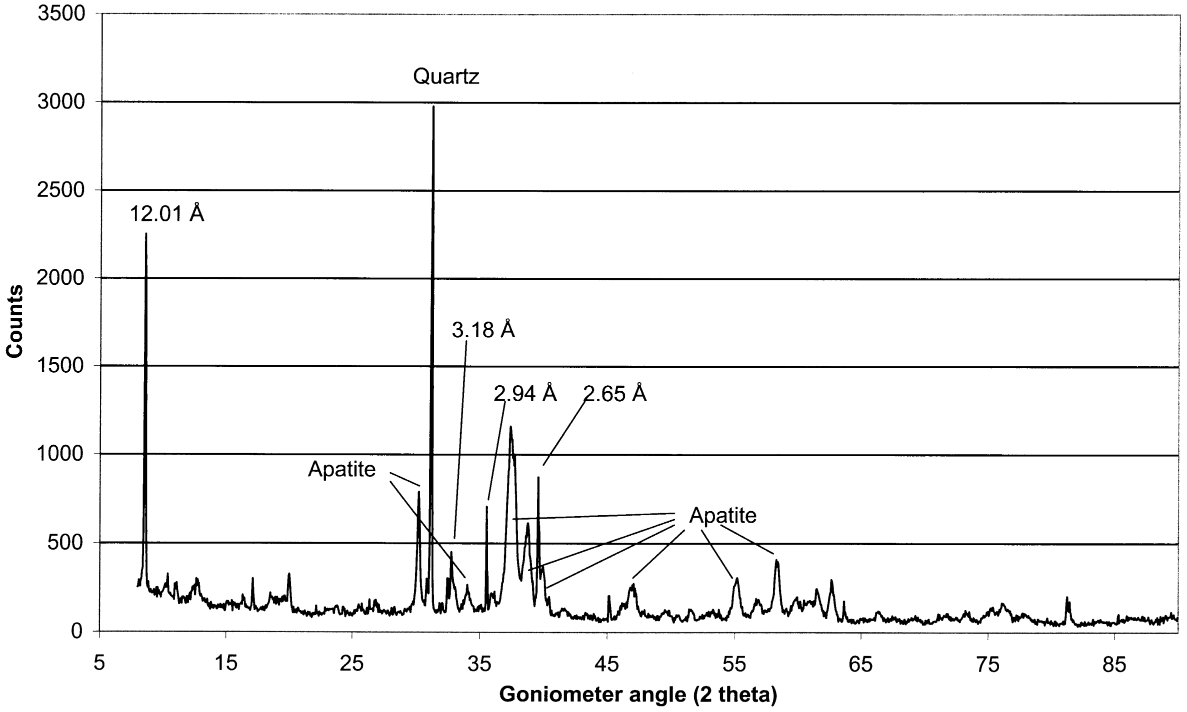


Figure 21. Unoriented high resolution XRD diagram of the less than 50 µm fraction of H7.

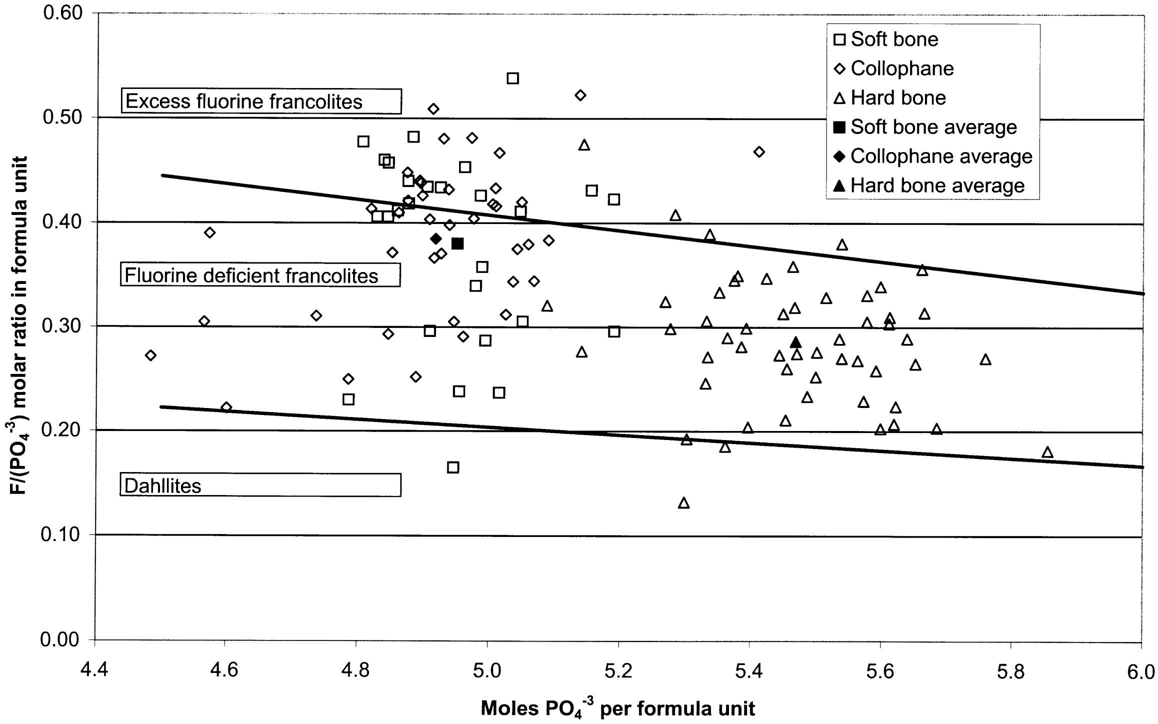


Figure 22. Molar ratio F/PO_4^{3-} versus moles PO_4^{3-} per formula unit for the individual microprobe observations belonging to the three categories in Table 12. The upper solid line separates fluorine deficient (below) from excess fluorine francolites (above). The lower solid line separates dahllites (below) from fluorine deficient francolites (above) according to the arbitrary limit of 1% F.

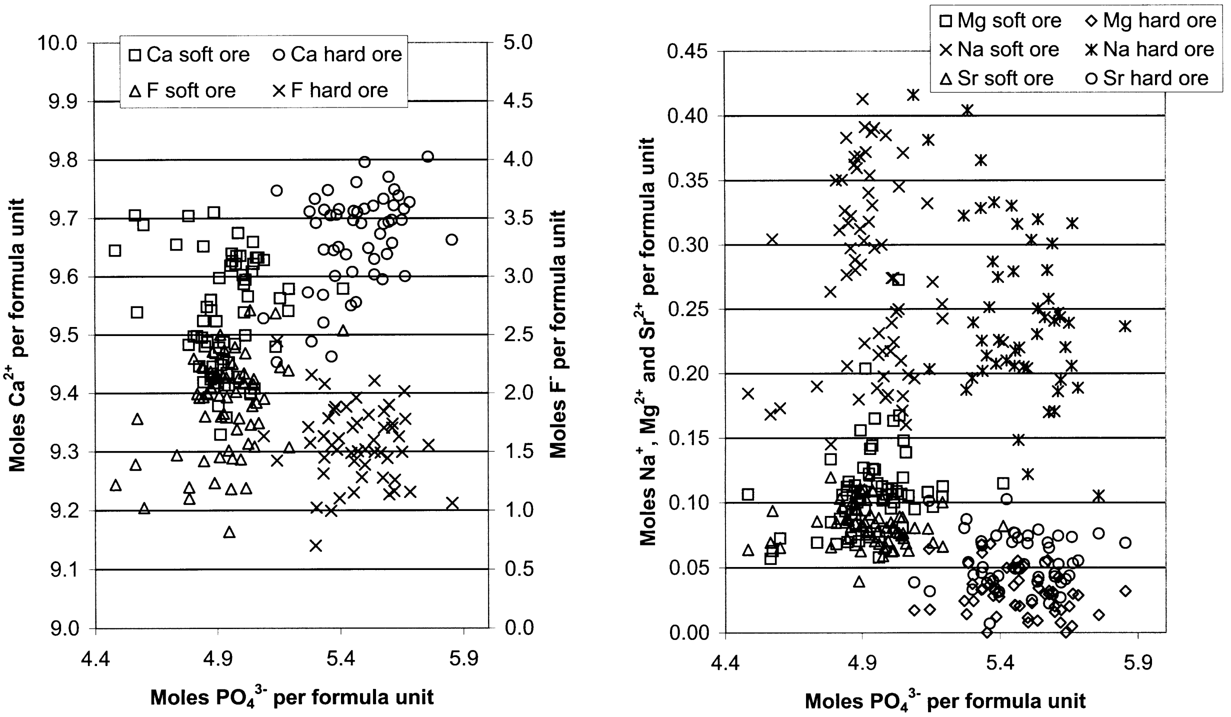


Figure 23. Molar contents of Ca^{2+} and F^- (left) and Na^+, Mg^{2+} and Sr^{2+} (right) per formula unit versus molar content of PO_4^{3-} for the individual microprobe observations belonging to the three categories in Table 12.

Based on the elemental composition of the microprobe observations of the various apatite fragments the content of cations and anions assuming 10 atoms in the Ca sites was calculated (Figure 22-Figure 23 and Table 12). In the calculations it was assumed that all Ca, Sr, Mg, Na, P and F enter the apatite phase whereas the remaining elements were ignored as assumed being either minor substituents in the apatite (Cd, U, S, Cl) or parts of a small fraction of silicate clays or other minerals (Si, Al, Fe, K, Ti).

Table 12. Average content of cations and anions based on 10 atoms in the Ca sites of the carbonate apatites.

Apatite type	Formula unit
Soft bone	$Ca_{9.535}Mg_{0.108}Na_{0.277}Sr_{0.081}[(PO_4)_{4.951}(CO_3)_?](F_{1.881}(OH)_?)$
Collophane	$Ca_{9.532}Mg_{0.108}Na_{0.275}Sr_{0.085}[(PO_4)_{4.918}(CO_3)_?](F_{1.898}(OH)_?)$
Hard bone	$Ca_{9.664}Mg_{0.030}Na_{0.251}Sr_{0.054}[(PO_4)_{5.469}(CO_3)_?](F_{1.563}(OH)_?)$

4.3 Discussion

XRD, FTIR, total chemical and SEM microprobe analyses presented in Chapter 4.2 together confirm that the main phosphate minerals in both the soft and hard Minjingu samples belong to the francolite series.

Both total chemical composition of bulk samples (Table 7) and SEM microprobe analyses (Figure 22 and Table 12) indicate that the hard ore is dominated by fluorine deficient francolites with less than 2 mol F^- per formula unit (carbonate hydroxyfluorapatites). For the soft ore samples, the microprobe analyses suggest a slight fluorine deficiency whereas total chemical analyses of bulk samples in general suggest a slight excess fluorine content. However, calculating an exact stoichiometric formula on the basis of bulk ore analyses is normally complicated by the presence of other mineral phases, and as the F/P_2O_5 ratio separating excess fluorine francolites from fluorine deficient francolites varies with molar content of PO_4^{3-} as shown in Figure 22, it may be difficult exactly to determine fluorine deficiency from the data in Table 7. In any case, it seems that the soft ore samples are being at the transition between fluorine deficient and excess fluorine francolites with an average fluorine content ranging close to 2 mol F^- per formula unit.

Previous morphological studies (Chapter 3.5.1) as well as the SEM pictures presented in Chapter 4.2 show that bone fragments are important constituents in both the soft and hard ore samples indicating that the fish bones were only partly digested and dissolved during ingestion and deposition of the guano. Originally the bone fragments may have consisted of dahllites, which may also have led to the previous suggestions that the Minjingu phosphates consist of dahllites and/or hydroxyapatites {97, 234} (Chapter 3.5). However, all previous analyses including the analyses presented by the authors suggesting the presence of dahllites show fluorine contents above 1% indicating that the Minjingu francolites have undergone a post-depositional diagenetical alteration similar to that observed for fish skeletons under marine conditions (Chapter 2.2). Present levels of F^- ranging between 400-1600 mg F^- dm^{-3} in other similar alkaline lakes in the Eastern Rift Valley (Lake Bogoria, Lake Magadi, Lake Natron) indicate that levels of fluorine in the environment may have been very high {225}. These high levels of fluorine have also led to the suggestion by Schlüter et al. {103} that swollen fossil fish bones (so called Tilly bones) found in the phosphorites at Minjingu are the result of hyperostosis, a biochemical reaction to high fluorine contents in the environment leading to higher than normal fluorine content in the bone apatites. Whether the rather high fluorine content of the bone fragments, at least compared to dahllite and most other guano derived phosphates, is a result of biochemical incorporation of high amounts of fluorine in the bone apatites of the fish and birds due to high levels of fluorine in Lake Manyara or is a result of secondary enrichment and substitution after deposition of the phosphates remains unclear, but it seems possible that both processes may have influenced the fluorine content of the apatites. On the basis of present salinity and paleolake volumes, Somi {250} estimated the salinity of the former paleolakes and suggested that Lake Manyara was virtually fresh (0.15-0.4 ‰) during the first and second lake stage. However, according to Schlüter et al. {229}, stromatolites are normally restricted to alkaline and highly alkaline conditions suggesting that Lake Manyara already during the first lake stages had an alkaline hydrochemistry.

The lower fluorine content of the hard ore is a remarkable feature and may possibly reflect a shorter period of submergence during which the diagenetic changes could happen. From the studies of the various lake stages it seems that the hard ore was only submerged during the first lake stage whereas the soft ore layers apparently were submerged during both the first and second stage (Chapter 3.1). The almost exact match between the second lake level (997-1006 m above sea level) and the border line between the hard and soft phosphates (995-1000 m) may partly explain the genetical, morphological and mineralogical difference between the two ore types.

The molar content of PO_4^{3-} in the francolites shown in Figure 22 indicate a significant substitution for PO_4^{3-} as the amount is significantly lower than required for full occupation of the tetrahedral sites. As no other of the PO_4^{3-} substituting anions occur in any significant amount (Table 11) and as FTIR spectra confirm the presence of CO_3^{2-} in the tetrahedral site (Figure 14), it is suggested that CO_3^{2-} or (CO_3^{2-}+F^-) substitute PO_4^{3-} in the tetrahedral sites in a 1:1 ratio resulting in an average carbonate substitution at the tetrahedral sites of approximately 1 and 0.5 mol CO_3^{2-} per formula unit for the soft and hard ore samples respectively (Table 12).

From Table 12 it is seen that Mg^{2+}, Na^+ and Sr^{2+} substitute a substantial amount of Ca^{2+} in both the soft and hard ore francolites. Apparently Mg^{2+} and Sr^{2+} substitution is less pronounced in the hard ore fragments whereas the Na^+ level on average is more or less the same between the two main ore types. The amount of Mg^{2+} and Na^+ substitution in the Minjingu samples corresponds quite well with the amounts found in other sedimentary excess francolites of marine origin with similar degree of carbonate substitution supporting that Mg^{2+} and Na^+ are directly linked to the carbonate substitution where especially Na^+ seems to play an important role in maintaining electroneutrality {53, 142}. On average about 25% and 50% of the reduction in negative charge caused by carbonate substitution is compensated by Na^+ for Ca^{2+} substitution in the soft and hard ore samples respectively. However, no correlation was found between Na^+ and PO_4^{3-} or Na^+ and $(CO_3+F)^{3-}$ per formula unit indicating that other factors also influence the francolite stoichiometry.

The relatively high content of Sr^{2+} is a remarkable characteristic of the Minjingu samples. Although Sr^{2+} has been found to substitute for Ca^{2+} in igneous apatites it is not a common feature of sedimentary francolites {246}. Inland phosphate deposits such as Minjingu may have formed under much more anomalous biogeochemical conditions compared to marine phosphorites due to the geographical limitation of the system. The intense volcanic activity including possibly hydrothermal activity in the area during Pliocene and Pleistocene followed by weathering may this way have introduced a number of specific elements such as F^-, Sr^{2+} and U^{4+} to the biogeochemical cycle of Lake Manyara, which then could be incorporated in the apatites through diagenetic alterations or during biochemical build up of the bone structures {11}. The correlation between P content and Sr^{2+} and U^{4+} of hard ore samples analysed by XRF at SEAMIC {234} indicate that both Sr^{2+} and U^{4+} are associated with the apatite (Figure 24) although some Sr^{2+} may also be associated with the unidentified secondary platy minerals found in the hard ore samples (Table 11). Similar contents of Sr^{2+} in modern and fossil bones suggest that it primarily enters the apatites during the life of the animals {195}. Although Cd^{2+} is often associated with apatites as substituent for Ca^{2+}, the high contents as estimated with the SEM microprobe (Table 11) are in strong disagreement with previous total elemental analyses (Table 8) suggesting that the SEM estimates of Cd are defective.

Assuming a 1:1 substitution of CO_3^{2-} for PO_4^{3-} the stoichiometric formulas in Table 12 can be recalculated on the basis of the general formula:

$$Ca_aMg_bNa_cSr_d(PO_4)_e(CO_3)_{(6-e)}F_f(OH)_{(2(a+b+d)+c-e-12-f)} \quad (5)$$

resulting in the formulas in Table 13. The variation in stoichiometric composition based on the microprobe observations and the theoretical composition of the three types are presented in Table 14 and Table 15.

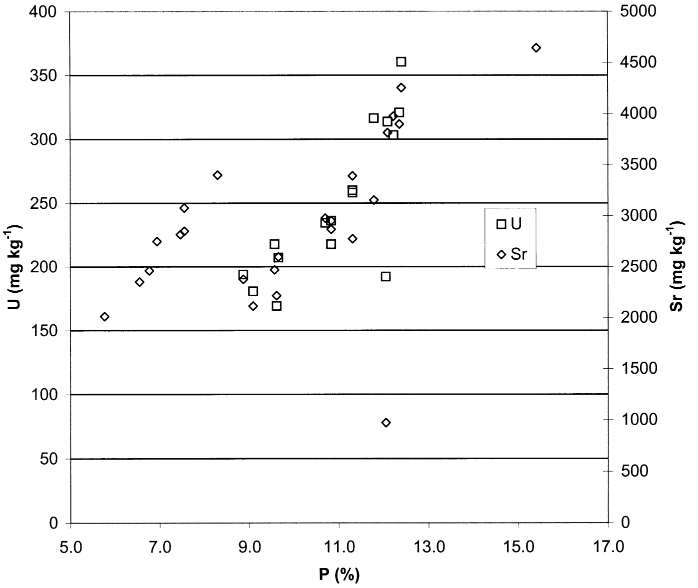


Figure 24. Strontium and uranium versus phosphorus in various hard ore samples analysed by SEAMIC {234}.

Table 13. Average stoichiometric formula of the various francolite fragments from Minjingu.

Apatite type	Formula unit	Molecular weight, g mol^{-1}
Soft bone	$Ca_{9.535}Mg_{0.108}Na_{0.277}Sr_{0.081}(PO_4)_{4.951}(CO_3)_{1.049}(OH)_{0.891}F_{1.881}$	1019
Collophane	$Ca_{9.532}Mg_{0.108}Na_{0.275}Sr_{0.085}(PO_4)_{4.918}(CO_3)_{1.082}(OH)_{0.910}F_{1.898}$	1018
Hard bone	$Ca_{9.664}Mg_{0.030}Na_{0.251}Sr_{0.054}(PO_4)_{5.469}(CO_3)_{0.531}(OH)_{0.718}F_{1.563}$	1021

Table 14. Average stoichiometry and 95% confidence interval of the soft and hard apatites based on the SEM microprobe analyses.

Element	Soft bone		Collophane		Hard bone	
		s		s		s
Ca	$9.535^a \pm 0.037$	0.09	$9.532^a \pm 0.032$	0.10	$9.664^b \pm 0.023$	0.08
Mg	$0.108^a \pm 0.016$	0.04	$0.108^a \pm 0.010$	0.03	$0.030^b \pm 0.005$	0.02
Na	$0.277^a \pm 0.030$	0.07	$0.275^a \pm 0.023$	0.07	$0.251^a \pm 0.020$	0.07
Sr	$0.081^a \pm 0.004$	0.01	$0.085^a \pm 0.006$	0.02	$0.054^b \pm 0.006$	0.02
PO_4	$4.951^a \pm 0.044$	0.11	$4.918^a \pm 0.053$	0.17	$5.469^b \pm 0.043$	0.16
CO_3	$1.049^a \pm 0.044$	0.11	$1.082^a \pm 0.053$	0.17	$0.531^b \pm 0.043$	0.16
OH	$0.891^a \pm 0.193$	0.49	$0.910^a \pm 0.173$	0.54	$0.718^a \pm 0.097$	0.35
F	$1.881^a \pm 0.180$	0.46	$1.898^a \pm 0.125$	0.39	$1.563^b \pm 0.092$	0.33

Letters after average values in each row indicate statistical significant differences at 5% level.

The two soft ore fragments (bone and collophane) are almost identical in average composition despite the large difference in morphology indicating a strong relation between the two fragment types. Even the variation in stoichiometry is similar (Table 14). It may therefore be suggested that the collophane aggregates in the soft Minjingu samples represent post-depositional precipitates formed from soluble phosphates originating from the guano leachates whereas the bone fragments probably due to the limited residence in the birds stomach avoided excessive dissolution during digestion. The bone fragments, which eventually were conveyed into the lake may this way have acted as primers for the precipitation of collophane francolites in the lake which hydrochemical composition apparently favoured the formation and precipitation of phosphate minerals primarily belonging to the carbonate apatite group.

The theoretical compositions in Table 15 are generally in agreement with the total elemental analyses shown in Table 7 except for calcium, which seems to be consistently lower than predicted from the theoretical values. There are no indications from Table 8 or Table 11 whatsoever, that other cations such as Ba^{2+}, Mn^{2+}, K^+, U^{4+} or rare earths should substitute for Ca^{2+} to any significant extent and the reason for the low Ca^{2+} content in the bulk samples or the higher Ca^{2+} content of the SEM microprobe analyses is puzzling.

Table 15. Theoretical composition based on stoichiometric formula (%).

		Apatite type	
	Soft bone	Collophane	Hard bone
CaO	54.54	54.43	54.62
MgO	0.44	0.44	0.12
Na_2O	0.88	0.87	0.79
SrO	0.85	0.89	0.57
P_2O_5	35.78	35.55	39.13
CO_2	4.70	4.85	2.36
F^-	3.64	3.67	2.99
H_2O (OH^-)	1.63	1.67	1.30
OH^-, F^- correction^a	-2.30	-2.33	-1.87
CaO/P_2O_5	1.52	1.53	1.40
F/P_2O_5	0.102	0.103	0.076

[a] Two F^- and two OH^- substitute for one O^{-2}.

The total CO_2 content of the bulk samples (Table 7) agrees quite well with the theoretical composition supporting the assumption that CO_3^{2-} substitute PO_4^{3-} according to formula (5).

The estimates of structurally bound CO_3^{2-} based on the XRD peak pair difference also suggest the average degree of CO_3^{2-} substitution to be 2-3 times larger in the soft compared with the hard ore samples. However, the estimates are highly variable within each ore type and the estimates based on the two different $\Delta 2\theta$

ranges are not well correlated. For the samples analysed, the high angle 402 peaks were generally identifiable but relatively broad and without a well-defined maximum indicating a relatively large variation in CO_3^{2-} substitution within the same sample. As the peak pair method is based on the crystallographic changes in *a*-cell dimension caused by CO_3^{2-} for PO_4^{3-} substitution in the main structure, the method is likely to fail for the fluorine deficient apatites in which CO_3^{2-}, as mentioned in Chapter 2.2, is able to substitute simultaneously at two different sites in the crystal structure. The peak pair method therefore seems to give relatively uncertain estimates on structurally bound CO_3^{2-} content for the Minjingu samples.

The CO_2-index calculated from the major FTIR C-O and P-O bands (Table 10) generally indicate that the Minjingu samples are among the medium to highly carbonate substituted excess fluorine francolites and so the figures do not agree at all with values typically found for fluorine deficient francolites {141}. This may either indicate the possible interference from free carbonates giving high background absorbencies around the C-O doublet or indicate an anomalously high degree of carbonate substitution. It is remarkable that even for those samples in which no carbonates were detected by XRD (S1, S3-6, S10 and all H samples, Table 10) the CO_2-index indicate a carbonate substitution corresponding to 0.86 and 0.79 mol CO_3^{2-} per formula unit for the soft and hard ore samples respectively {141, 268}.

The apparently high degree of carbonate substitution in the soft ore is in strong contrast to the measured *a*-cell values, which indicate a very low carbonate substituted excess francolite (Table 10 and Chapter 2.2). Even if the soft ore is regarded as a fluorine deficient francolite the carbonate content is disproportionally high compared to other similar francolites (Figure 2). *A*-cell values of the soft ore samples seem only to agree well with fluorine content (Figure 3) but the very high NAC solubility (around 2.6% P (6% P_2O_5)) is strongly contradicting the soft ore being a fluorine deficient francolite with *a*-cell values around 9.356 Å (Figure 5). This disagreement between *a*-cell values, NAC solubility and carbonate substitution is a remarkable and very crucial characteristic of the soft ore Minjingu indicating that the mineralogy and probably also the mode of formation is different from all other known francolites.

Carbonate substitution at the hexad sites, which could explain some of the differences is not demonstrated clearly on the FTIR spectra but the presence of a small inflection around 876-872 cm^{-1} on the C-O band at 865 cm^{-1} for most of the Minjingu samples, which is absent in R2 indicate that some of the CO_3^{2-} enters a different configuration than the normal tetrahedral sites in the apatites. This could either be attributed to the ν_2 vibrational mode of CO_3^{2-} in the hexad sites {50} or to minor amounts of calcite {209}, which were also detected by XRD in some of the soft samples. However, the total content of carbonates as estimated by ignition (Table 10) do not indicate excessive amounts of carbonates in addition to that substituting for PO_4^{3-}.

As can be seen from Table 13 the amount of OH^- required for electroneutrality is significant for both the soft and hard ore samples and one would expect OH^- contents of this size to be recognized by FTIR, which apparently was not the case {142}. Hence, it seems that filling up the hexad sites with OH^- may not be appropriate. What exactly provides electroneutrality is not known but both Ca vacancies as well as CO_3^{2-} substitution in the hexad site may contribute to this {53}.

Figure 22 and Figure 23 suggest that the francolites generally exhibit a large variation in fluorine and phosphorus content resulting in a large range in crystallographic properties. Hence, in addition to the suggestion by van Kauwenbergh {263} that the phosphates contain fragments with highly different reactivity (Chapter 3.5.1) Figure 22 also indicate that large differences in reactivity may exist even within the same kind of fragments.

A number of characteristics may therefore contribute to the discrepancies between *a*-cell values and NAC solubility:

1. Relatively small average crystal size compared with other carbonate substituted francolites (Table 10).
2. Anomalously high amount of structurally bound CO_3^{2-}, which may partly be residing in the hexad sites.
3. Ca^{2+} vacancies in the crystal structure distorting the crystal structure.
4. Significant amounts of structurally bound Sr^{2+}, which due to the larger ionic radius (1.12Å) compared with Ca^{2+} (0.99) may lead to distortion of the apatite structure and deviations from the general *a*-cell values typically found for francolites.
5. Apatite fragments of various kinds (bone and collophane) representing various crystal sizes and specific surface areas.

In contrast to the soft ore, the hard ore samples conform well to the general picture of the fluorine deficient francolites (Table 10, Figure 2, Figure 3 and Figure 5). This is a remarkable characteristic, as it seems that the hard ore represents a more weathered stage with less carbonate compared to the soft ore. Decarbonation with time is generally observed for francolites of marine origin and is interpreted as the transformation towards the thermodynamically more stable fluorapatite {145}. The presented geological and mineralogical data suggest that the distinction between the two rock types is due to different genetical histories. The hard phosphates probably experienced an intensive recrystallisation process with removal of parts of the carbonate due to the much longer exposure to the leaching influence by meteoric water while the soft rock stayed longer in a carbonate-phosphate-fluoride saturated solution. The shorter period of submergence of the hard rock may also explain the lower degree of substitution of OH^- by F^- compared with the soft rock and hence the more hydroxyapatitic composition. Figure 25 presents the proposed genetical relation between the soft and hard ore at Minjingu.

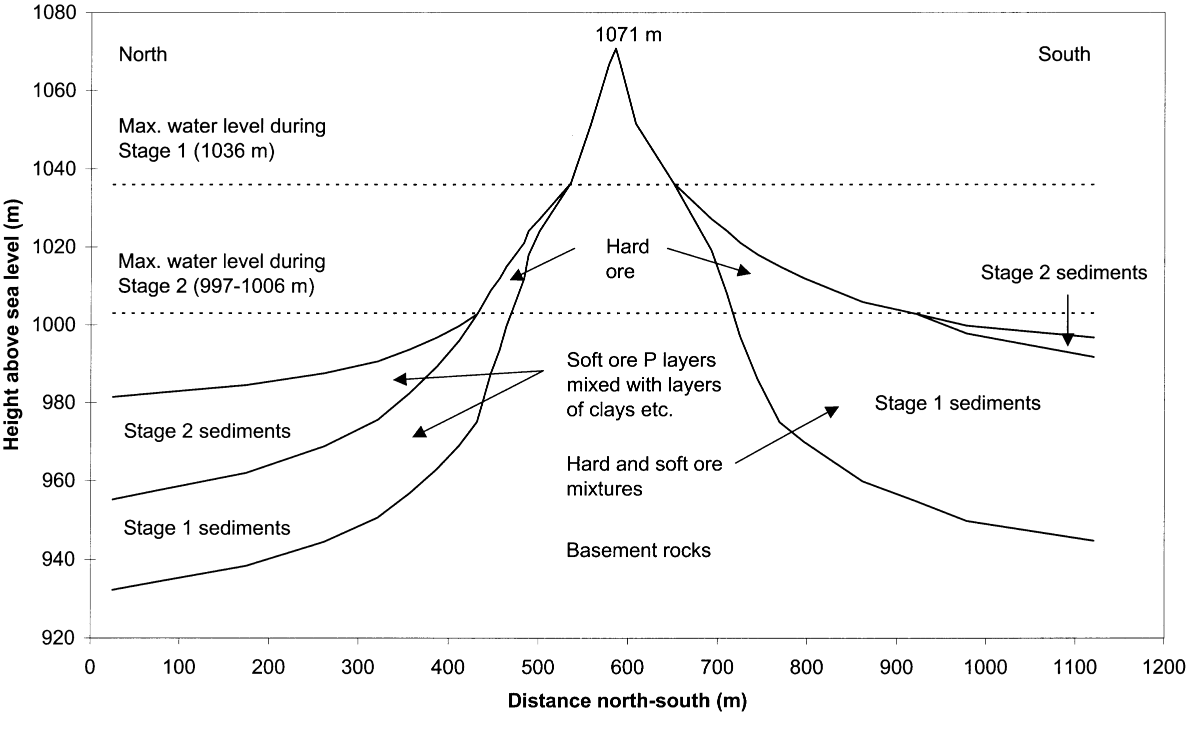


Figure 25. A north-south transect through the Minjingu summit showing the relation between the soft and hard ore phosphates.

4.4 Conclusion

The Minjingu phosphate deposit is an example of a continental sedimentary phosphorite, which has formed under conditions that are distinctively different from the marine phosphorites and even other guano derived phosphate deposits. There seems to be no doubt whatsoever, that guano particles are the main sources of the phosphates. All previous surveys, mineralogical and petrographical analyses including investigations on paleofossils, depositional facies and interpretations of the paleoenvironment indicate that guano produced by cormorants staying in large numbers on the isolated paleoisland of Minjingu is the source of the phosphates. Together with quartz, feldspar, mica, hornblende and other mineral grains originating from the weathering and erosion of the crystalline basement, the soluble phosphates and insoluble biogenic fragments were conveyed into the lake during periods of tropical rains forming the clastic phosphate sediments found around the Minjingu Hill and other similar nearby hills, which during Pleistocene projected over the much larger Lake Manyara. The stratification of the phosphate and clayey layers in the northern section of the deposit support the idea of sub-aqueous sedimentation in calm waters. The clay layers, which are primarily composed of expanding 2:1 layer silicates (montmorillonites) indicate alternating formation and sedimentation rates due to geologic or climatic events and it is very likely that they have formed in situ as a result of the contemporary volcanic activity in the area north of Lake Manyara.

It seems likely that the phosphate layers have formed during a relatively short period of time (<25,000 years) and only during a period where the Minjingu Hill was entirely surrounded by water corresponding to the first lake stage and first phase of the second lake stage. The exact age of the sediments is still relatively uncertain but 110,000-135,000 years have been proposed on the basis of studies of the various lake stages. After regression of the lake to the second lake stage, the hard phosphates were exposed whereas the soft phosphates remained submerged during the entire second lake stage. This has led to various petrographical, mineralogical and chemical differences between the two ore types.

The phosphates of the hard ore are fluorine deficient francolites consisting of weathered fragments of biogenic origin embedded in a matrix of detrital mineral grains, clays, calcite and colloidal silica, which gives the hard ore a cemented, hard and sometimes conglomeratic appearance. The reactivity, i.e. solubility in NAC, of the hard ore phosphates corresponds well with other fluorine deficient francolites with similar F^- content and reflects a medium to highly reactive phosphate rock suitable for direct application.

The soft ore phosphates are on average fluorine deficient francolite but ranges between fluorine deficient and excess fluorine composition. They mainly consist of original bone fragments and collophane particles embedded in a soft porous matrix of clays, calcite and dolomite. The structurally bound carbonate content of the soft ore phosphates is in strong disagreement with *a*-cell values normally found for fluorine deficient or excess fluorine francolites and also the high NAC solubility does not agree with the previously derived relations between crystallography and reactivity. The apparently high reactivity has been confirmed by field experiments and the soft Minjingu phosphates are normally regarded very suitable for direct application, at least in terms of agronomic performance.

This discrepancy between mineralogy and reactivity may be at result of a complicated crystallography of the soft Minjingu phosphates including a number of factors: a) high amounts of structurally bound carbonate leading to lattice instability and large free energy of dissolution, b) generally small crystallites compared with other highly reactive francolites and the presence of collophane representing a highly reactive and cryptocrystalline francolite, c) possible presence of Ca^{2+} vacancies in the apatite crystal structure, and d) significant amounts of structurally bound Sr^{2+}, which may distort the crystal structure due to the larger ionic radius compared to Ca^{2+} leading to the anomalous XRD determined *a*-cell values.

The high fluorine content of the Minjingu phosphates compared to dahllites indicates a post-depositional transformation with the fluorine derived from the lake water. The geographic location of Lake Manyara close to extensive areas of volcanic activity and the closed nature of the system have led to a highly different hydrochemical composition compared to sea water. It is suggested that the F^-, Sr^{2+} and U^{4+}, which occur as important constituents in the phosphates originate from hydrothermal activity or weathering of the extrusive alkaline rocks surrounding the lake.

5 Previous agronomic experimentation with the Minjingu phosphate rock

5.1 The MPR agronomic database

Since the discovery of the deposit in 1956 a large number of agronomic studies have been conducted with Minjingu phosphate rock and MPR derived products. During the initial explorative work at Minjingu in 1957-1961 about 20 tons of soft rock from zone B3 was distributed for agronomic trials at agricultural research institutes in Kenya and Tanzania {185}. However, although probably still existing in the archives of those institutes most of that information is not readily available. The first known agronomic results published in international agricultural journals were those of Anderson {5, 6}, Scaife {222} and Bromfield et al. {33}. Among the early work are also results from a pot study using MPR and TSP made from MPR as P source for wheat {71}. From the mid 1980s more work has been published especially from Sokoine University of Agriculture, Morogoro, Tanzania, but also from other agricultural research institutes in Tanzania, Kenya and elsewhere (Table 17 and Table 18).

In order to assess the agronomic potential of MPR on the basis of the previous experimental work all available agronomic data with MPR and MPR-related products were compiled into a MPR agronomic database. The only two criteria, which were required, were presence of a control for P and that same P rates were used for both the MPR product as well as the soluble P source. The content and present status of the database is presented in Table 16. At the initial stage of data entering no attempt has been made to exclude strange looking observations in the raw data. Adjustments and exclusion of deviant observations should preferably be done during the statistical interpretations after consultation of the original information sources for further explanations.

It is the intention that the database serves as a central future reference for all agronomic experimentation with the MPR and whenever new data are produced or when older data become available they should be entered into the database. The database is only effective as a mean of deriving important agronomic relations if it has a substantial size with a large number of observations of each combination of treatments from a range agro-ecological conditions. If the database is maintained and extended it can prove to be a valuable tool in the future evaluation of research needs regarding utilization of MPR in Tanzanian agriculture. The database structure and content is described in Appendix 1.4 with all the data available from the web.

From Table 18 it is clear that a large number of agronomic pot and field experiments already have been carried out and together with the data presented in Chapter 6 it should be possible to make recommendations for direct application of MPR.

Table 16. Data categories, variables and the present status of the database.

Data categories (No. of cases)	Variables (cases with registered data)
1. Site/soil (77)	Soil classification (66%), initial soil properties of surface layer (pH (92%), exchangeable cations (56%), CEC (61%), available P (90%), texture (53%), total C (87%), total N (62%)).
2. Agronomic (41 pot, 34 field exp.)	Agronomic data from pot and field experiments (treatment type and level (100%), crop species (maize 54%, sorghum 10%, legumes 21%, other 15%), season number (100%), dry matter or grain yield (100%), P uptake (39%), Ca uptake (16%)).
3. Dissolution (13 lab. exp., 36 pot, 14 field exp.)	Dissolution period, pH (55%), exchangeable Ca (44%), exchangeable Al (31%), available P (100%).

Table 17. Dissolution studies with Minjingu phosphate rock and related products.

Type[1]	Products[2]	No. of soils (classification)	Properties measured[3]	Source
L, P	TSP, MPR, MPR-COMP, MPR-FYM	1 (Ultisol)	pH, Ca_{ex}, Al_{ex}, P_{avail}	{40, 91, 92}
P	TSP, MPR, MPR-zeolite	1 (Inceptisol)	P_{avail}	{155}
P	TSP, MPR	4 (Ultisol, Oxisol, Entisol)	pH, Ca_{ex}, P_{avail}	{40, 153, 154}
L	TSP, MPR	2 (Ultisol)	pH, Ca_{ex}, P_{avail}	{156, 235}
F	TSP, MPR	4 (NA)	pH, P_{avail}	{67, 165}
P, F	TSP, MPR, PAPR	5 (Alfisol, Ultisol, Oxisol)	pH, Ca_{ex}, Al_{ex}, P_{avail}	{114-116}
P	MPR, MPR-FYM	1 (Ultisol)	P_{avail}	{119}
L, F	TSP, MPR	3 (Entisol, Ultisol)	P_{NaOH}	{34}
L	TSP, MPR, PAPR	3 (Ultisol, Alfisol, Inceptisol)	P_{avail}	{260}
F	TSP, MPR	1 (Alfisol)	P_{NaOH}	{172}
L[4]	MPR, MPR-S	1 (Oxisol)	pH, soluble P, Al, Mn	{102}
L[4]	MPR, MPR-S	no soil	pH, soluble P, EC	{129}
F	TSP, MPR	1 (Ultisol)	pH, P_{avail}	{40}
L, F	TSP, MPR, MPR-ORG	2 (Alfisol, Ultisol)	P_{avail}, P_{NaOH}	{12}
F	TSP, MPR, PAPR	1 (Ultisol)	pH, P_{avail}	{124}
F	TSP, MPR	1 (Ultisol)	P_{avail}	{189}
L	MPR	11 (Alfisol, Ultisol, Oxisol, Inceptisol)	P_{avail}, P_{NaOH}	{173}
L	MPR	2 (Inceptisol, Oxisol)	P_{NaOH}	{217}
P	TSP, MPR	6 (Inceptisol, Alfisol, Ultisol)	P_{avail}	{168}
P	TSP, MPR	5 (NA)	pH, Ca_{ex}, Al_{ex}, P_{avail}	{183, 184}
P	TSP, MPR	3 (Inceptisol, Alfisol, Ultisol)	pH, P_{avail}	{166}
L	TSP, MPR	2 (Alfisol, Inceptisol)	P_{NaOH}	{270}

[1] L = laboratory study, P = pot study, F = field study.

[2] TSP = triple superphosphate, MPR = Minjingu phosphate rock, MPR-COMP = mixtures with compost, MPR-ORG = mixtures with organic materials, MPR-FYM = mixtures with farm yard manure, MPR-S = mixtures with elemental S, PAPR = partially acidulated MPR, NBMPR = non-beneficiated MPR, SSP = single superphosphate, MPP = mono potassium phosphate, DSP = double superphosphate, NA = not available.

[3] P_{avail} = available P, P_{NaOH} = NaOH extractable P, Ca_{ex} = exchangeable Ca, Al_{ex} = exchangeable Al, EC = electric conductivity.

[4] Not included in database.

5.2 Database derivations

A few key relations have been derived as examples of the potential utility of the MPR agronomic database. Figure 26 presents all the presently contained agronomic data in a way where the yield response to a MPR product is related to the yield response to a soluble phosphate source at equal P levels. Yield response to each P source at each P level was assessed according to the following equation:

$$\text{P-response}\,(\%)=\frac{(\text{Yield with P source-Control yield})}{\text{Control yield}} \qquad (6)$$

From Figure 26 it is seen that yield response to either P source is highly variable and ranges between a negative response and up to 13-15 times the control yield. Most of the observations are showing yield increases below 200% corresponding to less than three times the control yield. A large part of the observations only show minor P response (0-20%) and apparently not all agronomic experiments were carried out with available P being the dominating constraint for crop performance. Other factors such as moisture stress, soil acidity or other nutrient constraints may also have influenced crop yields and thereby masked the effect of P.

Table 18. Agronomic studies with Minjingu phosphate rock and related products[1].

Type	Products	Crop	No. of harvests	No. of soils (classification)	Source
P, F	TSP, MPR, MPR-COMP, MPR-FYM	Maize	1	1 (Ultisol)	{40, 91, 92}
P, F	TSP, MPR, PAPR, NBMPR	Maize, Sorghum	2	5 (Alfisol, Ultisol, Oxisol)	{114-116}
F	SSP, MPR, MPR-S	Maize	5	1 (Oxisol)	{113, 214}
P	TSP, MPR, MPR-zeolite	Maize	1	1 (Inceptisol)	{155, 270}
P, F	TSP, MPR	Maize	1/6	2 (Ultisol, Oxisol)	{40, 238, 270}
P	TSP, MPR	Maize	2	4 (Ultisol, Oxisol, Entisol)	{40, 153, 154, 235, 237}
F	TSP, MPR	Pasture	5	1 (Ultisol)	{40, 235}
F	DSP, SSP, MPR	Groundnut	4	1 (NA)	{6, 113}
F	TSP, MPR	Maize	6	1 (Oxisol)	{101, 180}
F	TSP, MPR	Cotton	3-4	4 (NA)	{67, 165}
F	TSP, MPR	Sorghum	6	1 (Inceptisol)	{186, 187}
F	TSP, MPR	Maize	4	1 (Inceptisol)	{104}
P	MPP, MPR, MPR-Lime	Ryegrass	3	1 (NA)	{147}
P	MPR, FYM	Maize	1	1 (Ultisol)	{119}
F	TSP, MPR	Grapevine	2	3 (Entisol, Ultisol)	{34}
P	SSP, MPR, PAPR	Ryegrass	1	1 (Entisol)	{215}
F	TSP, MPR, PAPR	Clover	4	1 (Vertisol)	{81}
F	TSP, MPR	Maize	3	1 (Alfisol)	{172}
P	TSP, MPR, MPR-Lime	Bean	1	9 (NA)	{183, 184}
F	TSP, MPR, MPR-ORG	Maize	2	3 (Oxisol)	{95}
P, F	TSP, MPR	Maize	2 (P), 1 (F)	6 (Inceptisol, Alfisol, Ultisol)	{168, 177}
F	TSP, MPR	Bean	1	1 (Ultisol)	{210, 211}
F	TSP, MPR	Maize, Bean	1	1 (Ultisol)	{40}
F	TSP, MPR, MPR-ORG	Maize	1	1 (Ultisol)	{12}
F	TSP, MPR	Maize	1/6	1 (Ultisol)	{189}
F	TSP, MPR, PAPR	Maize	3	1 (Ultisol)	{124}
P	TSP, MPR	Maize	1	3 (Inceptisol, Alfisol, Ultisol)	{166}
F	TSP, SSP, MPR	Maize	1	1 (Alfisol)	{190}
F[2]	DSP	Cotton	6	1 (NA)	{222}
F[2]	DSP, MPR	Pasture	3	3 (Oxisol, Vertisol)	{5}
P	TSP, MPR	Maize[3]	2	2 (Alfisol, Andisol)	{272}
F	TSP, MPR	Maize	4	1 (NA)	{9}
F[2]	TSP, MPR	Maize	2	3 (Oxisol, Alfisol)	{262}
P	TSP, MPR	Maize, cowpea, pigeonpea	1	2 (Oxisol)	{164}
P	TSP, MPR	Maize	1	9 (NA)	{164}
F	TSP, MPR	Maize	2	2 (Oxisol)	{164}
F	TSP, MPR	Maize	2	2 (Oxisol)	{164}
F	TSP, MPR, FYM	Maize	2	2 (Oxisol)	{164}

[1] See description in Table 17. [2] Not included in database. [3] With maize, bean, pigeon pea and cabbage as initial crop.

While forcing the intercept of the regression line through zero the slope indicates the relative response of MPR products compared with a soluble P source. A slope of 1 corresponds to equal relative response whereas a slope of 0.5 corresponds to 50% response to that of the soluble P source. Table 19 list the slope values of various subsets of the data. A very important observation, which should always be taken into account when reviewing agronomic experiments with phosphate rock products, is the effect of time. The data in Table 19 clearly indicate that crop response to MPR is almost certainly lower in the first (70%) and second harvest (89%) than in subsequent harvests (99%). Hence, MPR seems to be comparable with a soluble P source after the second season. This trend has been observed previously and is mainly attributed to the delayed dissolution of MPR and hence lower P availability during the first season compared to the soluble P source. In subsequent seasons a larger fraction of available P originates from dissolved MPR resulting in the alleviation of the P constraints. As the data also contain experiments, which evaluate the residual P effect, a decreased effectiveness of the soluble P source compared with MPR could also contribute to this trend.

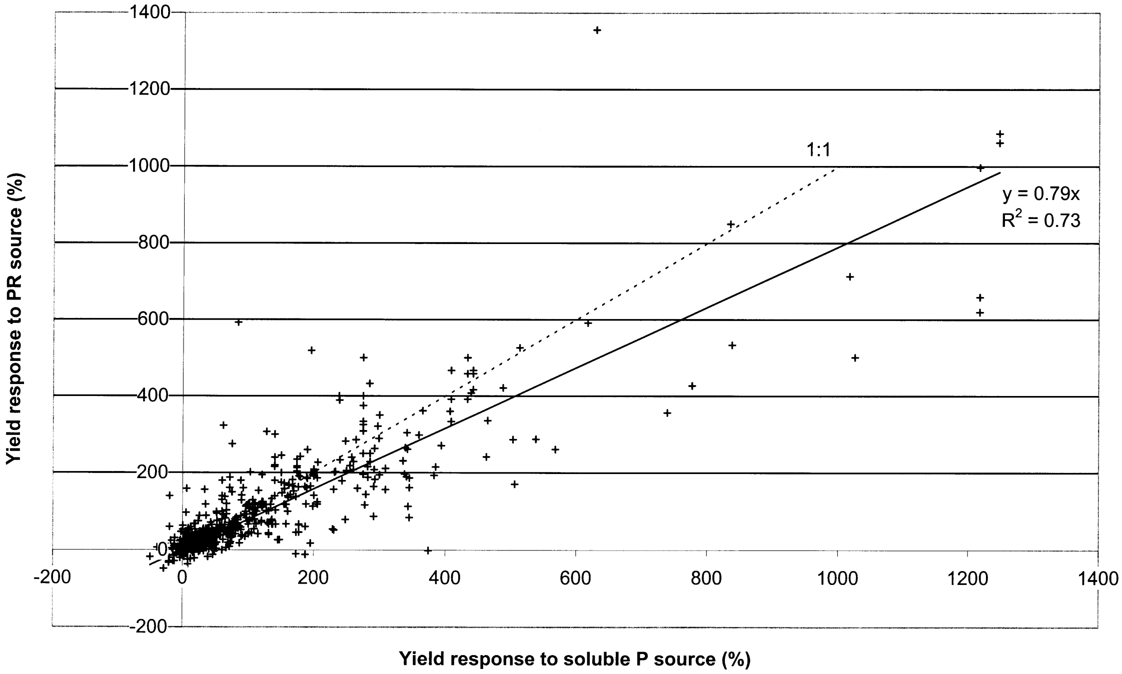


Figure 26. Yield response to MPR products compared with yield response to soluble P fertilizers at equal P level.

Table 19. Slope of regression line for various subsets of the agronomic data (intercept forced through zero).

Subset	No. of obs.	Slope	R^2
All data with positive P response (PPR)	557	0.80	0.83^{***}
First harvest (PPR)	301	0.70	0.82^{***}
Second harvest (PPR)	139	0.89	0.87^{***}
Third and subsequent harvests (PPR)	117	0.99	0.78^{***}

The mean MPR response to different classes of soil pH (pH_{water}) and P availability (Bray 1 P) respectively were also investigated on the data, which showed positive P response (Table 20). Although the statistical assumptions could be questionable due to the different number of observations in each group the analysis indicate that low soil pH and low level of available P are the most favourable conditions for the effective use of MPR. However, Table 20 also show that good MPR response is expected irrespective of soil pH if the P availability is low. The relatively high response to MPR at low pH but at high levels of available P may be attributed to the neutralizing effect of the phosphate rock. At high levels of available P and at high pH the response is normally low. When more observations on more fertile soils become available the database would enable a better estimation of the limits of soil pH, available P and crop species where MPR is expected to be effective.

Table 20. Simple pairwise t-test for comparison of MPR response means of various soil property classes.

Soil property	No. of obs.	Mean response (%)[1]
pH>6, $P_{avail.}>10$ mg P kg^{-1}	32	31^{a}
pH<6, $P_{avail.}>10$ mg P kg^{-1}	22	47^{ab}
pH>6, $P_{avail.}<10$ mg P kg^{-1}	55	99^{bc}
pH<6, $P_{avail.}<10$ mg P kg^{-1}	437	126^{c}

[1] Means with same letters are not significantly different at 5% level.

$P_{avail.}$ corresponds to Bray 1 extractable P.

5.3 Evaluation of suitable areas of Tanzania for direct application of MPR

A successful utilization of phosphate rocks as P source in tropical agriculture requires a strategic implementation in suitable areas close to the mine. However, a number of factors such as climate, soil characteristics and cropping traditions determine whether a particular area of the country is suitable for direct application and a countrywide analysis of the potential areas is necessary in order to optimise the utilization of the limited P sources from Minjingu. The compilation of soils, physiography and agro-ecological zones of Tanzania produced by de Pauw {51} basically gives the possibility for such an analysis.

In his study each of the 63 agro-ecological zones were described by their:

a) Climate (temperature regime, moisture characteristics, growing period and onset period).
b) Physiography (main land units and description of landform, slope, altitude and parent material).
c) Soils (relative distribution of main and associated soil units and a description of the soil characteristics in terms of chemical and physical properties).
d) Vegetation and land use (total area and cultivated area percentage, vegetation type, livestock carrying capacity and occurrence of tsetse fly).

On the basis of this information and with regard to the previous experiences with direct application of phosphate rocks, the combined effect of soil type and moisture regime on suitability for direct MPR application were classified as: 1) highly suitable, 2) suitable, 3) moderately suitable, and 4) not suitable (see appendix 1.2). Next step included calculation of the distribution of the area of each physiographic region to the four different suitability classes as well as the cultivated area of each class assuming the same cultivation percentage within each agroecologic zone irrespective of soil type (Figure 28 next chapter and Table 21).

Table 21. MPR suitability classification[1] of each physiographic region of Tanzania.

Zone[2]	Total area	Suitability (percent of total area)				Cultivation percentage				Cultivated area				Sum
		HS	S	M	NS	HS	S	M	NS	HS	S	M	NS	
	km^2		%				%				km^2			km^2
C	59371	3	59	24	14	100	57	46	56	1781	19966	6555	4655	32957
E	197429	34	21	39	6	29	39	27	19	19466	16169	20789	2251	58676
H	63255	33	52	15	-	68	51	53	-	14194	16775	5029	-	35998
N	48625	4	8	33	55	67	52	18	11	1303	2023	2888	2942	9156
P	313202	19	51	17	13	18	24	33	60	10712	38336	17571	24430	91048
R	26282	36	19	34	11	12	10	12	1	1135	499	1072	29	2736
S	62728	69	23	8	-	6	4	6	-	2597	577	301	-	3475
U	16654	81	5	14	-	53	53	53	-	7150	441	1236	-	8827
W	39427	57	22	21	-	54	49	54	-	12136	4250	4471	-	20857
Sum	826973									70474	99038	59912	34306	263730

[1] HS=highly suitable, S=suitable, M=moderately suitable, NS=not suitable.

[2] See Figure 28.

From Table 21 it is seen that highly suitable areas are found primarily on the Central, Inland and Eastern Plateau, in Ufipa, Rukwa and in the Western and Southern Highlands. When considering the most intensively cultivated areas especially the Central and Eastern Plateau and the Western and Southern Highlands are highly suitable.

However, as transport is among the most important constraints for direct application of reactive phosphate rocks, the distance from the mine to the potential areas must be considered. Figure 27 show the accumulated area ranked as highly suitable for direct MPR application in relation to the distance from the mine. Apparently, the bulk of the most suitable areas is more than 1000 km away from the mine. At the present situation, transport to areas such as the Western and Southern Highlands seems questionable from a economical point of view.

Assuming that the remaining resources at the Minjingu deposit contains 7 Mt of rock with an average P content of 10% P and with an annual potential production capacity of 100,000 tons of concentrate (13% P), the deposit is able to supply the Tanzanian agriculture with P for more than five decades. If applied at a P rate of 20 kg P ha^{-1} the annual production corresponds to 0.65 Mha indicating that not all potential areas can be supplied with MPR.

Although the cultivated area as defined by de Pauw may have included areas used for grazing and hence have overestimated the actual farmland, Figure 27 indicate that up to approximately 1 Mha of suitable farm land exist within a distance of 750 km from the mine. Hence, both from an agronomic and economical point of view it seems evident that these areas constitute a natural target area for a more detailed delineation of suitable areas, soil surveys, field experiments, demonstration plots, farmers and extension staff training and marketing.

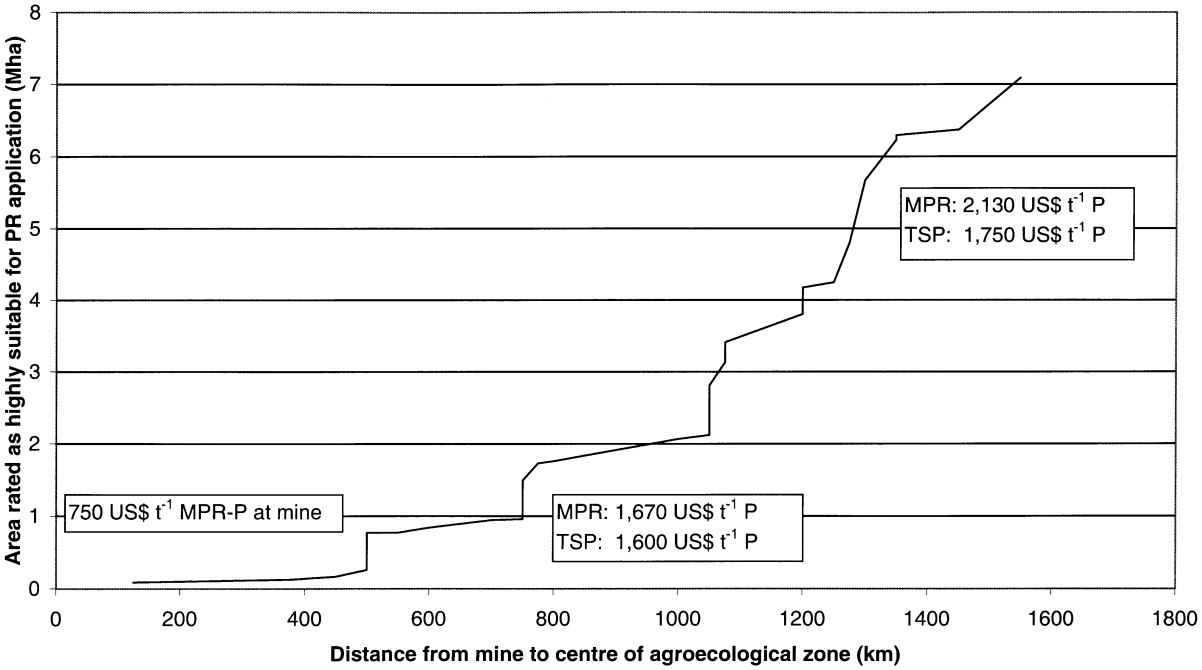


Figure 27. Accumulated area (Mha) of cultivated areas rated highly suitable for direct application of MPR as compared with the distance (km) from Minjingu. Also illustrated are present prices for MPR at the mine as well as estimated prices for MPR and TSP at Morogoro (740 km) and Sumbawanga (1780 km) respectively.

6 The main field experiment under the Phosphate Rock Utilization Project

As the use of MPR has showed promising opportunities in Tanzanian agriculture the Phosphate Rock Utilization Project (PRUP) was developed with the aim of determining the agro-ecological conditions under which MPR products could be suitable substitutes for water-soluble P fertilizers. The overall objective of PRUP is to fill the gaps in the knowledge of the use of MPR, and field experiments covering large differences in the agro-ecological environment were considered among the high priority research areas needed to address before appropriate agronomic recommendations for the future use of MPR in Tanzanian agriculture can be developed. Most of the previous experiments have been carried out under a limited range of agro-ecological conditions, often with limited background knowledge about the sites, and with a quite variable number of treatments so that it has been difficult to reach firm conclusions. Therefore, field experiments, all with similar layout, were started on ten different locations in the more humid parts of the country (Figure 28). The areas selected represent important agricultural areas of the country and the soils found at each site are commonly distributed in those areas. As maize is the dominant crop grown in the areas of Tanzania with plenty rainfall, it was selected as the test crop throughout the experimental period. A number of parameters describing the agro-ecological conditions are being collected during the experimental period in order to establish the information base required for interpretation of the field results as well as allowing the transfer of know-how to other areas with similar conditions. The specific objectives of the field experiments are to:

1) Evaluate the short and long term relative agronomic effectiveness of directly applied MPR for maize.
2) Evaluate the effect of mini-granulation of MPR on the relative agronomic effectiveness.
3) Evaluate the residual fifth year effect following four years of application of MPR.
4) Evaluate the effect of the mineralogical, chemical and physical properties of surface soils and subsoils on the relative agronomic effectiveness of MPR.
5) Evaluate the effect of climate, other nutrients and nutrient imbalances on maize yields and effectiveness of MPR
6) Support the previous results obtained from the use of MPR in Tanzania as well as giving stronger evidence of its relative agronomic efficiency under a wide range of agro-ecological conditions.
7) Develop agronomic recommendations for direct application of MPR as P source for maize production in various agro-ecological zones of Tanzania.

This chapter presents the methodology used and the results of the characterization of the experimental sites as well as the agronomic results from the first three growing seasons.

6.1 Materials and methods

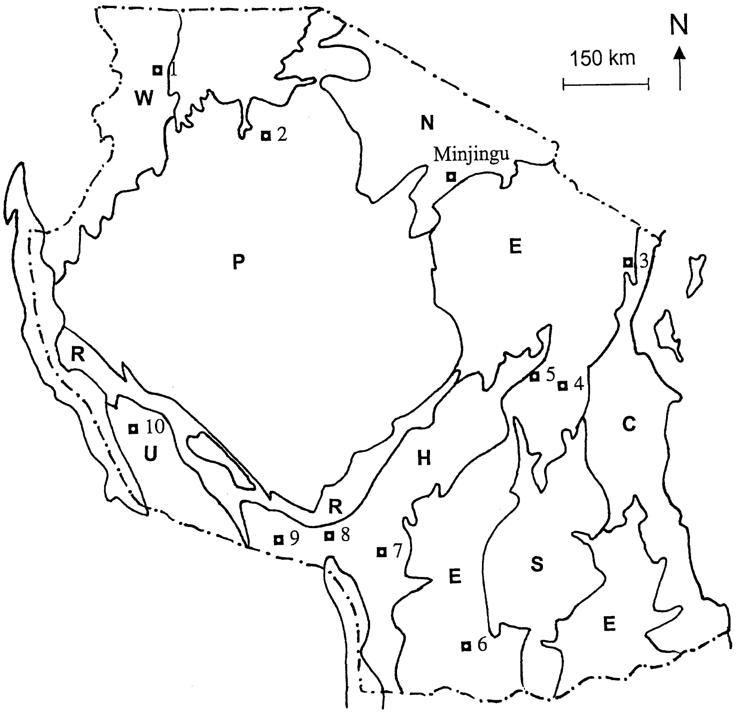
6.1.1 Selection of experimental sites and soil sampling

Site selection was done in order to:

a) Cover important agricultural areas of the sub-humid to humid parts of the country with acid soils where P deficiency occurs.
b) Include a large range of agro-ecological conditions especially with respect to soil properties.
c) Facilitate the management and supervision of the field experiments by involving either the extension service or agricultural research and training institutions.

Five of the sites are located at Tanzanian Agricultural Research Institutes (Ukiriguru, Mlingano, Ilonga (Msimba), and Uyole (Suluti, Nkundi)), one at Sokoine University of Agriculture (Magadu), one at a primary school farm (Mpangala), two at farmer’s fields (Lubonde, Sasanda) and one at a Farmers Training Centre

(Igabiro) (Figure 28). Igabiro, Ukiriguru, Msimba, Lubonde, and Mpangala were cultivated in the season prior to the setup of the experimental sites, whereas the remaining had been fallow for a number of years.



Site no:	
1.	Igabiro
2.	Ukiriguru
3.	Mlingano
4.	Magadu
5.	Msimba
6.	Suluti
7.	Lubonde
8.	Mpangala
9.	Sasanda
10.	Nkundi

Physiographic Region	
C	Coastal zone
E	Eastern Plateau and Mountain blocks
H	Southern Highlands
N	Northern Riftzone and volcanic Highlands
P	Central Plateau
R	Rukwa-Ruaha Riftzone
S	Inland sedimentary Plateau
U	Ufipa Plateau
W	Western Highlands

Figure 28. Physiographic regions of Tanzania {51} and location of field experimental sites and the Minjingu mine.

As part of each site description, a soil profile was excavated and horizons were identified, described and sampled according to FAO {60}. Horizon designation followed Schoenberger et al. {230}. Duplicate ring core samples of 100 cm^3 were collected from the centre of each horizon for bulk density measurement and evaluation of water retention properties. In addition, composite soil samples, each consisting of nine sub-samples collected from the surface layer (0-15 cm) from each of the blocks used in the field experiments, were collected. All soil samples were dried, crushed, sieved to pass a 2 mm sieve, and thoroughly mixed before analysis.

6.1.2 Geological background

The description of the geological background of the various sites is based on Schlüter {227} supplemented with information from geological maps at 1:125,000 scale. The Igabiro site is located near the crest of the Kamachumu plateau consisting of Neoproterozoic Igamba (Bukoba) sandstone composed of shales with dolorite sills overlain by orthoquartzite. The soil profile has developed on laminated, white and grey micaceous orthoquartzite {174}. The Ukiriguru soil profile is located on the footslope of a granitic Inselberg on the Tanzania Craton. The Inselberg is a remnant of early Precambrian (Archaean) alaskitic granites with massive, flesh pink appearance mainly composed of quartz, perthitic microcline, oligoclase feldspar, biotite and with some hornblende, epidote, sphene, magnetite, ilmenite, apatite and zircon {182}. The Mlingano site is located in the southeastern end of the Usambara Mountains, a fault bounded tectonic unit on the Neoproterozoic Mozambique Belt. The soil profile is developed in situ on pyroxene granulites containing garnet, biotite and hornblende {100}. The Magadu soil profile is located on the footslopes north of the Uluguru Mountains, a similar fault bounded tectonic unit as the Usambara Mountains. The parent material consists of alluvium originating from garnet-bearing hornblende-pyroxene granulites and migmatic biotite-muscovite bearing quartzo-feldspathic gneisses {219}. The Msimba soil profile is located on alluvium from the Ukaguru Mountains on the Mozambique Belt with parent material originating from kyanite-garnet-biotite gneisess containing quartz, microcline, oligoclase, apatite and zircon {65}. The Suluti soil profile is developed in situ on the peneplain of the Mozambique Belt on gneissose garnet-biotite, hornblende porphyroblastic granites with possible contents of tremolite and pyroxene {131}. The Lubonde soil profile is located on the Paleoproterozoic Usagaran Belt with parent material originating from granites containing quartz, oligoclase, andesine, microcline and biotite {63}. High contents of organic matter are probably due to a former thick forest cover although influx of pumiceous ash from the Rungwe volcanics about 40 km to the west is not unlikely {51}. The Mpangala soil profile is located on the Lupa terrane of the Paleoproterozoic Ubendian Belt. The parent material is various layers of recent volcanic pumiceous ash most probably from Mt. Ngozi overlying Pliocene-Pleistocene basaltic lavas from the Rungwe volcanics {256}. The pumice from Ngozi is light in colour and in contrast to the pumice from Mt. Rungwe, it often contains xenolithic materials up to 30 cm size such as syenite, phonolithic lavas and Ubendian gneiss. Pumice from Mt. Rungwe is normally cream-coloured and contains phyric feldspars crystallized prior to eruption {82}. The Sasanda soil profile is located on the Mbozi terrane of the Ubendian Belt. The parent material is volcanic pumiceous ash most probably from Mt. Rungwe with biotite-garnet-hornblende gneiss under the soil solum {132}. The Nkundi soil profile is formed in situ on the peneplain of the Ufipa terrane on the Ubendian Belt with parent material consisting of Paleoproterozoic acid biotite-garnet-silimanite-kyanite schists, gneisses and amphibolites {259}.

6.1.3 Chemical and physical properties

Profile samples were analysed for the following properties: pH measured in a 1:2.5 soil:solution mixture of water (pH_w), 0.01 M $CaCl_2$ (pH_{Ca}) and 1 M KCl (pH_{KCl}) respectively. Exchangeable bases (Ca, Mg, K, Na) and cation exchange capacity at pH 7 (CEC_7), by the silver thiourea method {93}, i.e. four hours shaking of 1-4 g of gently crushed soil (the amount depending on the estimated CEC) with 40 cm^3 of unbuffered or sodium acetate buffered (0.1 M, pH 7) silver thiourea solution (0.01 M Ag, 0.1 M thiourea) for exchangeable bases plus CEC_e and CEC_7 respectively. Calculation of CEC_7 was based on the decrease in Ag concentration after equilibration with the soil whereas CEC_e is the sum of exchangeable cations at soil pH. Atomic absorption spectrometry (AAS) was used for measurement of Ag, Ca and Mg and flame emission spectroscopy (FES) for K and Na. Total acidity (Al+H) by extraction with 1 M KCl at a soil:solution ratio of 1:2.5 during 1 hour, followed by filtration and titration of the filtrate with NaOH with and without addition of NaF. Exchangeable aluminium (Al) was estimated from the results of the titration and from the total exchangeable Al measured by AAS {257}. Total organic carbon (C) by quantitative measurement of the CO_2 evolved from combustion of a soil sample at 1250 °C in an oxygen flow {55}. Total inorganic P (P_{inorg}) by extraction of 0.5 g of soil, which had been ground to pass a 250 µm sieve with 5 cm^3 6 M H_2SO_4 for 15 min. at 70 °C, followed by addition of 5 cm^3 6 M H_2SO_4 and cooling for 1 hour before filtration and measurement of the P using the molybdenum blue method. Total P (P_{total}) was estimated using the same extraction procedure as just described but after heating a new soil sample to 550 °C for 1 hour. Total organic P (P_{org}) was calculated as the difference between P_{total} and P_{inorg}, $NaHCO_3$ extractable P (P_{Olsen}) by extraction of 5 g with 100 ml 0.5 M $NaHCO_3$ at pH 8.5 for 30 min. followed by filtration and measurement of P using the molybdenum blue method after acidification of the extract {191}.

P sorption isotherms were determined for the surface soils by seven days equilibration of ten batches of 2 g surface soil in a reciprocal shaker with 50 cm^3 0.01 M $CaCl_2$ solution initially containing concentrations of KH_2PO_4 up to either 8, 20, 40 or 80 mg P dm^{-3}. The maximum initial P concentration were approximately corresponding to the amount of P required to reach a preliminarily estimated adsorption maximum (see method described in Chapter 7.1.1). The difference between P concentrations before and after equilibration with the soil was considered to be sorbed P. The adsorption data were fitted to the Langmuir equation and the sorption maximum (P_{max}), and affinity parameter (K) were calculated using a least squares non-linear method. Standard P requirement, defined as the amount of P adsorbed at an equilibrium concentration of 0.2 mg P dm^{-3}, were also calculated using the Langmuir equation and the estimates for P_{max} and K. In addition, the P adsorption index (P_{index}) was determined by 16 hour equilibration with 120 mg P dm^{-3} at a soil:solution ratio of 1:25 followed by calculation of P adsorption (mg P kg^{-1}) on the basis of the difference between initial P concentration and equilibrium P concentration.

Oxalate extractable iron (Fe_o), aluminium (Al_o), silicium (Si_o) and phosphorus (P_o) was measured on fine earth fractions by shaking (end over end, 20 r.p.m.) of samples of 1 g soil with 40 cm^3 0.2 M ammonium oxalate solution (pH 3) for two hours in the dark, followed by measurement of Fe, Al and Si in the filtrate by AAS and P using the ammonium molybdate method {233}.

Dithionite-citrate-bicarbonate (DCB) extractable iron and aluminium (Fe_d, Al_d) were determined for the surface soils by extraction of 1 g soil with 40 cm^3 0.3 M Na-citrate, 5 cm^3 1 M $NaHCO_3$, and 1 g sodiumdithionite ($Na_2S_2O_4$) for 15 min. while stirring at 70 °C, followed by centrifugation and collection of the supernatant. The extraction with dithionite was repeated once more and finally after two washings with 0.3 M citrate, Fe and Al was measured in the collected supernatant by AAS {148}.

Extractable Zn and Cu by extraction with 0.5 M ammonium acetate/0.5 M acetic acid/0.02M Na_2-EDTA (sodium ethylenediaminetetraacetate) solution at pH 4.65 at a soil:solution ratio of 1:10 for 1 hour, followed by filtration and measurement of Zn and Cu by AAS {243}.

Separation of clay, silt and sand fractions and the particle size analysis was done after removal of the organic matter using the following method: 50 g of each sample (<2 mm) were moistened to field capacity with de-ionised water before addition of 10 ml 30% H_2O_2 and heating to 70 °C. The H_2O_2 treatment were repeated several times until only little reaction occurred after addition, or until no visible organic matter was present. During the treatment the moisture content was kept at flowing paste conditions by addition of water or by removal of excess moisture by heating. The pH was maintained between 5 and 6 by drop wise addition of 4 M NaOH. When the reaction ceased, excess H_2O_2 was removed by addition of 4 M NaOH to pH 8, and heating on boiling water bath until no reaction while keeping the soil moist by addition of water. Soluble salts were then removed by repeated washings with water and/or 96% ethanol and centrifugation. The first washings were done using only water followed by a mixture of water and ethanol and finally only ethanol to prevent dispersion of the fine clay at low electric conductivity. Before separation of the sand and coarse silt fractions from the finer particles (< 20 µm), the samples were dispersed using an ultrasonic vibrator for 6-10 min. while stirred. The separation was done using a repeated sedimentation technique, and a bottle where the finer particles could be removed by siphoning at a specific time calculated from Stokes equation using a mean separation diameter of 20 µm. In the case of visible aggregates in the sand fraction after separation, the ultrasonic treatment and separation by sedimentation and siphoning was repeated on the coarser particles (>20 µm). Finally the coarser particles (>20 µm) where dried and subjected to a particle size analysis using a vibrating sieve column with 50, 125, 250, 500 and 800 µm sieves for 30 min. Approximately 1 litre of the suspension of the finer particles (<20 µm) where used in a particle size analysis using the Andreassen's pipette apparatus where samples of 10 ml where taken at 0, 15, 45, 150, 390 and 1440 min. after initial mixing. Dispersion of the suspension was, if needed, insured by addition of sodium pyrophosphate at a final concentration of 0.002 M. The particle size limit at each sampling time was calculated from Stokes equation, and the fraction of particles in each size class was calculated as a weight fraction of the zero sample multiplied by the total weight of the finer particles (< 20 µm). The clay from the remaining suspension of the finer particles were separated using a particle size centrifuge and a centrifugation time so that the mean separation diameter was 2 µm. After separation both the clay and the fine silt were flocculated using $CaCl_2$ and repeatedly washed with water and/or 96% ethanol before drying and grinding using an agate mortar.

Both for the initial separation of the coarser particles, for the Andreassen's analysis and for the particle size centrifuge, 2.61 g cm^{-3} was used as mean density of the solids.

Water retention properties was measured according to Eijkelkamp {52} and the available water capacity (AWC) was calculated from the water retention curves using pF=2.5 and pF=4.2 as the limits for the field capacity and the wilting point respectively. The moisture content of the dry soil samples was estimated by heating a sub-sample to 110 °C until constant weight.

The composite surface samples were analysed for the following properties: pH_w and pH_{KCl} as described above. Exchangeable bases (Ca, Mg, K, Na) by extraction with 1 M NH_4-acetate using AAS for measurement of Ca and Mg, and FES for K and Na {181}. Cation exchange capacity at pH 7 (CEC_7) by saturation with neutral NH_4-acetate, followed by exchange with acidified KCl, distillation and titration {181}. Organic carbon (C), and $NaHCO_3$ extractable P (P_{Olsen}) as described above and Bray 1 available P (P_{Bray1}) by extraction with 0.025 M HCl/0.03 M NH_4F for one minute at a soil:solution ratio of 7, followed by P measurement using the molybdenum blue method {181}. Extractable Cu, Zn, Fe and Mn by extraction with 0.005 M DTPA and measurement of the metals by AAS {245}. Extractable B by extraction with hot water {110}.

All analyses except particle size analysis were carried out in duplo. Analyses were in most cases repeated if deviation between duplicates was larger than 5%.

6.1.4 Mineralogical properties

Approximately 3 g of the clay fraction was treated twice with dithionite-citrate-bicarbonate (DCB) using the same procedure as described above in order to remove the free iron oxides {148}. Both extractable iron (Fe_{d_clay}) and aluminium (Al_{d_clay}) were measured in the extract using AAS. After DCB extraction the clay was split into two fractions and saturated with either Ca^{2+} or NH_4^+ by four repeated additions of either 1 M $CaCl_2$ (pH 7) or 1 M NH_4-acetate followed by dispersion with ultrasound and centrifugation. The saturated samples were finally washed by addition of water and/or 96% ethanol followed by dispersion using ultrasonic treatment and centrifugation until the electric conductivity in the supernatant was less than 10-15 µS cm^{-1}. Before X-ray diffraction analysis (XRD), the air-dry samples were crushed and ground using an agate mortar.

X-ray diffraction analysis (XRD)

X-ray diffraction patterns were prepared from non-oriented powder samples of both Ca^{2+} saturated DCB treated and non-treated clay samples and non-treated silt samples using CoK_α radiation from a tube operated at 40 kV and 40 mA. Divergence, antiscatter and receiving slits were 1 mm, 0.6 mm and 0.1 mm wide respectively. Scanning speed were set to 0.3° 2θ min^{-1} over a scanning range of 8-75° 2θ. The diffraction patterns obtained were used for a first hand qualitative assessment of the minerals present in the samples and based on the results further XRD analyses were planned. In the case of 1:1 or 2:1 layer silicates oriented XRD patterns were obtained using the Ca^{2+} saturated DCB treated clay sample. The oriented scans were run at 0.3° 2θ min^{-1} over a scanning range of 3-35° 2θ using same settings as described above. Oriented samples were prepared by dispersion with ultrasonic treatment of 60 mg of sample in 5 cm^3 water and transfer of 1.5 cm^3 of the suspension to a glass plate, which was left drying overnight. After scanning at ambient temperature the samples were also scanned after heating to 350 °C and 550 °C during 1 hour respectively. In case of 2:1 layer silicates a glycerol treated sample was prepared after addition of one drop 1:2 glycerol:water solution to the suspension of the Ca^{2+} saturated clay sample. Calculation of d-spacings was done using Bragg's equation and 0.1791 nm as wavelength.

Fourier Transformed Infrared analysis (FTIR)

Ca^{2+} saturated DCB treated samples were used for qualitative assessment of the mineral components using a Perkin Elmer FT-IR 2000 infrared spectrometer. The absorption spectra were obtained using the KBr pellet method with 0.35 mg of sample in 300 mg KBr compressed at 150 MPa in an evacuated die. Spectra were recorded over the range 4000 to 400 cm^{-1}.

Total elemental analysis (TEA) and thermogravimetric analysis (TGA)

NH_4^+ saturated DCB treated clay samples were used for total elemental and thermogravimetric analysis. Digestion was done in 38% HF during 1 hour at 110 °C using an air tight teflon container followed by cooling before quantitative transfer of the digest into a 6% boric acid solution. Si, Al, Ca and Fe, Mg, were measured in the digest by AAS using N_2O and air as oxidizing agents respectively, and K and Na using FES. The weight losses were determined at the following temperature intervals using a muffle furnace: Room temperature-110 °C, 110-350 °C, 350-550 °C and 550-900 °C. Both analyses were carried out in duplo.

6.1.5 Phosphate sources

Commercially available, beneficiated Minjingu phosphate rock from the soft ore containing 13% total P is used as PR source {150}. The solubility in neutral ammonium citrate is 2.7% P (6.2% P_2O_5) corresponding to a medium to highly reactive phosphate rock. Granulation is, except for the first season, done by drum granulation with water as binding agent, followed by drying, crushing and sieving in order to obtain a final particle size range of 0.5-1 mm. For the first season the granulated material was obtained by manual mixing, drying, crushing and sieving a 1:1 mixture of MPR and water. The material used in the first season had a coarser particle size distribution compared to the material used in the subsequent seasons (Figure 29).

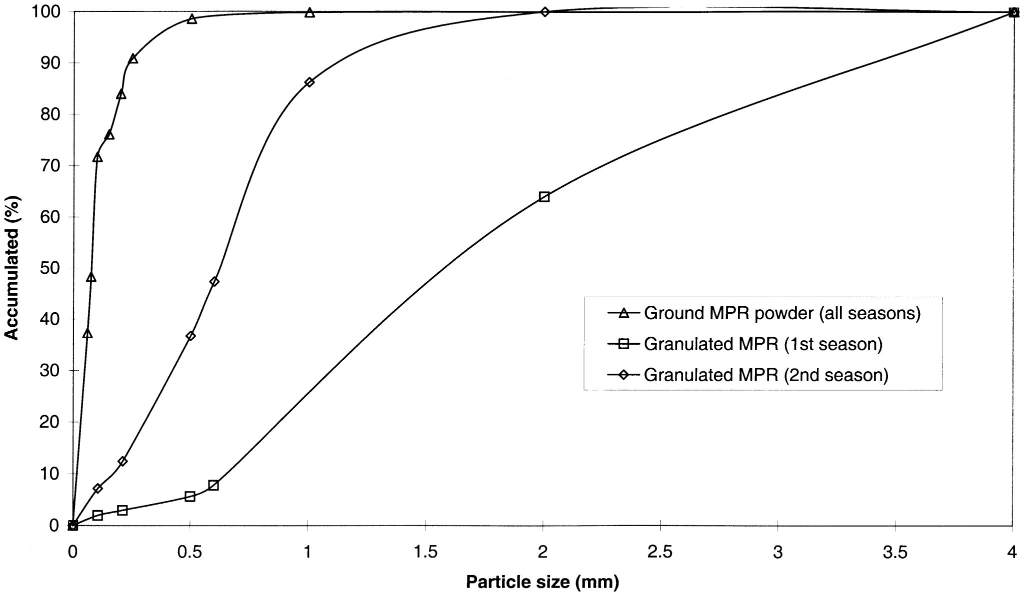


Figure 29. Particle size distribution of the ground and granulated MPR.

Prior to the granulation process a qualitative assessment on the granule strength of different binding agents, added at a 1:1 MPR:solution mixture, was carried out with the purpose of obtaining an appropriate method of mini-granulation. The test led to the following ranking according to decreasing granule strength: MPR+5% Urea > MPR+5% $MgSO_4$ = MPR+water > MPR+5% $(NH_4)_2SO_4$ = MPR+5% $MgCl_2$ > MPR+5% KCl. Heating to 60 °C improved the granule strength compared to air drying for all treatments. Water as binding agent was preferred from a field experimental point of view due to the absence of other nutritional effects from the granulated phosphate rock material, and because the relatively low strength was thought to benefit rapid granule disintegration in the soil and hence increase the contact between the phosphate rock and soil particles. Triple superphosphate supplied by Tanzania Fertilizer Company is used as water-soluble P source for comparison.

6.1.6 Field experimental design

Three levels of triple superphosphate (TSP) are compared over five seasons with equal levels of mini-granulated Minjingu PR (GPR), and non-granulated Minjingu PR (MPR) as well as with an absolute control and controls for N and P giving a total of twelve treatments at each experimental site (Table 22).

Table 22. Treatments introduced in the field experiment.

No.	Treatment and level
1	Absolute control (no application of any nutrients)
2	Control for P (basal nutrients and N at same level as treatment 4-12)
3	Control for N (basal nutrients and P as MPR at same level as treatment 10)
4-6	N and basal nutrients, and triple superphosphate (TSP) at 40, 80 and 120 kg P ha^{-1} respectively
7-9	N and basal nutrients, and granulated Minjingu PR (GPR) at 40, 80 and 120 kg P ha^{-1} respectively
10-12	N and basal nutrients, and non-granulated Minjingu PR (MPR) at 40, 80 and 120 kg P ha^{-1} respectively

A complete randomised block design with four blocks is used. Gross plot size is 35 m^2 with a harvested area of 25 m^2 (Appendix 1.3). After the fourth season the experiment is continued for one more season in order to evaluate the residual effect of the P sources applied. Either hybrid or composite maize varieties are grown depending on local conditions at a plant density of 40,000 plants ha^{-1}. All plots except for the absolute control receive basal nutrient applications according to soil and leaf analyses as indicated in Table 23.

Table 23. Basal nutrients and N applied at each experimental field (kg element ha^{-1}).

Nutrient	Site									
	Ig	Uk	Ml	Ma	Ms	Su	Lu	Mp	Sa	Nk
N as $(NH_4)_2SO_4$	2x40	2x40	2x40	2x40	2x40	2x40[3]	3x40[3]	2x50[3]	2x50[3]	2x50[3]
K as K_2SO_4	100[1]	100[2]	100[2]			100[1]				50[1]
Mg as $MgSO_4$ or $Mg(NO_3)_2$									25[1]	
Cu as $CuSO_4$		5				5	5	5	5	5
Zn as $ZnSO_4$	10	10	10[2]	5[2]	10[2]	10		10[1]	10[1]	10[2]
B as Na-borate		0.5[2]				1[2]	1[2]	1[2]	1[2]	

[1] From the second season only (50 kg Mg ha^{-1} at Sasanda and 100 kg K ha^{-1} at Nkundi in the third season).

[2] From third season only.

[3] In the third season: 100 kg N ha^{-1} in four splits at Suluti, 100 kg N ha^{-1} in three splits at Lubonde, Mpangala and Nkundi, and 120 kg N ha^{-1} in four splits at Sasanda.

All the applied nutrients except N are broadcasted and incorporated into the surface 0-15 cm by hand cultivation prior to planting. N is topdressed as a two or three split application during the growing season. Total rainfall is recorded daily throughout the growing season. Surface runoff is minimized by establishment and maintenance of tied ridges throughout the growing season. Stalk borers, termites and other pests are, as far as possible, controlled by spraying appropriate insecticides when needed. All plots are kept weed free by regular hand weeding. At 50% tasseling, fifteen ear leaves randomly selected among the plants in each plot are collected each season and stored for the sake of total elemental analysis. At crop maturity the total grain weight per plot is recorded, and a sub-sample of the grain is used for a quadruplicate moisture determination using a digital moisture meter (Agromatic) and stored for the possible analysis of total P. All yield data were adjusted to 12.5% moisture content.

For the evaluation of the general nutrient uptake at the various experimental sites, leaf samples from five of the twelve treatments from a block randomly selected at each field experiment were selected for total elemental analysis during the three seasons. The randomly sampled leaves were cleaned, air dried, ground to pass a 1 mm sieve and mixed thoroughly before wet digestion using a combination of conc. H_2SO_4 and conc. H_2O_2 while heating {98}. Total Ca, Mg, Zn, Cu and Mn were estimated by AAS, K by FES and P and N by flow injection analysis. All analyses were carried out in duplo.

6.1.7 Moisture stress

An estimate of the daily soil moisture deficit, expressed as the ratio between actual and potential available soil moisture within the effective root depth was calculated on the basis of accumulated precipitation recorded on-site during the growing season, accumulated actual evapotranspiration based on monthly averages of potential evapotranspiration from nearest meteorological station, and the effective available water holding capacity of the soil determined from water retention curves, using the following model:

$$MD_i = \left[1 - \frac{\sum\limits_{n=1}^{i} (P-E)}{EMC_i} \right] \cdot 100 \qquad (7)$$

where MD_i is the soil moisture deficit on day *i* (%), *n* the first day of the rain season, which contributes to the moisture supply of the crop, P and E the daily precipitation and actual evapotranspiration respectively (mm), and EMC_i the potential effective available soil moisture content on day *i* (mm). The model assumes that surface run-off and interception by the crop is zero as long as the soil is dry. When filled to field capacity to the maximum effective root depth, surplus precipitation is considered lost by leaching or runoff. Under adequate moisture conditions, it is assumed that a maximum rooting depth of 150 cm is reached at 50% tasseling stage. In case of inadequate moisture during the vegetative stage, the root depth is assumed to be restricted to the soil wetting depth, which is estimated from the net precipitation and total soil water holding capacity at pF=2.5. In case of strong subsoil acidity, it is assumed that the root growth is restricted to 75 cm. Average moisture deficit (%) at the critical grain filling stage (MDG), assumed to be the first half of the period between 50% tasseling and harvest was calculated as:

$$MDG = \left[\frac{\sum\limits_{i=t}^{t+0.5\cdot(h-t)} MD_i}{(h-t)\cdot 0.5} \right] \cdot 100 \qquad (8)$$

where *t* is the day of 50% tasseling, *h* is the day of harvest, and MD_i is the calculated moisture deficit (%) on day *i* of the growing season.

6.1.8 Statistical analysis

Effect of rate and type of P on maize yield

For the evaluation of the effect of P during the first three seasons, treatments number 2 and 4-12 (Table 22) were selected. The statistical analysis was made using a mixed linear model with blocks as random effect and harvest, site and treatment as fixed effects {128}:

$$Y_{ijkl} = \mu + \alpha_i + \beta_j + \gamma_k + \alpha\beta_{ij} + \alpha\gamma_{ik} + \beta\gamma_{jk} + \alpha\beta\gamma_{ijk} + u_{l(k)} + v_{l(jk)} + w_{l(ik)} + \varepsilon_{ijkl} \qquad (9)$$

where

Y_{ijkl} = grain yield (t/ha) at 12.5% moisture for the i^{th} treatment, j^{th} harvest, k^{th} site and l^{th} block	1..1200
α_i = effect of the i^{th} treatment (fixed)	1..10
β_j = effect of the j^{th} harvest (fixed)	1..3
γ_k = effect of the k^{th} site (fixed)	1..10
$u_{l(k)}$ = random effect of blocks within sites (four blocks per site)	$N(0, \sigma_u^2)$
$v_{l(jk)}$ = random interaction of blocks within sites and harvest	$N(0, \sigma_v^2)$
$w_{l(ik)}$ = random interaction of blocks within sites and treatment	$N(0, \sigma_w^2)$
ε_{ijkl} = random residual error	$N(0, \sigma^2)$

Relative agronomic effectiveness

In case of significant effect of TSP on grain yield the relative agronomic effectiveness (RAE) was calculated using the following equation after averaging the yield values from all four blocks:

$$\text{RAE }(\%) = \left[\frac{\text{Yield}_{\text{PR}} - \text{Yield}_{\text{Control}}}{\text{Yield}_{\text{TSP}} - \text{Yield}_{\text{Control}}}\right] \cdot 100 \qquad (10)$$

Response curves

Likewise the coefficients of Mitcherlich's exponential yield response equation were calculated using the Mitcherlich equation:

$$Y = Y_{\max} \cdot \left[1 - 10^{-c(x+b)}\right] \qquad (11)$$

where Y is the yield with nutrient quantity x added as fertilizer, plus b, the effective quantity of the nutrient supplied by the seeds and the soil and expressed in the same units as x, $Y_{\max}$ the maximum yield attainable as x increases indefinitely, and c the proportionality factor {20}.

Effect of N, P and other nutrients on maize yield

For the evaluation of the effect of N, P and other nutrients during the first three seasons, treatments number 1, 2, 3 and 10 (Table 22) where selected. The statistical analysis was made using the same model (9) as described above only modified by the number of treatments included.

6.2 Results

6.2.1 Site characteristics

Figure 28 shows the location of the Minjingu phosphate rock deposit and the ten experimental sites. The sites cover eight agro-ecological zones in five physiographic regions of the country {51} (Table 24).

Table 24. Geographical and climatical characteristics.

Site	Region/ district	Location	Altitude m	PRE[1] (PET) mm	TEMP[2] (MIN-MAX) ºC	AEZ[3]
Igabiro	Kagera/ Muleba	S 01.8198 E 031.55270	1508	1510 (1316)	19.9 (14.0-25.7)	W3
Ukiriguru	Mwanza/ Magu	S 02.71778 E 033.03093	1230	1002 (1596)	22.4 (17.6-27.2)	P8
Mlingano	Tanga/ Muheza	S 05.11471 E 038.86882	160	1179 (1386)	26.5 (21.7-31.3)	E6
Magadu	Morogoro/ Morogoro	S 06.85183 E 037.64165	568	892 (1429)	24.0 (18.8-29.1)	E4
Msimba	Morogoro/ Kilosa	S 06.74959 E 037.05107	430	1063 (1525)	26.7 (21.9-31.5)	E9
Suluti	Ruvuma/ Songea	S 10.54447 E 036.08035	924	1118 (1396)	21.8 (16.4-27.2)	E7
Lubonde	Iringa/ Njombe	S 09.33577 E 034.57393	2131	1336 (1047)	15.2 (9.7-20.6)	H5
Mpangala	Iringa/ Makete	S 08.98872 E 033.93526	2250	1336 (1047)	15.3 (8.9-21.6)	H5
Sasanda	Mbeya/ Mbozi	S 09.16039 E 033.03262	1650	883 (1268)	19.0 (13.0-24.9)	H5
Nkundi	Rukwa/ Nkansi	S 07.87022 E 031.42288	1927	823 (1345)	17.2 (11.1-23.3)	U

[1] PRE = Total annual precipitation, PET = Potential evapotranspiration (based on data from nearby agrometeorological stations {59}).
[2] TEMP = Mean annual air temperature, MIN/MAX = Mean minimum and maximum annual air temperature {73}.
[3] AEZ = Agro-ecological zone {51}.

Climatically the sites are all characterized by one growing season long enough to support one maize crop per year followed by a long dry season (winter drought) with strong soil moisture deficit for several months, typical for an Ustic soil moisture regime. A slightly bimodal rainfall pattern is found at Ukiriguru, Mlingano and Magadu. From Table 24 and Figure 30 it can be seen that the total amount of rain and the pattern of the rain season vary between the sites and between the years.

Three sites, i.e. Igabiro, Lubonde and Mpangala are characterized by humid climate whereas the climate at the remaining sites is sub-humid {74}. The vertical bars in (Figure 30) show that the rainfall pattern during the first three seasons in general was far from normal, which may partly be attributed to the aftermath of El Niño, which caused excessive rains during the 1997/98 season and normally causes unstable conditions in the following years. Several sites experienced severe water deficiency during parts of the three growing seasons (Table 46). At Ukiriguru and Magadu, yields were strongly affected by soil moisture stress after tasseling in all three seasons due to low available soil water holding capacity, limited root depth, leaching and runoff and erratic distribution of the rainfall (Figure 30, Table 27 and Table 46). Yields at Igabiro, Msimba and Mpangala were also affected by soil moisture deficiency in some seasons (Table 46).

The average annual temperature is mainly determined by the elevation and especially at high altitudes, the lower temperatures have a large impact on the length of the period required to mature the maize crop. At Lubonde and Mpangala the growing period exceeds 8 months, whereas approximately 5 months are sufficient at lower altitudes (Table 46). Soil temperature regime, as inferred from air temperatures (Table 24), is characterized as Isohyperthermic for all sites except for Lubonde, which is Isothermic and Mpangala and Nkundi, which are Thermic {73} (Table 25).

Physiographically the sites are located on gentle slopes (1-9%) except for Mpangala, which is located in a steep-sided valley with 17% slope (Table 25). Despite the gentle slopes and generally well-drained soils with good porous soil matrix, sheet and rill erosion were observed at several sites during the first three seasons. About 10% of the rainfall observations exceeded 30 mm day^{-1} with few events ranging between 100-200 mm day^{-1}, which in most cases led to some erosion despite the tied ridges. Especially the Magadu soil, which does not possess any soil structure easily developed crusts during heavy showers leading to ponding and erosion despite a high subsoil porosity and hydraulic conductivity.

Horizon designations and some macro-morphological characteristics are presented in Table 26 (see also soil profile descriptions in Appendix 1.1). Evidence of clay illuviation was generally difficult to identify in the field despite the designation of Bt horizons at Ukiriguru, Mlingano, Magadu and Msimba. Except for Msimba where the clay cutans were easily detectable on ped faces, clay and iron oxide accumulations appeared more as faint thin cutans in patches of the matrix. Neither Ukiriguru nor Nkundi showed any visible signs of clay accumulation in the subsoil despite the large increases in clay content with depth (Table 27). None of the soil profiles excavated, except at Msimba, reached the bedrock and only Lubonde had a compact layer, possibly a cultivation pan, just below the lower Ap horizon. Where mottling occurred they were generally signs of iron accumulations either as concretions or as patches with higher chroma in the matrix indicating that some iron may be translocated by redox processes caused by temporary water saturation during heavy showers despite the soils being well drained. In some of the soil profiles dark mottles resembling old root remnants were present. The volcanic soils typically contained distinct pieces of pumice with strong colours at depth.

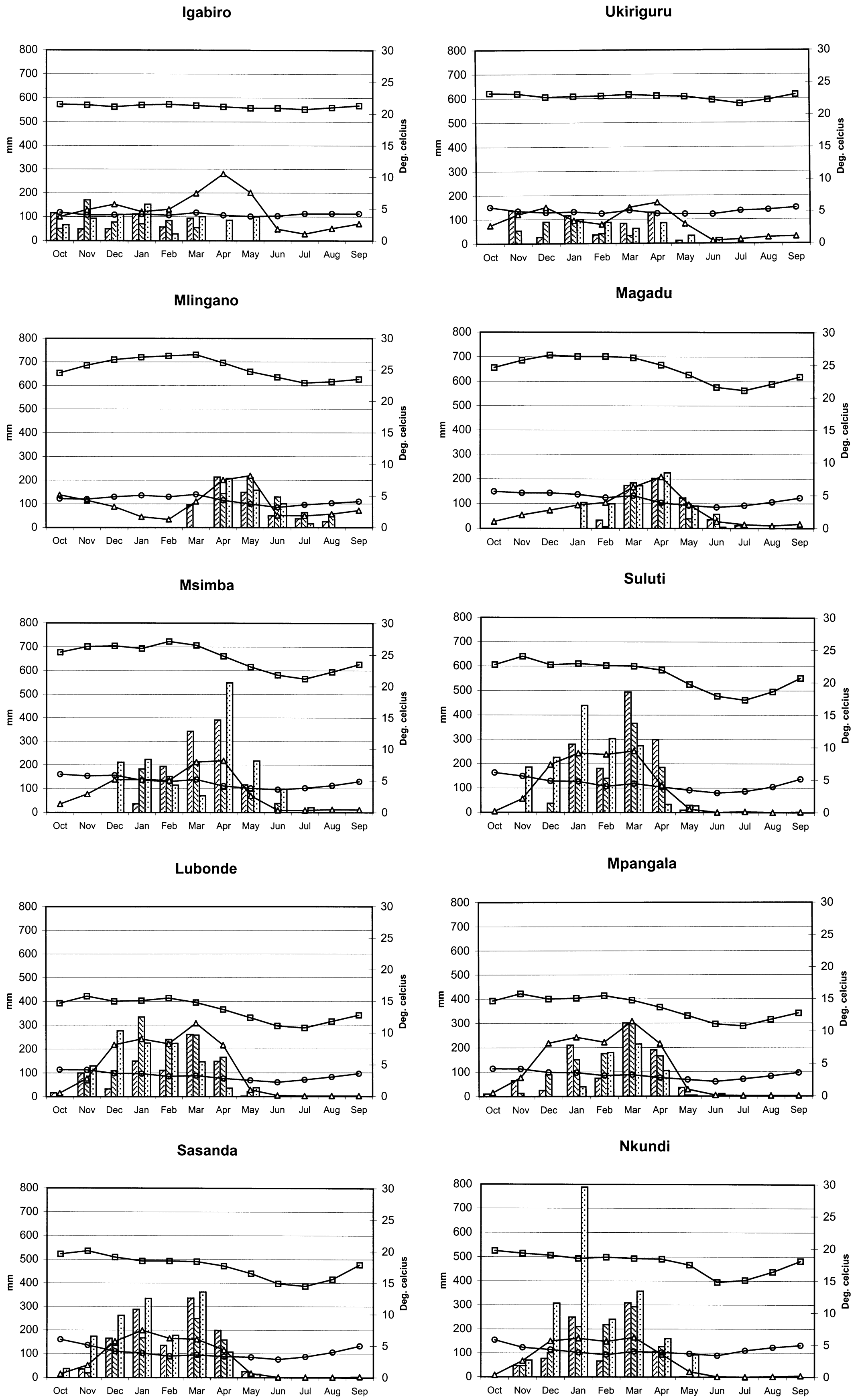


Figure 30. Climatical characteristics derived from nearby meteorological stations {59}, and observed precipitation during the first three growing seasons (first bar = 1998/1999, second bar = 1999/2000 and third bar = 2000/2001, square=temperature, circle=potential evapotranspiration, triangle=precipitation).

Table 25. Classification and physiography.

Site	Diagnostic horizons epipedon/subsurface Soil Taxonomy[1]	Classification Soil Taxonomy	WRBSR[2]	Physiography, parent material and drainage
Igabiro	Umbric/Oxic	Isohyperthermic, fine loamy, kaolinitic Typic Haplustox	Umbric Ferralsol	Upper part of a straight slope on the hilly dissected Kamachumu Plateau formed by parallel ridges and intervening narrow valleys. G: 6-8% towards ENE, PM: Quartzite rich sandstone, D: Well drained.
Ukiriguru	Ochric/Argillic	Isohyperthermic, coarse loamy, kaolinitic Kanhaplic Haplustult	Haplic Acrisol	Upper part of a straight footslope of an Inselberg on the flat to gently undulating plains of the Central Plateau. G: 5-9% towards SE, PM: Granite, D: Well drained.
Mlingano	Ochric/Kandic	Isohyperthermic, very fine, kaolinitic Rhodic Kandiustox	Rhodic Ferralsol	Crest of the undulating to rolling plains of the Eastern Plateau. G: 1-2% towards NE, PM: Intermediate metamorphic rocks, D: Well drained.
Magadu	Ochric/Argillic	Isohyperthermic, very fine, kaolinitic Kanhaplic Haplustult	Chromic Acrisol	Lower part of alluvial fan of the Uluguru Mountains in stretching out into the Ngerengere valley, which slightly dissects the undulating to rolling plains of the Eastern Plateau. G: 2% towards NW, PM: Intermediate metamorphic rocks, D: Well drained.
Msimba	Ochric/Argillic	Isohyperthermic, fine, mixed Ultic Haplustalf	Haplic Luvisol	Lower part of the undulating to rolling footslopes of the Ukaguru Mountains bordering the flat alluvial Mkata plains of the Eastern Plateau. G: 4-8% towards E, PM: Kyanite-garnet-biotite gneiss, D: Well drained.
Suluti	Ochric/Kandic	Isohyperthermic, very fine, kaolinitic Rhodic Kanhaplustalf	Rhodic Acrisol	Flat dissected plain of the Eastern Plateau. G: 2% towards E, PM: Intermediate metamorphic rocks, D: Well drained.
Lubonde	Mollic/Oxic	Isothermic, fine, kaolinitic Humic Rhodic Haplustox	Humic Ferralsol	Middle part of a straight slope on the undulating to rolling plains and plateau of the Southern Highland with mountainous ridges and steep-sided valleys. G: 6-7% towards NE, PM: Basement complex rocks, D: Well drained.
Mpangala	Mollic/Cambic	Thermic, fine-silty, mixed, Andic Dystrustept	Andic Cambisol	Lower part of a straight slope on the undulating to rolling plains and plateau of the Southern Highland with mountainous ridges and steep-sided valleys. G: 17% towards NE, PM: Basement complex rocks and basaltic lavas covered with volcanic pumice and ash from the Mt. Ngozi area, D: Well drained.
Sasanda	Umbric/Cambic	Isohyperthermic, medial, mixed Dystric Haplustand	Umbric Andosol	Lower part of a straight slope on the undulating medium to high altitude plateau of the Southern Highland. G: 2-5% towards S, PM: Gneissic rocks covered by volcanic pumice and ash from the Rungwe area, D: Well drained.
Nkundi	Ochric/Kandic	Thermic, fine, kaolinitic Acruoxic Kandiustult	Chromic Acrisol	Middle part of a straight slope on the flat to very gently undulating high altitude plains of the Ufipa Plateau. G: 4-5% towards S, PM: Gniesses and schists, D: Well drained.

[1] {249}. [2] WRBSR: World Reference Base for Soil Resources {61}, G: Gradient at soil profile, PM: Parent material, D: Drainage.

Physically most of the non-volcanic soils show no or very weak soil macro structure (Table 26). For the kaolinitic soils only the surface horizon show weak granular or sub-angular blocky structure, whereas the subsoil in most cases appears structure less. However, the overall porosity is generally high due to the normally large content of very fine to medium channels in the otherwise massive matrix. The higher organic matter content in the upper horizons generally results in a darker colour and a more well developed granular or blocky structure with the resulting positive effects on workability, water infiltration and reduced erodibility. Except for Lubonde, which apparently due to the high content of organic matter is both soft and friable, most of the kaolinitic soils are only friable when moist. In the dry state they are all hard to very hard and are either slightly sticky and slightly plastic or non-sticky and non-plastic when wet. These properties can mainly be attributed to the dominance of low activity clay minerals and content of sesquioxides. In contrast, the volcanic soils are both very soft when dry and friable when moist resulting in a very high infiltration capacity and good workability.

The textural composition vary among the sites ranging from loamy sands to loam, clay and silt loam (Table 27). Except for the volcanic soils and Ukiriguru, the soils have relatively high clay contents, which in several cases increases with depth from the surface horizon indicating that clay eluviation-illuviation or other processes resulting in textural differentiation have taken place. In case of the kaolinitic soils, with exception of Lubonde, the silt:clay ratio is low indicating a high rate of weathering {58}. The large fraction of silt in Lubonde is possibly due to high contents of gibbsite present in both the clay and fine silt fractions. Ukiriguru deviates from the other soils by having a very coarse sandy composition reflecting the very coarse-grained granitic parent material. The content of fine gravel (2-4 mm) increases with depth and the lowest horizon contain more than 25% fine gravel indicating a transition zone towards the quartz-rich saprolite. The silty composition of the volcanic soils probably reflects the composition of the ash, which was deposited in the Mt. Rungwe area during Pleistocene and up to recent times {82}. Bulk density among the non-volcanic soils is generally medium to high in the surface horizon and shows either a constant or decreasing value down through the soil profile (Table 27). For Magadu and Suluti, the higher bulk density in the surface soil probably reflects the effect of mechanical compaction compared to the stable, clayey and very porous subsoil. Lubonde generally show a low bulk density even in the two upper horizons, which are probably a result of the deep cultivation and high content of organic matter. The two volcanic soils have very low bulk densities reflecting the typical porous characteristics of recent ash-pumice type deposits containing poorly crystalline aluminium silicates {242}. The decreasing bulk density with depth in Mpangala reflects a more advanced weathering stage in the surface horizons compared with the subsurface horizons (see below).

Available water holding capacity (AWC) in the upper meter of the soil profiles is ranging from 60 mm at Ukiriguru up to 230 mm at Sasanda (Table 27). Multiple regression showed that 96% of the variation in AWC can be explained by the content of clay (<2 µm), fine silt (2-20 µm) and sand (50-250 µm) ($AWC = 0.077 \cdot clay\% + 0.437 \cdot fine\ silt\% + 0.127 \cdot sand\%$). The contribution of organic matter to AWC was not significant indicating that the inorganic constituents are the most important factors for AWC in these soils. The differences in AWC also show that the moisture reserve in case of dry spells or early cutting off of rains is quite different among the sites.

Table 26. Macro-morphological characteristics.

Horizon[1]	Depth	Matrix colour (moist)	Mottling[2]		Field texture[3]	Struc-ture[4]	Consistence[5]		Poro-sity[6]
	cm		Abundance /contrast	Colour (moist)			dry/ moist	wet	
Igabiro									
Ap	0-18	7.5YR 2.5/3	-	-	l	mm-cg	s/	s, p	m
A	18-43	7.5YR 2.5/3	f/d	5YR 4/4	l	pm	/f	s, p	m
AB	43-65	7.5YR 2.5/2	f/d	5YR 4/4	l	pm	/f	s, p	m
Bo1	65-110	7.5YR 3/4	c/d	5YR 4/4	l	pm	/f	s, p	m
Bo2	110-180	5YR 4/4	f/p	7.5YR 2.5/2	scl	pm	/f	s, p	h
Ukiriguru									
Ap	0-28	7.5YR 3/3	-	-	csl	wfsb	s/	ns, np	m
AB	28-49	7.5YR 3/3	-	-	csl	pm	/f	ns, np	m
Bt1	49-75	7.5YR 3/4	f/f	5YR 4/6	csl	pm	/f	ns, np	m
Bt2	75-132	7.5YR 3/4	c/f	5YR 4/6	cls	pm	/f	ns, np	m
BC	132-180	7.5YR 3/4	c/f	5YR 4/6	cls	pm	/f	ns, np	m
Mlingano									
Ap	0-25	2.5YR 3/4	-	-	sc	wmg	/f	ss, sp	h
Bto	25-52	10R 3/4	-	-	sc	pm	/f	ss, sp	m
Bo1	52-105	10R 3/4	-	-	scl	pm	/f	ss, sp	m
Bo2	105-180	10R 3/4	-	-	scl	pm	/f	ss, sp	m
Magadu									
Ap	0-10	7.5YR 3/4	-	-	cl	pm	h/	s, p	m
Bo	10-47	5YR 4/6	-	-	cl	pm	sh/	ss, sp	m
Bto1	47-125	5YR 4/6	vf/d	10YR 5/6	cl	pm	/f	ss, sp	h
Bto2	125-180	5YR 4/6	c/d	10YR 5/6	cl	pm	/f	ss, sp	h
Msimba									
Ap	0-18	2.5YR 2.5/1	-	-	sl	mvfab	h/	ss, sp	m
AB	18-33	5YR 3/3	-	-	sc	pm	/f	s, p	m
Bt	33-64	5YR 3/4	f/d	7.5YR 2.5/2	sc	mfsb	/f	s, p	m
BC	64-90	5YR 3/4	-	-	sc	pm	/f	s, p	m

Macro-morphological characteristics, continued.

Horizon	Depth	Matrix colour (moist)	Mottling		Field texture	Structure	Consistence		Porosity
	cm		Abundance /contrast	Colour (moist)			dry/ moist	wet	
Suluti									
Ap	0-15	2.5YR 3/3	-	-	sl	pm	h/	ss, sp	m
AB	15-25	2.5YR 4/4	-	-	sl	pm	vh/	ss, sp	m
Bo1	25-70	2.5YR 3/6	-	-	cl	pm	/f	ss, sp	h
Bo2	70-120	2.5YR 3/6	-	-	cl	pm	/f	ss, sp	h
Bo3	120-180	2.5YR 3/6	-	-	cl	pm	/f	ss, sp	h
Lubonde									
Ap1	0-25	2.5YR 2.5/2	-	-	sl	vwvfg	/f	ss, sp	h
Ap2	25-55	2.5YR 2.5/2	-	-	sl	wmsb	/f	ss, sp	h
Bom	55-64	2.5YR 3/4	-	-	scl	pm	/fi	s, p	m
Bo1	64-125	10R 3/4	-	-	sl	pm	/f	ss, sp	h
Bo2	125-180	10R 3/4	-	-	sl	pm	/fi	ss, sp	m
Mpangala									
Ap	0-20	7.5YR 2.5/1	-	-	ls	wmg	/f	ns, np	vh
A	20-55	7.5YR 2.5/2	-	-	sl	wmsb	/f	ns, sp	vh
Bw1	55-95	7.5YR 2.5/3	-	-	sl	wm-csb	/f	ss, sp	h
Bw2	95-150	7.5YR 3/4	-	-	l	pm	/f	s, sp	h
Bw3	150-180	7.5YR 4/6	-	-	l	pm	/f	s, sp	h
Sasanda									
Ap	0-32	7.5YR 2.5/2	-	-	sil	wmg	/f	ns, np	vh
Bw1	32-65	7.5YR 3/4	-	-	l	wmg	/f	s, sp	vh
Bw2	65-125	7.5YR 3/4	-	-	l	wmsb	/f	s, sp	vh
Bw3	125-180	7.5YR 3/4	-	-	l	wmsb	/f	s, sp	vh
Nkundi									
Ap	0-8	7.5YR 2.5/2	-	-	ls	mmg	sh/	ss, sp	h
A	8-29	7.5YR 3/4	-	-	ls	wvf-fsb	sh/	ss, sp	m
AB	29-62	5YR 4/6	f/d	10YR 2/1	ls	vwvfsb	sh/	ss, sp	m
Bo1	62-135	5YR 4/6	f/d	10YR 2/2	sl	vwfsb	sh/	ss, sp	m
Bo2	135-180	5YR 4/6	f/d	10YR 2/2	sl	vwfsb	sh/	ss, sp	m

[1] Horizon designation follows Schoenberger et al. {230}.

[2] Mottling: vf/:very few, f/:few, c/:common, /d:distinct, /p:prominent {60}.

[3] Field determined texture: cls:coarse loamy sand, csl:coarse sandy loam, sl:sandy loam l:loam, scl:sandy clay loam, cl:clay loam, sc:sandy clay, sil: silty loam

[4] Structure: pm:porous massive, vwvfg:very weak very fine granules, wmg:weak medium granules, mmg:moderate medium granules, mm-cg:moderate medium to coarse granules, vwvfsb:very weak very fine sub-angular blocky, wvf-fsb:weak very fine to fine sub-angular blocky, wfsb:weak fine sub-angular blocky, wmsb:weak moderate sub-angular blocky, wm-csb:weak medium to coarse sub-angular blocky, mfsb:moderate fine sub-angular blocky, mvfab:moderate very fine angular blocky {60}.

[5] Consistence: dry: (s:soft, sh:slightly hard, h:hard), moist: (f:friable, fi:firm), wet: (ns:non-sticky, ss:slightly sticky, s:sticky, np:non-plastic, sp:slightly plastic, p:plastic) {60}.

[6] Porosity: m:medium, h:high, vh:very high {60}.

Table 27. Physical characteristics.

Horizon	Depth	Clay	Silt[1]			Sand[2]							AWC[4]	Bulk density
			F	C	T	VF	F	M	C	VC	T	TC[3]		
	cm	%											vol-%	g cm^{-3}
Igabiro														
Ap	0-18	26	4	2	6	5	35	25	3	<1	68	SCL	11	1.4
A	18-43	29	3	3	6	4	36	21	4	<1	65	SCL	11	1.2
AB	43-65	31	4	3	7	6	32	21	3	<1	62	SCL	11	1.2
Bo1	65-110	32	3	3	6	4	35	19	4	<1	62	SCL	12	1.3
Bo2	110-180	35	3	3	6	4	30	23	2	<1	59	SC	12	1.4
Ukiriguru														
Ap	0-28	9	4	4	8	9	21	20	17	16	83	LS	5	1.6
AB	28-49	13	5	6	11	5	15	15	19	22	76	SL	6	1.4
Bt1	49-75	15	6	5	11	8	15	14	16	21	74	SL	6	1.6
Bt2	75-132	14	6	6	12	6	11	10	17	30	74	SL	7	1.6
BC	132-180	11	5	4	9	6	6	6	17	45	80	SL	6	1.6
Mlingano														
Ap	0-25	54	5	1	6	4	13	9	9	5	40	C	7	1.4
Bto	25-52	66	1	<1	1	1	11	9	7	5	33	C	6	1.3
Bo1	52-105	62	2	3	5	3	9	9	7	5	33	C	10	1.2
Bo2	105-180	49	9	5	14	8	10	8	6	5	37	C	10	1.3
Magadu														
Ap	0-10	55	4	5	9	6	15	8	5	2	36	C	11	1.4
Bo	10-47	65	3	3	6	5	11	8	4	1	29	C	10	1.1
Bto1	47-125	65	4	4	8	6	9	6	4	2	27	C	13	1.1
Bto2	125-180	60	6	7	13	7	12	4	3	1	27	C	14	1.1
Msimba														
Ap	0-18	27	12	7	19	9	18	14	8	5	54	SCL	9	1.4
AB	18-33	39	8	8	16	7	13	11	9	5	45	SC	9	1.6
Bt	33-64	49	8	6	14	6	10	9	7	5	37	C	9	1.3
BC	64-90	47	6	<1	6	5	8	9	10	15	47	SC	8	1.5
Suluti														
Ap	0-15	24	3	6	9	11	25	19	8	4	67	SCL	9	1.5
AB	15-25	53	2	3	5	7	17	11	5	2	42	C	8	1.4
Bo1	25-70	62	3	3	6	5	11	10	3	3	32	C	7	1.2
Bo2	70-120	55	5	3	8	6	16	10	3	2	37	C	9	1.2
Bo3	120-180	51	5	6	11	7	17	8	4	2	38	C	8	1.1
Lubonde														
Ap1	0-25	43	19	4	23	4	8	10	7	5	34	C	16	0.8
Ap2	25-55	48	18	4	22	4	8	9	5	4	30	C	23	1.0
Bom	55-64	51	24	2	26	2	6	7	5	3	23	C	19	1.2
Bo1	64-125	47	20	5	25	5	8	7	5	3	28	C	19	1.0
Bo2	125-180	53	15	3	18	3	8	8	6	4	29	C	12	1.2
Mpangala														
Ap	0-20	30	22	6	28	3	10	20	7	2	42	CL	18	0.9
A	20-55	27	22	6	28	3	12	21	7	2	45	L	17	0.9
Bw1	55-95	25	30	8	38	3	8	18	6	2	37	L	21	0.8
Bw2	95-150	25	35	13	48	8	7	8	3	1	27	L	31	0.6
Bw3	150-180	28	41	9	50	6	6	6	3	1	22	CL	31	0.6
Sasanda														
Ap	0-32	35	34	7	41	7	11	4	1	1	24	CL	21	0.7
Bw1	32-65	28	39	14	53	6	9	3	1	<1	19	SICL	21	0.7
Bw2	65-125	25	46	14	60	7	7	1	<1	<1	15	SIL	27	0.6
Bw3	125-180	25	35	13	48	8	7	8	3	1	27	L	24	0.7
Nkundi														
Ap	0-8	18	4	7	11	15	30	18	6	2	71	SL	16	1.4
A	8-29	28	2	2	4	12	35	14	5	2	68	SCL	11	1.4
AB	29-62	34	3	7	10	15	24	11	4	2	56	SCL	14	1.3
Bo1	62-135	40	3	6	9	20	21	7	2	1	51	SC	13	1.2
Bo2	135-180	45	3	10	13	17	18	4	2	1	42	C	12	1.3

[1] Clay (<2 µm), F:fine silt (2-20 µm), C:coarse silt (20-50 µm), T:total silt {230}.

[2] VF:very fine sand (50-100 µm), F:fine sand (100-250 µm), M:medium sand (250-500 µm), C:coarse sand (500-1000 µm), VC:very coarse sand (1000-2000 µm), T:total sand {230}.

[3] Textural class: LS:loamy sand, SL:sandy loam, SCL:sandy clay loam, L:loam, SC:sandy clay, CL:clay loam, C:clay, SICL:silty clay loam, SIL:silt loam {230}.

[4] AWC: Available water content (pF2.5-pF4.2).

Table 28 show some chemical properties of the soils. The sites are generally slightly acid to acid except for Msimba, which is close to neutral. The ΔpH (pH_{KCl}-pH_{water}) is negative in all cases, indicating that all the soils possess net negative charge despite most of them being dominated by low activity clay minerals and contain sesquioxides (Table 32 and Table 33). The pH values are generally rather constant down through the soil profile, even in Magadu and Nkundi despite increasing levels of exchangeable acidity in the subsoil. CEC_e is low for Igabiro, Ukiriguru, Mlingano, Suluti, Lubonde, Sasanda and Nkundi, intermediate in case of Magadu and Mpangala and high for Msimba reflecting the combined effect of the clay mineralogy, organic matter content and soil pH. The large difference between CEC_7 and CEC_e for the soils with low CEC_e values reflects the high content of variable charge components and relatively low soil pH values. Especially Sasanda show very strong pH dependent charge with the organic matter being almost entirely responsible for the exchange capacity. The difference between CEC_e and CEC_7 for Msimba is small and reflect the combined effect of soil pH and presence of permanently charged clay minerals. The CEC_7 values are generally in agreement with the content and type of clay and the amount of organic matter (Table 29 and Table 33). Except for the subsoils of Magadu and Nkundi the effective base saturation (BS_e) is exceeding 70% indicating relatively low amounts of total exchangeable acidity of which exchangeable aluminium (Al) in most cases is dominating. Base saturation in the subsoil based on CEC_7 is below 50% except for Msimba, Suluti and Lubonde. Exchangeable calcium (Ca) is the dominating exchangeable base cation in the surface soil horizons except for Mlingano where levels of exchangeable magnesium (Mg) are higher. Except for Msimba, the levels of exchangeable Ca are low, especially for Ukiriguru, Mlingano, Suluti and Sasanda. In case of Mlingano, Magadu, Sasanda and Nkundi exchangeable Ca in the subsoil is considered very low and make up only a minor fraction of the exchangeable base cations. In case of Mlingano and Magadu exchangeable Mg is dominating whereas exchangeable potassium (K) is dominating in Sasanda and Nkundi giving high ratios of K to Ca+Mg. Levels of exchangeable Mg in the surface horizon are low especially for Ukiriguru, Suluti and Sasanda. In the subsoil especially Ukiriguru, Lubonde, Sasanda and Nkundi have low levels of exchangeable Mg. Levels of exchangeable K are very low for Igabiro, Ukiriguru, Mlingano, Suluti and Nkundi and contributes only a little to the exchangeable base cations. An exception to this is the high ratios of K to other base cations especially in the subsurface horizons of Sasanda and Nkundi. Exchangeable sodium (Na) is generally negligible.

Table 28. Soil chemical characteristics.

Horizon	Depth	pH$_w$	pH$_{KCl}$	Exchange capacity and exchangeable cations									
				Ca	Mg	K	Na	H+Al	CEC$_e$	CEC$_7$	Al-sat.	BS$_e$	BS$_7$
	cm			cmol(+) kg^{-1}							%	%	%
Igabiro													
Ap	0-18	5.6	4.2	1.8	1.1	<0.1	<0.1	0.4	3.4	6.8	12	88	44
A	18-43	5.4	4.1	1.3	0.7	<0.1	<0.1	0.8	2.9	6.4	28	71	32
AB	43-65	5.0	4.1	1.6	0.7	0.1	0.1	0.6	3.1	6.8	19	81	37
Bo1	65-110	5.6	4.1	1.1	0.7	<0.1	0.1	0.8	2.7	7.2	30	72	27
Bo2	110-180	5.7	4.3	1.7	0.6	0.1	0.1	0.4	2.9	6.8	14	86	37
Ukiriguru													
Ap	0-28	5.3	4.1	0.9	0.2	0.1	<0.1	0.3	1.5	2.5	20	80	48
AB	28-49	5.7	4.1	1.6	0.2	0.1	<0.1	0.3	2.2	4.1	14	88	47
Bt1	49-75	5.6	4.2	1.5	0.2	0.1	<0.1	0.2	2.0	3.6	10	92	51
Bt2	75-132	5.6	4.3	0.6	0.2	0.1	0.1	0.1	1.1	2.3	9	91	43
BC	132-180	5.7	4.5	1.0	0.4	0.1	<0.1	0.1	1.6	3.1	6	96	49
Mlingano													
Ap	0-25	5.3	4.1	0.7	0.9	0.2	<0.1	0.6	2.4	7.3	25	76	25
Bto	25-52	5.1	4.1	0.8	0.7	0.1	<0.1	0.7	2.3	8.5	30	70	19
Bo1	52-105	5.4	4.3	0.6	0.6	<0.1	0.1	0.5	1.8	5.0	28	74	27
Bo2	105-180	5.4	4.3	0.2	1.5	<0.1	0.1	0.3	2.1	4.0	14	88	46
Magadu													
Ap	0-10	4.9	3.8	2.9	1.7	0.6	0.1	1.4	6.7	11.6	21	79	46
Bo	10-47	4.8	3.7	1.4	1.4	0.2	0.1	3.4	6.5	15.0	52	48	21
Bto1	47-125	5.3	3.8	0.2	1.6	0.2	0.1	3.7	5.8	13.0	64	36	16
Bto2	125-180	5.5	3.8	0.2	1.5	0.1	0.2	3.8	5.8	12.2	66	34	16
Msimba													
Ap	0-18	6.5	5.2	9.7	2.7	1.3	0.1	<0.1	13.8	16.3	0	100	85
AB	18-33	6.8	5.3	9.4	3.0	0.7	<0.1	<0.1	13.2	15.9	0	99	83
Bt	33-64	6.5	5.1	7.9	3.7	0.5	0.1	<0.1	12.2	16.9	0	100	72
BC	64-90	6.4	5.0	7.1	3.9	0.3	0.2	<0.1	11.5	16.7	0	100	69
Suluti													
Ap	0-15	6.2	4.8	1.5	0.6	0.2	<0.1	<0.1	2.4	4.7	1	98	50
AB	15-25	6.1	4.8	1.8	0.7	0.1	0.1	<0.1	2.7	5.5	1	100	49
Bo1	25-70	6.3	5.2	2.0	1.2	0.1	<0.1	<0.1	3.4	6.4	1	98	52
Bo2	70-120	6.5	5.8	1.4	1.0	0.1	<0.1	<0.1	2.5	6.2	0	100	41
Bo3	120-180	6.6	5.7	1.2	0.7	0.3	<0.1	<0.1	2.3	3.6	1	97	62
Lubonde													
Ap1	0-25	5.7	4.4	3.8	0.9	0.6	<0.1	0.1	5.4	10.7	2	99	50
Ap2	25-55	5.6	4.4	4.1	1.0	0.3	<0.1	0.2	5.6	11.6	4	97	47
Bom	55-64	5.7	4.5	2.9	0.9	0.3	<0.1	0.1	4.2	9.7	2	99	43
Bo1	64-125	6.2	5.1	1.7	0.6	0.1	<0.1	<0.1	2.4	4.6	0	100	53
Bo2	125-180	6.4	5.6	1.5	0.6	<0.1	<0.1	<0.1	2.2	4.0	0	98	54
Mpangala													
Ap	0-20	6.0	4.8	5.9	1.6	1	<0.1	0.1	8.6	12.5	1	99	68
A	20-55	6.0	4.7	3.3	1.4	0.9	0.1	0.1	5.8	11.5	2	98	50
Bw1	55-95	6.0	4.7	2.4	1.7	0.8	0.1	0.1	5.1	10.4	2	98	48
Bw2	95-150	6.0	4.9	2.4	1.9	0.7	0.2	0.1	5.3	13.5	2	98	39
Bw3	150-180	6.0	4.9	1.7	2.5	0.5	0.3	0.1	5.1	13.7	2	98	36
Sasanda													
Ap	0-32	5.5	4.6	1.2	0.6	0.5	<0.1	0.2	2.5	10.1	8	93	23
Bw1	32-65	6.0	4.7	0.1	0.5	0.5	0.1	0.2	1.4	10.1	14	86	12
Bw2	65-125	6.2	5.0	0.1	0.4	0.6	0.2	0.1	1.4	9.6	7	93	14
Bw3	125-180	6.3	4.9	0.2	0.2	1.4	0.2	0.2	2.2	10.1	9	91	20
Nkundi													
Ap	0-8	5.9	4.7	2.1	1.5	0.2	<0.1	<0.1	3.9	6.4	1	98	60
A	8-29	5.3	4.1	0.2	0.2	0.1	<0.1	0.8	1.3	3.2	62	39	16
AB	29-62	5.2	4.1	0.2	0.1	0.1	<0.1	0.9	1.3	4.3	69	32	10
Bo1	62-135	5.9	4.3	0.1	<0.1	0.3	<0.1	0.7	1.2	5.5	58	38	8
Bo2	135-180	5.8	4.3	<0.1	0.1	0.4	<0.1	0.8	1.4	4.6	57	41	13

Table 29. Organic carbon and extractable elements.

Horizon	Depth	C	Total P		Extr. P	Extractable micronutrients		Oxalate extr. elements			
			P_{inorg}	P_{org}	P_{Olsen}	Cu	Zn	Fe_o	Al_o	Si_o	P_o
	cm	%	mg P kg^{-1}								
Igabiro											
Ap	0-18	1.5	150	180	5	2.4	0.3	1060	1610	360	28
A	18-43	1.2	90	190	2	2.0	0.2	990	1680		14
AB	43-65	1.2	110	130	1	2.1	0.2	930	1520		13
Bo1	65-110	0.8	90	160	1	2.8	0.1	1040	1750		15
Bo2	110-180	0.6	100	120	1	2.0	0.2	970	1690		14
Ukiriguru											
Ap	0-28	0.3	140	70	19	0.4	1.0	460	550	240	90
AB	28-49	0.3	40	70	1	0.4	0.1	530	790		17
Bt1	49-75	0.3	50	70	1	0.4	0.1	400	670		11
Bt2	75-132	0.2	50	80	1	0.5	0.1	270	470		11
BC	132-180	0.1	40	50	2	0.9	0.1	290	370		15
Mlingano											
Ap	0-25	1.2	90	90	2	6.2	0.8	800	1310	470	15
Bto	25-52	0.5	70	70	1	5.0	0.3	820	820		10
Bo1	52-105	0.4	50	50	1	3.6	0.2	760	770		8
Bo2	105-180	0.2	40	30	<1	2.6	0.4	820	690		7
Magadu											
Ap	0-10	1.2	260	160	31	1.4	14.4	910	1440	440	117
Bo	10-47	0.7	70	150	1	1.3	0.7	610	1580		11
Bto1	47-125	0.4	80	90	1	1.2	0.1	500	1630		7
Bto2	125-180	0.3	50	100	1	1.3	0.2	440	1550		9
Msimba											
Ap	0-18	2.3	210	230	10	4.3	1.7	990	960	670	83
AB	18-33	1.3	150	200	2	5.0	0.3	980	1070		29
Bt	33-64	0.9	140	200	1	5.0	0.3	1090	1310		17
BC	64-90	0.7	140	210	2	4.4	0.5	960	1200		21
Suluti											
Ap	0-15	1.0	260	210	12	0.9	0.7	980	820	320	145
AB	15-25	0.4	220	270	5	0.7	0.2	800	1190		55
Bo1	25-70	0.2	170	110	4	0.5	0.2	660	1100		31
Bo2	70-120	0.1	70	160	<1	0.5	0.3	470	850		7
Bo3	120-180	0.1	50	190	<1	0.4	0.2	460	820		6
Lubonde											
Ap1	0-25	2.6	390	360	9	0.5	1.4	2540	4250	1540	158
Ap2	25-55	2.3	270	290	3	0.4	0.9	2200	4670		78
Bom	55-64	1.3	180	130	1	0.2	0.2	990	2240		20
Bo1	64-125	0.5	190	40	1	0.2	0.2	530	1620		19
Bo2	125-180	0.3	190	10	1	0.1	0.3	550	1530		19
Mpangala											
Ap	0-20	2.9	240	410	4	0.5	1.8	5070	6320	6560	187
A	20-55	1.4	150	320	1	0.2	0.8	6610	9280		108
Bw1	55-95	0.8	100	110	1	0.2	1.2	6350	10180		54
Bw2	95-150	0.9	110	140	<1	0.2	0.9	3660	22040		37
Bw3	150-180	0.5	220	100	1	0.2	1.0	6630	25540		15
Sasanda											
Ap	0-32	3.4	190	240	1	2.6	0.6	4430	22680	17550	115
Bw1	32-65	1.5	120	130	<1	0.2	0.3	5480	24370		39
Bw2	65-125	1.2	100	120	<1	0.2	0.2	5150	36550		2
Bw3	125-180	0.8	70	120	<1	0.1	0.6	4450	14430		3
Nkundi											
Ap	0-8	2.0	100	120	4	1.5	1.9	590	640	340	30
A	8-29	0.6	70	110	2	1.8	0.2	550	810		14
AB	29-62	0.5	70	140	1	1.3	0.0	410	990		15
Bo1	62-135	0.2	70	130	1	1.0	0.0	350	1050		12
Bo2	135-180	0.1	100	130	1	0.9	0.1	440	1120		18

The organic matter content is reasonably high in most surface horizons. An exception is Ukiriguru and partly Suluti containing low amounts of organic matter in all horizons, which could be attributed to the rapid mineralization in the sandy soil and relatively low biomass production at Ukiriguru, and low input of organic matter to the soil due to the widespread fires during the dry season at Suluti. The two volcanic soils and Igabiro and Lubonde exceed 16 kg C m^{-2} down to 180 cm. The high contents of organic matter in Lubonde may partly be explained by the indications of a former forest cover and partly to the very deep cultivation during preparation of the large ridges used in the traditional farming system. At Igabiro, the high content of organic matter in the subsurface horizons may be a result of collovial processes as the soil profile is located at the lower part of a cultivation terrace. High contents of organic matter in the two volcanic soils are probably a result of metal-humus complexes, which protects the organic matter from mineralization {29}.

The total P content of the various horizons vary between 67 mg P kg^{-1} in the subsoil of Mlingano to 750 mg P kg^{-1} in the surface soil of Lubonde respectively. The content is largest in the surface soil and decreases with depth indicating a combined effect of previous fertilization and translocation (pumping effect) of P through the biomass from lower horizons to the surface horizon. Based on the history of the sites, fertilization seems to have played a role for the increase in total P content in the surface soil at Igabiro, Ukiriguru, Magadu and Suluti. Lubonde, Mpangala and Sasanda. Total organic P generally constitutes approximately half of the total P emphasising the importance of the organic matter in the soil P cycle. However, there is no relation between available P and total inorganic or organic P indicating that the majority of the soil P is not participating in the immediate exchange reactions and hence is unavailable at least for the short term supply of P to the plants.

Despite the possible P fertilization at a number of sites the amount of available P as assessed by $NaHCO_3$ (P_{olsen}) generally show low levels. Particularly the subsoil show very low levels at all sites. Based on the values of the surface horizons, sites such as Igabiro, Mlingano, Mpangala, Sasanda and Nkundi seem to be strongly P deficient. Msimba, Suluti and Lubonde intermediate P deficient and Ukiriguru and Magadu apparently having sufficient levels of available P. As the analyses of the samples of each block places Magadu among the strongly deficient sites (Table 34), the surface soil must have been contaminated with P either before or after sampling. In fact it was realized that sewage from Morogoro town was dumped right next to the experimental field with some sludge flowing right into the soil profile indicating that this could also have happened before sampling of the soil in that pit.

P sorption isotherms for the surface soil samples are given in Figure 31 with details in Table 30. Phosphate adsorption maximum (P_{max}), as calculated from the experimental data fitted to the Langmuir equation, show that the sites are characterized by low (Ukiriguru, Msimba, Suluti, Nkundi), medium (Igabiro, Mlingano, Magadu), high (Lubonde, Mpangala) to very high (Sasanda) phosphate adsorption capacity.

Although being highly correlated with the content of sesquioxides, the experimentally determined adsorption maxima (P_{max}) are significantly lower than expected (P_{calc}), considering the content of less crystalline sesquioxides (Fe_o and Al_o) and crystalline iron oxides (Fe_d-Fe_o) using the pedotransfer function of Borggaard et al. {30} (Table 30). The discrepancy may primarily be attributed to the experimental design of the adsorption study in which the initial P concentrations were adjusted to the expected P_{max} of the particular soil in order to avoid excessive equilibrium P concentrations, which normally result in the absence of a well-defined adsorption maximum (a Freundlich type curve progress). A continued increase in P sorption at high equilibrium concentrations may involve precipitation reactions in addition to specific adsorption and hence overestimate the actual adsorption {232}. By adjusting the maximum initial P concentration so it corresponds to approximately 100% saturation of the expected P_{max}, the first part of the curve is much better described as the data points are evenly distributed in the low concentration range and fitting to the Langmuir equation is more successful, which is also indicated by the high regression coefficients in Table 30. From a mechanistically point of view it seems evident that description of the first part of the isotherm in the low concentration range where P retention primarily is a result of specific adsorption, is more relevant than at higher concentrations. Based on the regression curves in Figure 31 it seems that most of the soils are close to P saturation at equilibrium concentrations, which are significantly lower than normally seen for similar P adsorption studies {193}. More evidence that P_{max} may have been underestimated in this study compared to adsorption studies at higher initial P concentrations is also demonstrated by the experimentally determined P_{index} shown in Table 30. The P_{index} was determined as a single observation at an initial P concentration of 120 mg P dm^{-3} corresponding to several times the estimated P_{max} for most soils. The P_{index}, excluding Sasanda, is highly correlated with P_{calc} (P_{calc}=P_{index}, R^2=0.98***) indicating that initial P concentration may have large impact on the apparent P adsorption. Sasanda represents a special case because most of the P adsorption capacity is related to the content of poorly crystalline aluminium silicates. As soils of this kind were not part of the data set from which the pedotransfer function were developed, deviations are expected due to the differences in adsorption capacity and specific surface area of these minerals. A slight overestimation of P_{calc} compared to the P_{index} is also observed in Msimba and Mlingano and could be attributed to a high crystallinity of the hematite present in the clay fraction, which leads to an overestimation of the predicted contribution to P adsorption by the crystalline iron oxides (Fe_d-Fe_o) {31, 193}.

The estimates of the affinity parameter (K) in Table 30 are also variable between the sites. For sites with similar P_{max} values (Ukiriguru = Msimba = Suluti = Nkundi < Igabiro = Mlingano = Magadu < Lubonde = Mpangala < Sasanda) it may reflect the soils relative affinity for P. Hence, applied P is expected to be stronger retained at Suluti and Nkundi than at Ukiriguru and Msimba despite the similar P adsorption capacity. This is also indicated by the estimated standard P requirement (SPR) and may be a result of the present composition and degree of P saturation of the adsorbents, i.e. the type and availability of P adsorbing sites. In this way SPR gives a good picture of the combined effect of the soil's affinity and capacity for P adsorption and as a rough estimate, assuming that applied P will get in contact with 1250 tons of surface soil per hectare, fertilizer P requirements range from 66 kg P ha^{-1} at Msimba to 1980 kg P ha^{-1} at Sasanda, indicating highly variable fertilizer requirements among the sites. Figure 31 also indicates a highly variable P buffer capacity among the sites. It is evident from the graph that relatively small additions of P through fertilizers at sites such as Ukiriguru, Msimba and Nkundi lead to a dramatic increase in the soil solution concentration of P whereas same P additions to sites such as Lubonde, Mpangala and Sasanda only increase the soil equilibrium P concentration to a small extent. On the other hand when the latter sites once have been supplied with large amounts of fertilizer P, the capacity of releasing P to the soil solution will last for a number of years under the assumptions that the P is not irreversibly fixed. Hence, the suitability for P recapitalization by large single applications of P is highly different between the sites.

Table 30. P adsorption characteristics of the surface soils.

Soil	P_{max} mg P kg^{-1}	K dm^{-3} mg P^{-1}	R^2 %	SPR^a	P_{calc}^{b}	P_{index}^{c}	Fe_o	Al_o	Fe_d	Al_d
							mg kg^{-1}			
Igabiro	493	4.24	99	226	757	885	1058	1609	11550	2786
Ukiriguru	219	1.61	98	53	237	231	462	550	2830	517
Mlingano	462	4.51	99	219	1025	746	804	1309	24178	1859
Magadu	528	2.95	99	196	896	940	911	1436	18252	2822
Msimba	266	1.36	99	57	638	479	985	955	13051	1078
Suluti	209	3.70	99	89	448	411	976	820	7392	944
Lubonde	970	3.35	98	389	1527	1556	2541	4246	14364	3054
Mpangala	1017	4.50	98	482	1936	1815	5074	6320	7674	2822
Sasanda	2430	9.30	95	1580	5978	2812	4430	22684	11359	7829
Nkundi	181	3.74	99	77	356	363	585	644	6134	1359

^{a}SPR: Standard P requirement, the amount of P required to increase equilibrium concentration to 0.2 mg P dm^{-3} using the experimentally determined Langmuir parameters.

^{b}P_{calc}= $0.221 \cdot Al_o + 0.115 \cdot Fe_o + 0.05 \cdot (Fe_d - Fe_o) + 0.3$ {30} (all units in mmol kg^{-1}).

^{c}Single determination of P sorption at an initial concentration of 120 mg P dm^{-3} with a soil:solution ratio of 1:25, shaken for 16 hours.

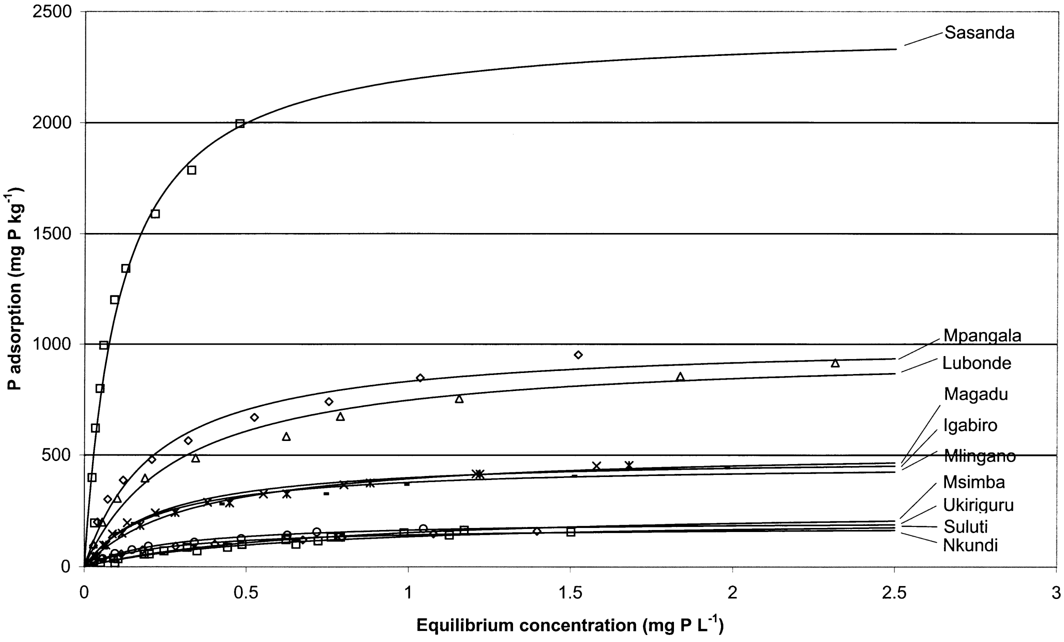


Figure 31. P adsorption isotherms for the surface soil samples from each experimental site.

Total elemental composition and total DCB extractable Fe and Al (Fe_{clay} and Al_{clay}) of the clay fraction from each horizon is presented in Table 32. Mineralogically most of the soils are strongly weathered and leached and only Ukiriguru and Msimba, which are located on the slopes of mountains composed of crystalline rocks and the two volcanic ash soils contain appreciable amounts of primary minerals other than quartz in the silt fractions (Table 31). The X-ray diffraction patterns indicate that the K-feldspars are distinctively different between the two volcanic soils on one side and the non-volcanic soils on the other side. Whereas sanidine is prevalent in Sasanda and Mpangala, microcline seems to be dominant in the other soils indicating different temperature conditions during formation of the parent material. The clay fractions of Mlingano, Magadu, Suluti, Lubonde and Nkundi are almost entirely composed of kaolinite and sesquioxides whereas Mpangala and Sasanda developed on Neogene volcanic ash show only few signs of secondary minerals other than poorly crystalline aluminium silicates (imogolite and allophane) and unordered kaolinites/halloysites (Table 33). Except for the two volcanic soils no variation with depth were observed from the XRD and FTIR spectra and hence only the average composition of the soil profile is given. The two volcanic soils did show a slight decrease in the content of kaolinite/halloysite with depth indicating a more weathered stage above and less weathered pumice at depth. Msimba showed a higher content of smectite in depth in accordance with clay illuviation processes. For most of the non-volcanic soils, residual accumulation of secondary iron minerals is also indicated by the strong reddish and yellowish subsoil colours. Ferrihydrite seems to be prevalent in the two volcanic soils due to the high amount of organic matter and relatively high rate of weathering whereas either goethite or hematite is dominating in the other soils depending on the degree of weathering, soil drainage and climatical conditions. The larger weight loss in the 110-350 ºC interval compared with the other soils and the XRD analyses indicate that the Lubonde soil contains a significant amounts of gibbsite. The high porosity and large P adsorption capacity of Lubonde may also be attributed to this high gibbsite content.

The non-volcanic soils have developed from rather different kinds of parent materials over time on relatively stable surfaces in a primarily udic to ustic soil moisture regime and with isothermic or isohyperthermic temperatures. The main soil pedogenetical process, which has acted on the soils, is desilication although some clay illuviation may have been or still is active at some sites, e.g. Msimba {35, 58}. These conditions have favoured the development of old, strongly weathered and leached soils dominated by low activity clays. Only Ukiriguru and Msimba contain some primary minerals besides quartz indicating the slightly younger soils developing on slopes of crystalline mountains. The presence of gibbsite at Lubonde may be a result of a higher degree of desilication due to a present or formerly stronger leaching environment and lower pH of this soil {35}. Lateritization may also be active at some sites indicated by the subsoil mottling caused by accumulation of iron minerals. Although well-developed plinthite was actually not seen at any of the sites, iron stone layers were found in the surroundings of the Igabiro and Nkundi soil profiles.

In contrast to the non-volcanic soils, the volcanic ash soils are much younger in age indicated by the presence of fresh pumice, low bulk density and the small content of secondary minerals. Weathering in the volcanic soil is fast and the soils will change into more mature soils and the non-crystalline aluminium minerals will gradually weather into more well crystallised secondary minerals with types depending on the prevailing conditions and the nature of the parent material.

Table 31. Mineralogical composition of the silt fraction of the surface horizon as inferred from unoriented XRD.

Site	Quartz	K-feldspars	Illite or other 2:1 layer silicates	Kaolinite/ halloysite	Gibbsite
Igabiro	xxxx	tr.	tr.		
Ukiriguru	xxx	xx	tr.		
Mlingano	xxx	tr.		xx	
Magadu	xxxx	tr.	tr.		
Msimba	xxx	xx			
Suluti	xxx	x		tr.	
Lubonde	tr.	x		xx	xx
Mpangala[1]	tr.	xx		tr.	
Sasanda[1]	tr.	xx		tr.	
Nkundi	xxxx	tr.		tr.	

xxxx>90%, xxx=50-90%, xx=10-50%, x=2-10%, tr.<2%

[1] The reminder being probably volcanic glass.

Table 32. Total DCB extractable Fe and Al of the non-treated clay fraction and total elemental analysis and thermogravimetric analysis of the DCB treated clay fraction.

Horizon	Depth	Non-treated clay		DCB-treated clay									Weight loss		
		Fe_{d_clay}	Al_{d_clay}	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ign. loss	Sum	110-350 °C	350-550 °C	550-900 °C
	cm	%													
Igabiro															
Ap	0-18	5.6	1.4	44.4	34.9	4.4	0.03	0.4	0.3	0.01	14.7	99.1	3	9	2
A	18-43	5.3	1.2	44.1	35.0	5.0	0.01	0.4	0.3	0.01	14.5	99.3	3	9	2
AB	43-65	5.6	1.5	45.2	34.5	4.2	0.01	0.3	0.3	0.01	14.4	98.9	3	10	2
Bo1	65-110	5.4	1.4	44.2	35.3	4.2	0.01	0.4	0.3	0.01	14.7	99.1	4	10	2
Bo2	110-180	5.5	1.4	44.5	35.5	4.2	0.01	0.2	0.3	0.01	14.5	99.2	3	10	2
Ukiriguru															
Ap	0-28	3.6	0.6	48.5	29.7	5.6	0.01	0.7	2.6	0.01	12.4	99.5	3	8	2
AB	28-49	3.5	0.7	47.3	30.5	5.5	0.01	0.8	2.4	0.01	13.0	99.5	3	8	2
Bt1	49-75	3.5	0.7	47.7	30.2	5.5	<0.01	0.8	2.2	0.01	13.1	99.5	4	8	2
Bt2	75-132	3.3	0.7	48.1	30.3	5.3	<0.01	0.8	2.4	0.01	12.7	99.6	3	9	2
BC	132-180	3.5	0.6	48.7	29.4	5.6	0.01	0.8	2.7	0.01	12.4	99.6	3	8	2
Mlingano															
Ap	0-25	6.9	0.4	44.1	36.0	4.6	<0.01	0.1	0.2	0.01	14.7	99.7	2	11	<1
Bto	25-52	7.0	0.4	45.5	36.3	2.8	<0.01	0.2	0.2	0.01	14.4	99.4	2	11	1
Bo1	52-105	6.6	0.3	43.8	36.0	5.0	<0.01	0.1	0.2	0.01	14.5	99.6	3	11	1
Bo2	105-180	6.8	0.3	44.0	36.2	4.0	<0.01	0.1	0.2	0.01	14.7	99.2	3	11	1
Magadu															
Ap	0-10	5.0	0.7	44.9	33.2	6.8	0.01	0.3	0.3	0.01	14.0	99.5	4	9	2
Bo	10-47	5.0	0.7	44.9	33.4	6.3	0.01	0.3	0.3	0.01	14.2	99.4	3	10	2
Bto1	47-125	5.0	0.8	44.7	33.8	6.3	<0.01	0.3	0.3	0.01	14.2	99.6	3	9	2
Bto2	125-180	4.9	0.8	44.9	33.6	6.4	<0.01	0.3	0.3	0.01	14.0	99.5	3	9	2
Msimba															
Ap	0-18	6.2	0.5	48.1	28.0	7.6	0.1	2.0	1.4	0.01	12.3	99.5	4	7	1
AB	18-33	5.8	0.4	47.6	29.8	7.0	0.02	1.3	1.1	0.02	12.7	99.5	4	8	1
Bt	33-64	5.2	0.5	46.6	30.1	7.0	0.02	1.3	0.9	0.01	13.5	99.4	4	9	1
BC	64-90	4.9	0.5	46.4	29.9	7.5	<0.01	1.4	0.8	0.01	13.4	99.4	6	8	2

Total DCB extractable Fe and Al of the non-treated clay fraction and total elemental analysis and thermogravimetric analysis of the DCB treated clay fraction (continued).

Horizon	Depth	Non-treated clay		DCB-treated clay									Weight loss		
		Fe_{d_clay}	Al_{d_clay}	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ign. loss	Sum	110-350 °C	350-550 °C	550-900 °C
	cm	%													
Suluti															
Ap	0-15	4.2	0.5	43.4	36.9	2.9	0.02	0.1	0.2	0.01	15.3	98.8	4	10	1
AB	15-25	4.0	0.4	43.2	37.9	2.6	<0.01	0.1	0.2	0.01	15.0	99.0	4	10	1
Bo1	25-70	3.9	0.4	43.4	38.1	2.3	0.01	0.1	0.2	0.01	15.2	99.3	3	11	1
Bo2	70-120	4.0	0.4	43.2	38.3	2.3	<0.01	0.1	0.2	0.01	15.2	99.3	4	11	1
Bo3	120-180	4.9	0.4	42.6	38.5	2.4	<0.01	0.1	0.2	0.01	15.3	99.1	4	11	1
Lubonde															
Ap1	0-25	3.6	0.7	35.4	41.2	2.6	0.02	0.1	0.3	0.01	19.2	98.8	10	9	2
Ap2	25-55	3.8	0.7	34.9	41.5	2.6	0.01	0.2	0.3	0.01	19.7	99.2	11	10	2
Bom	55-64	4.0	0.6	30.3	45.8	2.0	<0.01	0.1	0.2	0.01	21.1	99.5	11	8	2
Bo1	64-125	4.0	0.5	28.1	46.3	2.9	<0.01	0.1	0.2	0.01	21.6	99.2	13	9	3
Bo2	125-180	4.0	0.5	28.2	46.9	2.4	<0.01	0.1	0.2	0.01	21.4	99.2	13	10	3
Mpangala															
Ap	0-20	2.6	1.0	45.6	34.6	2.3	0.04	0.2	0.7	0.1	15.6	99.1	6	10	2
A	20-55	3.4	1.0	45.0	35.1	2.3	0.1	0.2	0.7	0.1	15.3	98.8	6	9	2
Bw1	55-95	2.5	1.2	45.8	35.0	2.1	0.1	0.1	0.7	0.1	14.5	98.4	6	9	2
Bw2	95-150	2.6	1.0	44.8	34.7	2.0	0.1	0.1	0.8	0.1	15.6	98.2	6	8	3
Bw3	150-180	3.4	1.3	43.6	35.4	1.7	0.03	0.1	0.4	0.03	16.3	97.6	9	6	3
Sasanda															
Ap	0-32	3.7	1.9	43.8	34.5	3.2	0.1	0.2	1.0	0.1	15.8	98.7	6	8	2
Bw1	32-65	3.6	1.8	42.4	35.2	2.4	0.1	0.2	1.0	0.1	17.2	98.6	9	7	2
Bw2	65-125	3.7	2.0	42.7	34.7	1.9	0.1	0.2	1.2	0.1	16.8	97.7	10	6	3
Bw3	125-180	3.7	1.4	44.7	35.0	2.0	0.04	0.1	0.9	0.1	15.4	98.2	8	8	2
Nkundi															
Ap	0-8	2.4	0.6	44.2	33.7	6.8	0.1	0.3	0.4	0.01	13.8	99.3	3	10	2
A	8-29	3.4	0.9	44.8	35.2	4.4	<0.01	0.2	0.4	0.01	14.7	99.7	3	10	1
AB	29-62	3.6	0.9	44.2	36.5	4.3	0.01	0.2	0.4	0.01	14.4	100.0	3	11	1
Bo1	62-135	2.8	0.9	44.2	36.3	4.0	<0.01	0.2	0.3	0.01	14.4	99.4	3	11	2
Bo2	135-180	2.8	0.8	44.9	35.8	4.1	<0.01	0.2	0.3	0.01	14.2	99.5	3	11	1

Table 33. Average mineralogical composition of clay the fraction based on DCB extraction, TEA, TGA, XRD and FTIR.

Horizon	Quartz	K-feldspars	Illite	Smectite	HIM	Kaolinite	Halloysite	Allophane/ Imogolite	Gibbsite	Goethite	Hematite	Ferrihydrite
Igabiro	tr.				x	xxxx				x	tr.	
Ukiriguru	x	x	xx			xxx				x		
Mlingano	tr.					xxxx			tr.		x	
Magadu	tr.		tr.			xxxx				x		
Msimba	x	x	x	xx		xx				tr.	x	
Suluti	tr.					xxxx			x	tr.	x	
Lubonde	tr.	tr.				xxx			xx	tr.	x	
Mpangala		x	x				xxx	xx				tr.
Sasanda		x	x				xxx	xx		tr.		tr.
Nkundi	x		tr.			xxxx				x		

xxxx>90%, xxx=50-90%, xx=10-50%, x=2-10%, tr.<2%

With regard to classification according to Soil Taxonomy {249} and WRBSR {61} most epipedons fail to fulfil the requirements of either Umbric or Mollic epipedons due to either too low organic carbon (Ukiriguru), too light colours (Mlingano, Magadu, Suluti, Nkundi) or consistence being harder than moderately hard when dry (Magadu, Msimba, Suluti) (Table 25 and Table 26). Despite having andic soil properties the epipedon of Sasanda is not Melanic due to insufficient levels of organic carbon. The diagnostic subsurface horizons vary from Cambic, Argillic, Kandic to Oxic according to pedogenic development, mineralogical composition and textural differentiation. The soils cover five soil orders according to Soil Taxonomy {249}. Except for Msimba, which shows clear signs of clay illuviation and contains appreciable amounts of expanding 2:1 layer silicates giving a slightly higher cation exchange capacity, all the Alfisols and Ultisols are characterized by the dominance of low activity clays resulting in the Kandic or Kanhaplic great group levels. The Acruoxic subgroup level of Nkundi indicates the extremely low CEC of the clay fraction in that soil. Also World Reference Base for Soil Resources (WRBSR) classifies the soils into five different categories with the lower level names indicating specific properties. There is good agreement between the two classification systems.

Table 34 presents mean values of some chemical characteristics of the composite surface soil samples collected within each of the four blocks at each of the ten field experimental sites. As the soil profile was excavated near the blocks one would expect the values to be in the same range as for the surface horizons of the soil profiles. However, some discrepancies, which might result from differences in actual sampling depth, field variation and methods of analysis, can be observed among the parameters analysed. The pH values are generally in agreement between the two sample types and the confidence intervals generally indicate little variation in pH among the blocks. The levels of exchangeable Ca are also similar except for Magadu, Sasanda and Nkundi where the levels are higher for the profile samples. Levels of exchangeable Mg, K and Na are generally in the same magnitude. The effective base saturation is generally high for most sites except for Magadu and Sasanda. Aluminium saturation ranges between almost zero at Msimba and up to 11% and 28% at Sasanda and Magadu respectively. CEC_7, which is showing only little variation among blocks, is in some cases deviating considerably from the profile samples, which could be attributed to the differences in analytical methods. Especially the two volcanic soils seem to have larger CEC_7 when determined using the NH_4-method. Organic matter content, which is also showing little variation among blocks, agrees well with the values from the profiles. Available P assessed as Bray1 is in most cases showing large variation among blocks. It seems that Mlingano and Magadu are strongly P deficient, Igabiro, Msimba, Sasanda and Nkundi intermediate P deficient and the remaining sites having sufficient levels of plant available P. P_{Olsen} values varies less between blocks except at Lubonde where one block apparently contains high levels of available P. Based on P_{Olsen} sites such as Mlingano, Magadu, Sasanda and Nkundi seems to be strongly P deficient whereas Igabiro, Msimba and Mpangala are intermediate and Ukiriguru, Suluti and

Lubonde are having sufficient levels of available P. DTPA extractable levels of Cu from the blocks indicate Cu deficiency at Ukiriguru, Magadu, Suluti, Lubonde, Mpangala, Sasanda and Nkundi whereas Igabiro and Msimba have medium and Mlingano sufficient levels. Zn is deficient at Igabiro, Ukiriguru, Magadu, Suluti, Sasanda and Nkundi whereas Mlingano, Msimba, Lubonde and Mpangala have medium levels. Neither Mn nor Fe show near deficient levels in any of the soils whereas extractable B generally show very low levels. Especially Ukiriguru, Suluti, Lubonde, Mpangala and Sasanda show very low levels indicating that soil B may represent a major constraint for crop production. Nitrogen is also assumed to be a major fertility constraint at all sites despite some sites showing low response to N during the first season (Table 41 and Table 42). Generally the values from the blocks are in agreement with the values from the surface horizons of the soil profiles and they do not change the general view of the chemical properties of the soils.

Table 35 summarises the general site productivity characteristics of the experimental sites. As the relatively variable bulk densities among the different soils and soil layers have a significant effect on the amount of nutrients per soil volume, Figure 32 summarises some of the soil properties expressed on the basis of the amounts per hectare or as a weighted average in the upper 100 cm. Included in the calculations is also the effect of varying moisture contents of the air dry soil samples (Figure 32). It is seen that large differences exist in the way the plants may experience the amount of nutrients. For instance, the low effective cation exchange capacity of the soil material at Sasanda is further aggravated by the low bulk density leading to generally very small amounts of exchangeable bases available for plant uptake.

Table 34. Selected surface soil properties at each experimental site as mean of four composite samples (95% confidence interval in italic).

Site	$\mathrm{pH_w}$	$\mathrm{pH_{KCl}}$	Exchange capacity and exchangeable cations												DTPA extractable micronutrients				Hot water extr.
			Ca	Mg	K	Na	Al+H	$\mathrm{CEC_e}$	$\mathrm{CEC_7}$	$\mathrm{BS_e}$	$\mathrm{Al_{sat}}$	C	$\mathrm{P_{Olsen}}$	$\mathrm{P_{Bray1}}$	Cu	Zn	Mn	Fe	B
			cmol(+) $\mathrm{kg^{-1}}$							%	%	%	mg $\mathrm{kg^{-1}}$						
Igabiro	5.6	4.3	2.5	1.2	0.1	<0.1	0.3	4.2	9.3	93	4	1.6	9	18	2.5	0.4	54	32	0.2
	0.1	*0.1*	*0.7*	*0.3*	*0.1*	*<0.1*	*0.1*	*0.9*	*0.7*	*4*	*4*	*0.1*	*2*	*9*	*0.9*	*0.2*	*8*	*3*	*0.2*
Ukiriguru	6.4	4.7	1.1	0.4	0.4	0.1	0.1	2.1	3.8	94	2	0.6	14	36	0.6	0.3	93	13	<0.1
	0.1	*0.1*	*0.5*	*0.1*	*0.1*	*0.2*	*<0.1*	*0.5*	*0.5*	*4*	*3*	*0.1*	*3*	*13*	*<0.1*	*0.1*	*2*	*1*	*<0.1*
Mlingano	5.6	4.3	0.7	1.0	0.5	0.1	0.3	2.5	5.7	87	6	1.3	2	4	5.0	0.7	134	11	0.6
	0.3	*0.1*	*0.3*	*0.3*	*0.1*	*<0.1*	*0.1*	*0.5*	*0.7*	*11*	*8*	*0.1*	*<1*	*1*	*0.1*	*0.1*	*4*	*1*	*0.1*
Magadu	4.9	3.6	1.2	1.3	0.8	<0.1	1.8	5.2	11.0	65	28	0.9	3	6	1.2	0.6	75	21	0.4
	0.1	*<0.1*	*0.1*	*0.2*	*<0.1*	*<0.1*	*0.2*	*0.2*	*0.8*	*5*	*7*	*0.1*	*<1*	*2*	*<0.1*	*0.1*	*6*	*1*	*0.1*
Msimba	6.9	5.6	9.4	2.0	1.2	<0.1	0.1	12.7	12.6	99	0	2.0	9	17	2.0	0.8	125	15	0.3
	0.3	*0.3*	*2.7*	*0.1*	*0.1*	*<0.1*	*<0.1*	*2.8*	*1.0*	*0*	*0*	*0.2*	*2*	*6*	*0.1*	*0.1*	*12*	*2*	*<0.1*
Suluti	6.1	4.7	1.2	0.6	0.3	<0.1	0.1	2.2	5.8	95	0	1.2	11	34	0.4	0.3	140	12	0.2
	0.1	*<0.1*	*0.2*	*0.1*	*<0.1*	*<0.1*	*<0.1*	*0.3*	*0.7*	*1*	*0*	*0.3*	*1*	*4*	*0.1*	*0.1*	*26*	*1*	*0.4*
Lubonde	5.9	4.5	4.6	1.0	0.7	<0.1	0.2	6.6	14.1	97	1	3.0	18	55	0.3	1.8	118	26	0.2
	0.2	*0.1*	*1.0*	*0.1*	*0.2*	*<0.1*	*<0.1*	*1.2*	*1.5*	*1*	*1*	*0.2*	*7*	*29*	*0.1*	*0.4*	*15*	*3*	*0.1*
Mpangala	5.9	4.6	4.0	1.3	1.2	<0.1	0.2	6.8	17.0	97	1	2.6	6	27	0.1	1.1	71	30	0.1
	0.2	*0.1*	*1.7*	*0.3*	*0.1*	*<0.1*	*<0.1*	*2.0*	*0.6*	*1*	*0*	*0.3*	*1*	*12*	*<0.1*	*0.1*	*8*	*2*	*0.1*
Sasanda	5.7	4.5	0.7	0.6	0.9	0.1	0.4	2.7	22.8	85	11	3.7	3	18	0.9	0.3	45	19	<0.1
	0.1	*0.1*	*0.1*	*0.4*	*0.3*	*0.1*	*0.1*	*0.7*	*1.1*	*5*	*7*	*0.2*	*1*	*2*	*0.2*	*<0.1*	*5*	*1*	*<0.1*
Nkundi	5.9	4.3	0.6	0.7	0.3	<0.1	0.2	1.8	5.3	90	3	1.1	3	13	1.4	0.3	51	28	0.4
	0.3	*0.1*	*0.2*	*0.2*	*<0.1*	*<0.1*	*<0.1*	*0.2*	*1.3*	*5*	*4*	*0.1*	*<1*	*13*	*0.1*	*0.1*	*6*	*2*	*<0.1*

Table 35. General relative site productivity characteristics based on soil and leaf analyses and moisture balance.

Site	Igabiro	Ukiriguru	Mlingano	Magadu	Msimba	Suluti	Lubonde	Mpangala	Sasanda	Nkundi
pH	l	m	l	vl	h	m	m	m	m	m
Al saturation (surface)	m	h	h	h	l	l	l	l	m	l
Al saturation (subsoil)	h	m	m	vh	l	l	l	l	m	vh
Effective CEC	m	l	l	h	vh	m	m	m	vl	vl
Exch. Ca	m	m	vl	m	vh	m	h	h	vl	l
Exch. Mg	m	vl	l	m	vh	m	m	h	l	l
Exch. K	vl	vl	vl	m	vh	vl	m	vh	m	l
Base saturation	m	m	l	vl	h	m	h	h	l	l
P adsorption	m	l	m	m	l	l	h	h	vh	l
Available P (surface)	m	h	l	vl	m	m	m	l	vl	vl
Available P (subsoil)	l	l	l	l	l	m	l	vl	vl	l
Available Zn	vl	vl	m	l	h	vl	m	h	vl	vl
Available Cu	m	vl	h	l	h	vl	vl	vl	vl	l
Available B	l	vl	m	l	l	l	l	vl	vl	l
Organic C	h	vl	l	l	h	vl	h	h	h	l
Workability	good	good	poor	poor	poor	poor	good	good	good	poor
AWC	m	l	l	m	l	l	h	h	h	m
Mineralogy	kaolinite	kaolinite	kaolinite	kaolinite	kaol. + 2:1	kaolinite	kaolinite	halloysite	halloysite	kaolinite
Rainfall distribution	good	erratic	good	erratic	erratic	good	good	good	good	good
Main productivity constraints for optimum crop performance	Subsoil Al, pH, N, P, K, Zn, B	N, CEC$_e$, Mg, K, Cu, Zn, B, organic matter, rainfall, low AWC	pH, N, P, CEC$_e$, Ca, K, AWC	Subsoil Al, pH, soil structure, N, P, Ca, Cu, rainfall, AWC	N, B, AWC, Rainfall	N, K, Cu, Zn, B, workability when dry, organic matter	N, Cu, B	N, P, Cu, B	CEC$_e$, P adsorption, N, P, Ca, Mg, Cu, Zn, B	Subsoil Al, pH, CEC$_e$, BS$_e$, N, P, Ca, Mg, K, Zn, organic matter

vl=very low, l=low, m=medium, h=high, vh=very high.

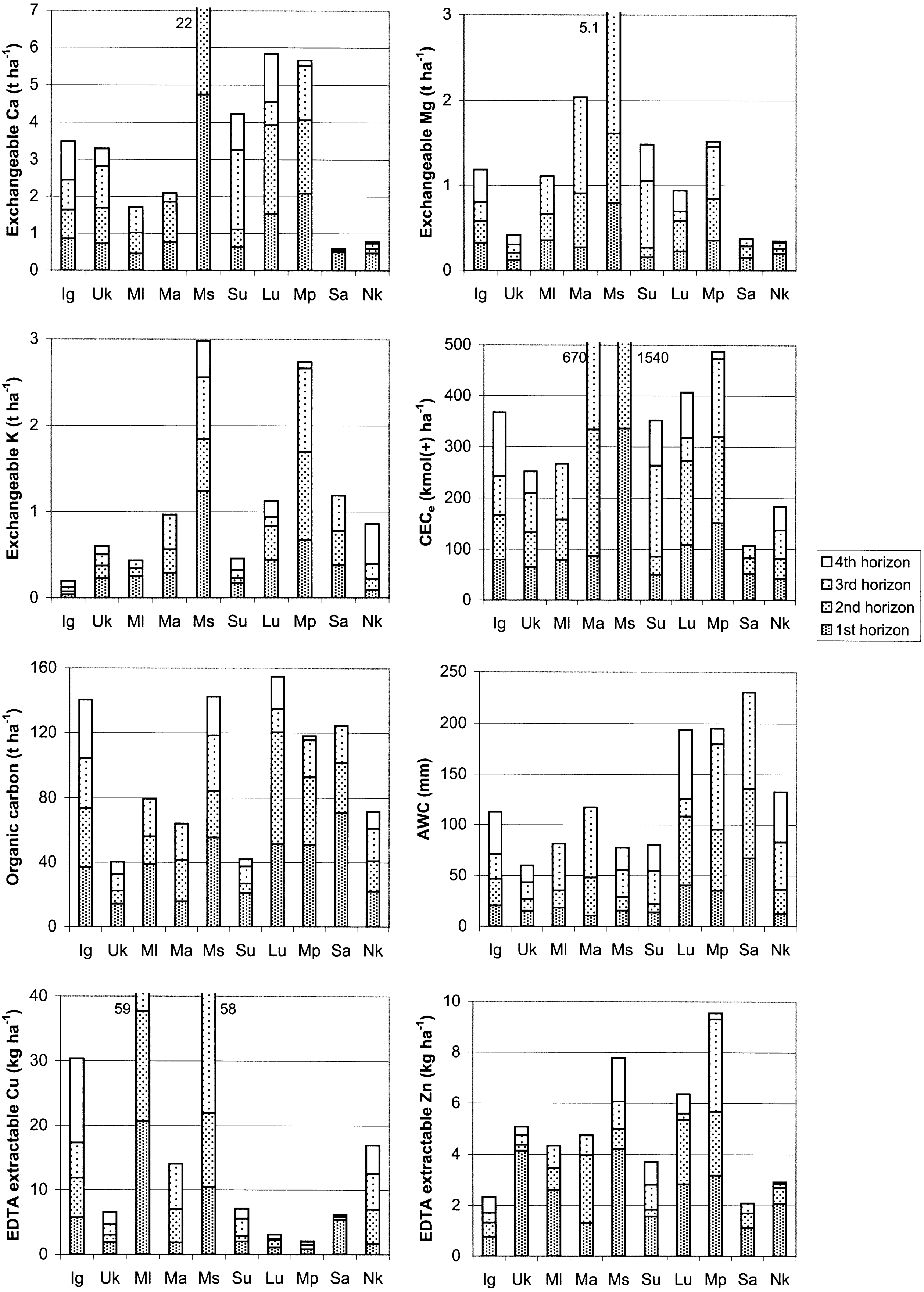


Figure 32. Soil characteristics in the upper 100 cm expressed on the basis of amounts per hectare (Ca, Mg, K, CEC$_e$, P$_{olsen}$, C, Zn, Cu, AWC, P$_{inorg}$, P$_{org}$, Fe$_o$, Al$_o$) or as weighted average (pH$_w$, Al-saturation and moisture content of air-dry soil samples) (Zn and P$_{olsen}$ for the upper horizon at Magadu was estimated to 1 and 3 mg kg^{-1} respectively).

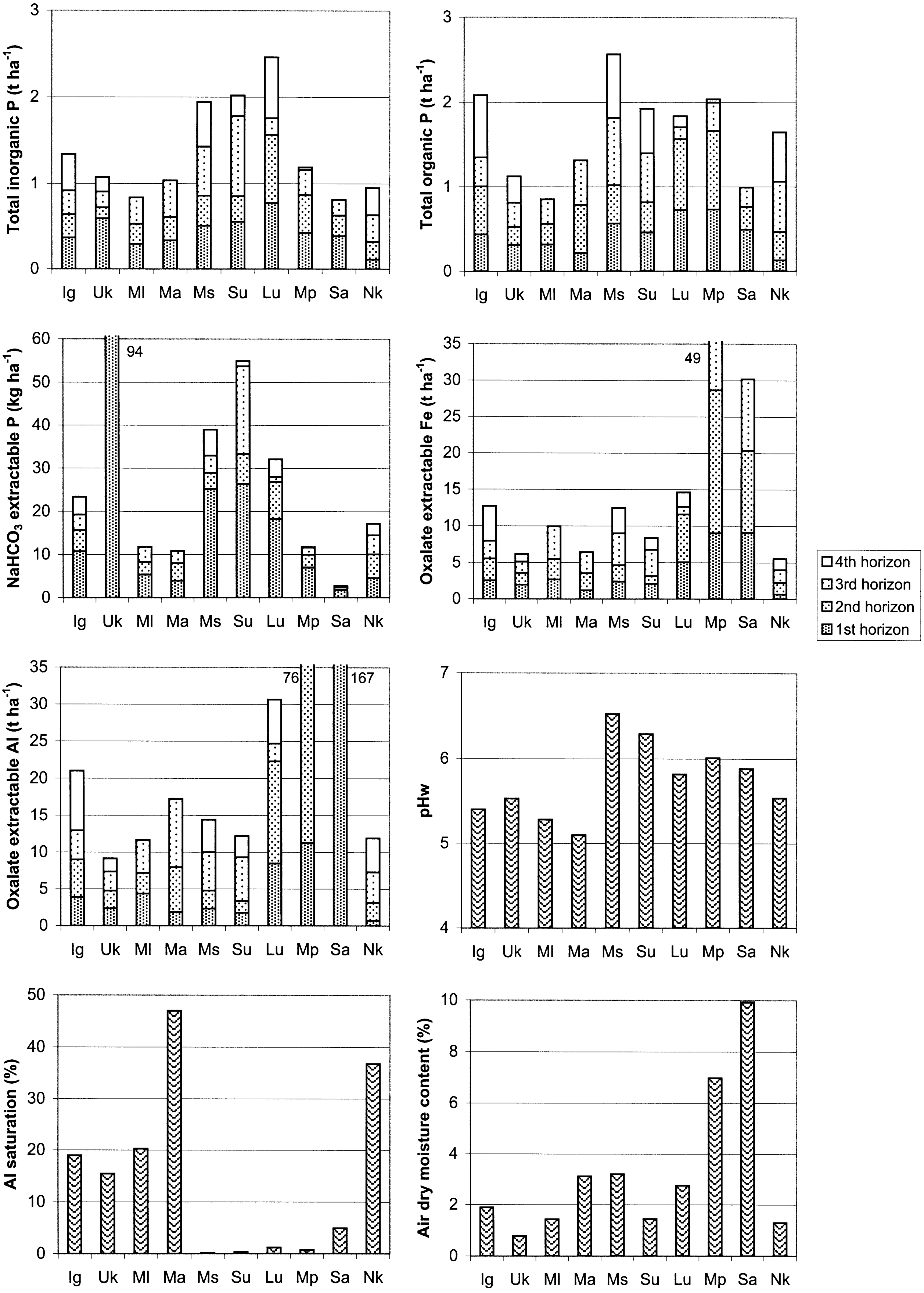


Figure 32. Continued.

6.2.2 Field experiments

Before running the statistical analysis of the P response on maize yield, the assumptions on normality of residuals and variance homogeneity within class variables were tested on non-transformed as well as on square root and logarithm transformed yield values {254}. Although not significantly conforming to the normal distribution, square root transformation increased normality of residuals slightly compared with non-transformed values whereas the logarithm showed to be an unsuitable transformation. The variance in the non-transformed yield values showed to be homogeneous among harvests, blocks and treatments but not among sites, which were dealt with by calculating the covariance parameter estimates for each site during the analysis using Proc Mixed (SAS ver 8.1) {128}. As both the square root and non-transformed yield values gave comparable results in the model control, the non-transformed values were used as the dependent variable in the statistical test of fixed effects and their interaction.

The statistical analysis showed that all main effects, two-way interactions and three-way interactions were strongly significant ($p<0.001$), and each combination of harvest, site and treatment must therefore be evaluated separately. In order to simplify presentation and interpretation of the results some orthogonal contrasts were evaluated (Table 36). Looking at these comparisons it can be seen that yield increase due to P application was significant at Mlingano, Sasanda and Nkundi in all seasons. In the third season, maize yield at Magadu and Mpangala was also increased significantly by P application. For those sites showing a significant P response, the response became more pronounced with time and differences between P sources became smaller.

Table 36. Significance level[1] for differences between treatment groups for the first three seasons (effect of level and source of P on maize grain yield).

		Site									
Harvest	Contrast[2]	Ig	Uk	Ml	Ma	Ms	Su	Lu	Mp	Sa	Nk
1998/1999	Control vs. TSP			**						***	***
(1st season)	Control vs. GPR			**						***	**
	Control vs. MPR									***	***
	GPR vs. TSP									**	***
	MPR vs. TSP										*
	GPR vs. MPR									*	
	40 P vs. 80 P									**	*
	40 P vs. 120 P			*						***	*
	80 P vs. 120 P								*		
1999/2000	Control vs. TSP			*						***	***
(2nd season)	Control vs. GPR									***	***
	Control vs. MPR									***	***
	GPR vs. TSP										**
	MPR vs. TSP										
	GPR vs. MPR										
	40 P vs. 80 P									***	
	40 P vs. 120 P									***	*
	80 P vs. 120 P									***	
2000/2001	Control vs. TSP			***	*				***	***	***
(3rd season)	Control vs. GPR			***	*				***	***	***
	Control vs. MPR			**	*				***	***	***
	GPR vs. TSP										
	MPR vs. TSP								**		
	GPR vs. MPR										
	40 P vs. 80 P									***	
	40 P vs. 120 P				*				*	***	
	80 P vs. 120 P								**	***	

[1] Non-significant (blank), *p<0.05, **p<0.01, ***p<0.001.

[2] The first named treatment group being significantly lower than the group for which the comparison is made.

P application at Sasanda led to highly significant P response in all seasons but also Nkundi responded very well to P. At Mlingano GPR seemed to give a better response than MPR whereas the opposite was generally the case at Sasanda and Nkundi. GPR was significantly inferior to TSP and MPR at Sasanda but only in the first season. At Nkundi, both MPR and GPR were inferior to TSP in the first season whereas only GPR was inferior in the second season. In the third season all significant differences between the P sources vanished except at Mpangala, which should be viewed at with caution due to high within block variation caused by a high small scale variation in soil properties and nutritional constraints leading to erroneous observations for several treatments during the first two seasons. In the third season the Mpangala site suffered from severe moisture stress at the critical grain filling stage (Table 46).

Least square means of maize grain yield including least significant differences (LSD) from the first three seasons are presented in Table 37. Yield levels varies considerably among the sites and reflect primarily differences in the productivity potential of the sites due to soil properties, availability of plant nutrients and climate. The sites, which experienced water stress at the critical stage during some or all growing seasons (Igabiro, Ukiriguru, Magadu, Msimba and Mpangala) (Table 46) generally had low yields. An exception to this is Igabiro, which had relatively high yields during the first two seasons despite suffering from moisture stress. Poor crop establishment at Lubonde due to erratic rainfall during the first period of the second season was probably the main reason for the large decrease in yield from first to second season. At Mpangala, yields were sub-optimal in the two first seasons apparently due to strong B deficiency, which were supported by increased yields after B application in the third season although water stress might have masked the potential effect of B. Also at Sasanda yields were sub-optimal in the first season. A better crop establishment during the second season along with addition of magnesium (Mg) (Table 23), and a second year effect of the applied P were probably the main reasons for the large increase in yields at Sasanda in the second season.

The P control yields range from almost zero at Sasanda up to 6.5 t ha^{-1} in the first season at Lubonde representing sites showing very large and no P response respectively. Absolute yield increases due to P application, i.e. the difference between the P treated and the P control yields are generally moderate during the first season but increases up to around 3.5 t ha^{-1} as average of each P source at Sasanda during the second and third season (Table 38). For sites showing significant P response the relative average yield increases range between 50-200% of control yields for Mlingano, Mpangala and Nkundi whereas Sasanda generally show dramatic average yield increases of up to 40 times the control yield. Figure 33 presents the P response functions for sites showing significant P response. Grouping of the P sources have been done according to the findings presented in Table 36. In most seasons, the Mitcherlich response function fitted the data well at Sasanda, Nkundi and Magadu (Table 39). Neither a logarithmic nor an exponential response function improved the description of the yield response to P application compared with the Mitcherlich expression for any of the sites.

The response to increasing levels of P were important at Sasanda, which even seems to respond to P levels beyond 80 kg P ha^{-1} (Table 36 and Figure 33). At Nkundi, the response curves indicate only a slight effect of increasing P levels on maize grain yield, which is also confirmed by the statistics in Table 36 and Table 39. The yields at the 40 kg P ha^{-1} level at Nkundi range between 85% and 99% of the maximum yields according the Mitcherlich response curve whereas for Sasanda less than 50% and for Magadu and Mpangala in the third season 67% and 70-90% of maximum yield is obtained at 40 kg P ha^{-1} respectively. The lower response to increasing P levels at Mlingano, Mpangala and Nkundi compared with Sasanda and Magadu is also indicated by the larger proportionality factor corresponding to a steeper initial slope of the curve for the former (Figure 33 and Table 39). The estimates of the amounts of initial phosphorus present in the soil and seed indicate that Sasanda is extremely deficient in P, which is also confirmed by almost zero yields in the control treatments. The strong P depletion of the control treatments of Mlingano and Nkundi with time is also illustrated by the decrease in the initial amounts of P. Sasanda do not show this decrease in initial P availability as the site is already completely depleted.

Table 37. Least square means of maize grain yield (t ha^{-1}) for the first three seasons (effect of level and source of P on maize grain yield).

Harvest	Treatment	Site										
		Ig	Uk	Ml	Ma	Ms	Su	Lu	Mp	Sa	Nk	All sites
1998/1999	Control	5.45	1.13	1.82	2.45	2.13	5.52	6.50	2.42	0.04	4.22	3.17
(1st season)	40 TSP	6.00	1.08	2.70	2.63	2.31	5.29	6.70	3.08	0.90	5.39	3.61
	80 TSP	4.41	0.96	2.70	3.10	2.06	5.10	6.63	2.87	1.76	6.04	3.56
	120 TSP	5.18	1.18	2.99	2.79	1.80	5.83	6.98	3.42	2.02	6.15	3.83
	40 GPR	5.17	1.23	2.37	2.41	2.42	5.84	6.15	3.56	0.58	5.02	3.48
	80 GPR	5.29	1.20	3.01	2.69	2.10	5.74	6.46	1.70	1.15	5.13	3.45
	120 GPR	4.84	1.06	3.08	2.83	2.69	5.60	6.97	3.07	1.51	5.18	3.68
	40 MPR	4.50	0.91	2.19	2.37	2.51	5.62	6.66	2.17	1.20	4.99	3.31
	80 MPR	5.49	1.14	2.39	2.43	2.00	5.49	6.89	2.81	1.54	5.59	3.58
	120 MPR	5.59	1.08	2.75	2.71	2.15	4.95	6.25	2.90	1.77	5.58	3.57
1999/2000	Control	4.62	1.65	0.97	0.49	2.53	3.86	3.42	0.13	0.01	2.28	2.00
(2nd season)	40 TSP	4.87	1.59	1.82	0.86	1.99	4.21	3.36	0.55	2.82	5.33	2.74
	80 TSP	4.93	1.39	1.62	0.91	2.07	3.74	3.45	0.31	3.52	5.55	2.75
	120 TSP	5.06	1.84	1.66	0.63	2.09	4.29	3.77	0.66	4.49	5.65	3.01
	40 GPR	4.80	1.39	1.45	0.75	2.29	3.94	2.67	0.84	2.48	4.88	2.55
	80 GPR	4.38	1.76	1.85	0.96	1.73	3.95	3.51	0.13	3.64	4.78	2.67
	120 GPR	5.25	1.30	1.65	0.72	2.42	4.39	3.42	0.61	4.46	5.13	2.94
	40 MPR	5.30	1.23	1.37	0.69	2.44	4.28	3.31	0.27	2.55	4.83	2.63
	80 MPR	5.12	1.83	1.34	0.80	2.13	4.38	3.74	0.32	3.70	5.37	2.87
	120 MPR	5.33	1.69	1.76	0.98	2.41	4.22	3.27	0.28	4.23	5.65	2.98
2000/2001	Control	3.88	3.01	1.76	1.33	3.17	3.90	2.68	0.89	0.09	3.89	2.46
(3rd season)	40 TSP	3.87	2.43	3.31	1.73	3.32	4.50	3.22	3.52	2.03	5.67	3.36
	80 TSP	3.99	2.95	3.20	2.03	3.41	3.93	3.12	3.08	3.22	5.64	3.46
	120 TSP	3.79	3.29	3.73	2.17	3.31	4.29	3.08	4.35	3.95	5.81	3.78
	40 GPR	3.60	3.13	2.66	1.70	3.26	4.08	3.37	2.93	2.43	5.60	3.28
	80 GPR	4.13	3.11	3.54	2.40	2.89	3.79	3.21	2.49	3.31	5.52	3.44
	120 GPR	3.96	3.07	3.17	2.16	3.46	4.25	2.94	4.15	3.89	5.76	3.68
	40 MPR	3.60	3.18	2.87	1.82	2.97	4.24	2.99	2.71	2.51	5.30	3.22
	80 MPR	3.83	3.14	2.68	1.93	2.78	4.56	3.14	3.09	3.18	5.51	3.38
	120 MPR	3.75	3.15	3.32	2.42	3.37	4.14	3.10	2.76	3.84	5.51	3.54
Average yield (all seasons)		4.67	1.90	2.39	1.80	2.54	4.60	4.37	2.07	2.43	5.23	3.20
Least significant difference (95%)		0.90	0.62	0.86	0.73	0.65	0.81	0.85	1.02	0.62	0.72	0.25
LSD/average yield (%)		19	33	36	41	26	18	19	49	26	14	8

Table 38. Maize grain yield increases (t ha^{-1}) due to P application.

Harvest	Treatment	Site										
		Ig	Uk	Ml	Ma	Ms	Su	Lu	Mp	Sa	Nk	All sites
1998/1999 (1st season)	TSP	-0.25	-0.05	0.98	0.39	-0.07	-0.11	0.27	0.71	1.53	1.65	0.50
	GPR	-0.35	0.03	1.00	0.19	0.28	0.20	0.03	0.35	1.04	0.89	0.37
	MPR	-0.25	-0.08	0.62	0.05	0.10	-0.16	0.10	0.21	1.47	1.17	0.32
1999/2000 (2nd season)	TSP	0.34	-0.04	0.73	0.31	-0.48	0.22	0.10	0.38	3.60	3.23	0.84
	GPR	0.19	-0.17	0.68	0.32	-0.38	0.24	-0.22	0.40	3.52	2.65	0.72
	MPR	0.63	-0.07	0.52	0.33	-0.20	0.44	0.01	0.16	3.48	3.00	0.83
2000/2001 (3rd season)	TSP	0.01	-0.12	1.65	0.65	0.18	0.34	0.46	2.76	2.98	1.82	1.07
	GPR	0.02	0.09	1.36	0.76	0.03	0.14	0.49	2.30	3.13	1.74	1.01
	MPR	-0.15	0.14	1.19	0.73	-0.13	0.41	0.40	1.96	3.09	1.55	0.92
	LSD[1]	0.73	0.51	0.70	0.59	0.53	0.66	0.69	0.84	0.51	0.59	0.20
All seasons	TSP	0.03	-0.07	1.12	0.45	-0.12	0.15	0.28	1.28	2.70	2.23	0.80
	GPR	-0.04	-0.01	1.01	0.42	-0.02	0.20	0.10	1.02	2.56	1.76	0.70
	MPR	0.08	0.00	0.78	0.37	-0.08	0.23	0.17	0.78	2.68	1.91	0.69
	LSD[2]	0.61	0.29	0.58	0.44	0.35	0.52	0.57	0.73	0.29	0.43	0.15

[1] Least significant difference (yield increase) for each site when comparing sources within or between seasons.
[2] Least significant difference (yield increase) for each site (all seasons).

Table 39. Parameter estimates of Mitcherlich response function.

Site	Season	P source	Max. yield (Y_{max}) t ha^{-1}	Prop. factor (c)	Initial nutrient (b) kg P ha^{-1}	Regression coefficient R^2
Ml	1	All	3.19	0.00596	61.8	0.29
	2	All	1.67	0.01809	21.1	0.32
	3	All	3.38	0.01314	24.4	0.36
Ma	1	-	-	-	-	-
	2	-	-	-	-	-
	3	All	2.60	0.00490	62.7	0.51
Mp	1	-	-	-	-	-
	2	-	-	-	-	-
	3	TSP+GPR	3.98	0.01052	11.3	0.43
	3	MPR	2.92	0.02606	6.1	0.40
Sa	1	TSP+MPR	2.23	0.00697	0.9	0.79
	1	GPR	3.72	0.00189	1.7	0.92
	2	All	4.86	0.00797	0.3	0.94
	3	All	4.35	0.00775	1.3	0.94
Nk	1	TSP	6.36	0.00915	51.4	0.88
	1	GPR+MPR	5.45	0.01141	56.1	0.73
	2	TSP+MPR	5.62	0.01937	11.7	0.94
	2	GPR	4.97	0.03539	7.6	0.92
	3	All	5.63	0.03904	17.5	0.78

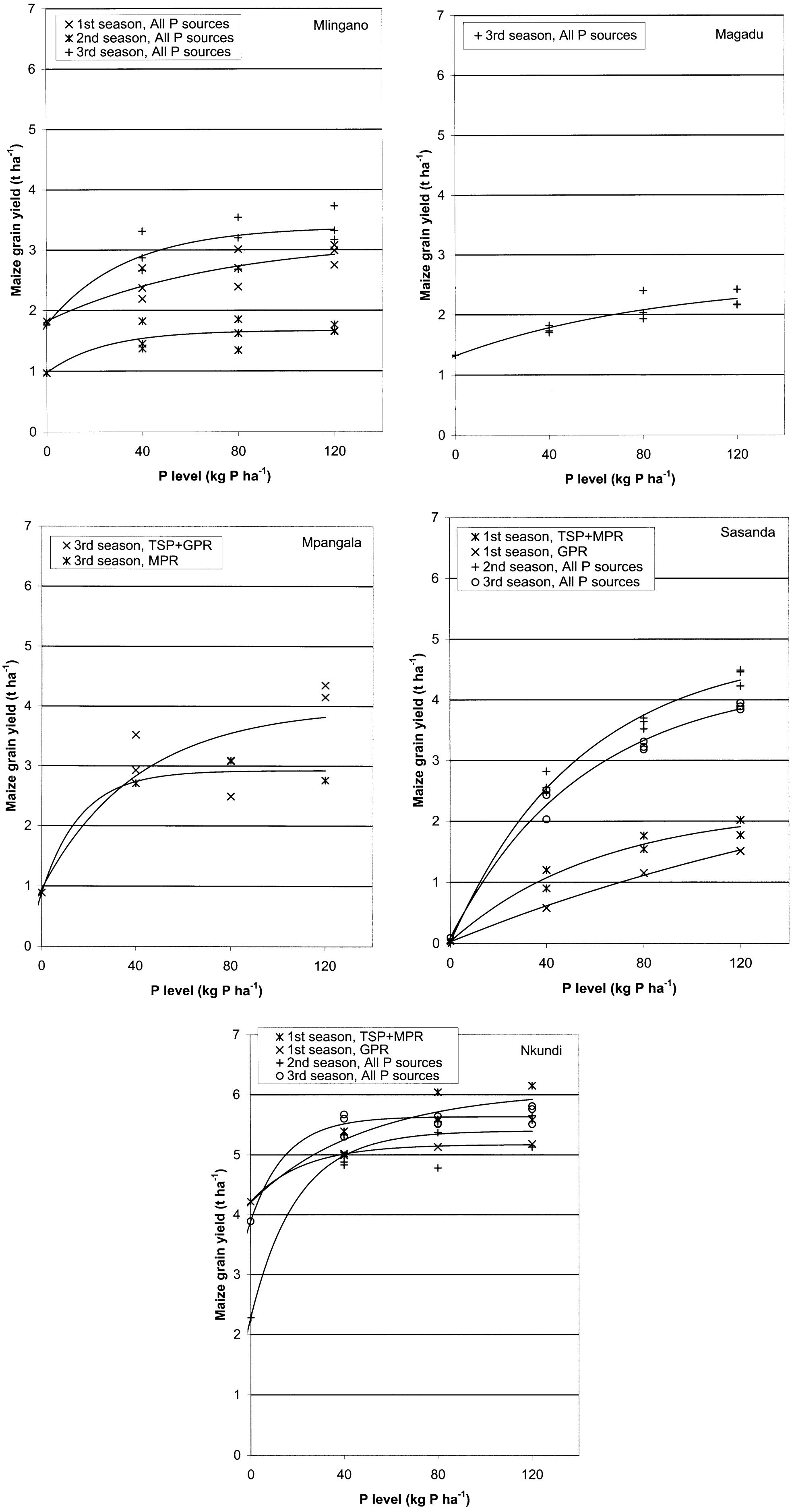


Figure 33. Maize grain yield response to P application.

The relative agronomic effectiveness (RAE) of the two PR products at the different sites showing significant P response is shown in Table 40. At Sasanda and Nkundi, RAE was significantly smaller for GPR compared to MPR in the first season but from the second season, differences were small, even between levels and the PRs were on average comparable with TSP (82-107%). RAE is consistently higher for GPR than MPR at Mlingano, which is explained by the high variability in the yield data with GPR treatments in the second block performing significantly better than MPR. Hence, interpretation of RAE for Mlingano should be made with caution. The data do not show any trend in RAE according to P level.

Table 40. Relative agronomic effectiveness (RAE) based on maize grain yield for sites showing significant P response (% ± 95% confidence interval).

Harvest	Treatment			Site			
		Ml	Ma	Mp	Sa	Nk	All sites
1998/1999	GPR						
(1st season)	40 P	62	-	-	63	68	64±5
	80 P	135	-	-	64	50	83±76
	120 P	108	-	-	74	50	77±50
	All levels	102±62	-	-	67±11	56±18	75±18
	MPR						
	40 P	42	-	-	134	66	81±81
	80 P	64	-	-	87	75	75±19
	120 P	80	-	-	87	71	79±14
	All levels	62±31	-	-	103±46	71±8	78±16
	Both PR						
	40 P	52	-	-	99	67	73±26
	80 P	99	-	-	76	63	79±25
	120 P	94	-	-	81	60	78±16
	All levels	82±28	-	-	85±22	63±9	77±11
1999/2000	GPR						
(2nd season)	40 P	57	-	-	88	85	77±29
	80 P	137	-	-	104	77	106±51
	120 P	99	-	-	99	85	94±14
	All levels	97±67	-	-	97±14	82±8	92±14
	MPR						
	40 P	47	-	-	90	84	73±40
	80 P	58	-	-	105	95	86±42
	120 P	115	-	-	94	100	103±18
	All levels	73±61	-	-	97±13	93±14	87±14
	Both PR						
	40 P	52	-	-	89	84	75±15
	80 P	97	-	-	104	86	96±22
	120 P	107	-	-	97	92	99±8
	All levels	85±30	-	-	97±6	87±7	90±9
2000/2001	GPR						
(3rd season)	40 P	58	93	78	121	96	89±22
	80 P	124	152	73	103	93	109±29
	120 P	71	99	94	99	97	92±11
	All levels	84±59	115±55	82±19	107±20	96±4	97±11
	MPR						
	40 P	72	120	69	125	80	93±26
	80 P	64	85	101	99	92	88±14
	120 P	79	130	54	97	84	89±26
	All levels	72±13	111±40	75±40	107±26	86±11	90±10
	Both PR						
	40 P	65	106	73	123	88	91±14
	80 P	94	118	87	101	93	99±14
	120 P	75	114	74	98	91	90±12
	All levels	78±20	113±21	78±14	107±10	91±6	93±7
All seasons	Both PR						
	40 P	56±9	106	73	104±23	80±9	82±9
	80 P	97±32	118	87	94±13	80±14	92±10
	120 P	92±15	114	74	92±8	81±15	89±7
	All levels	82±12	113±21	78±14	96±8	80±6	88±5

Table 41 show the results of the statistical analysis of the effect of N, P and other nutrients on maize grain yields. Interpretation of the table is complicated by the fact that not all combinations of treatments and control treatments are present. For instance, evaluation of the effect of N without P (T1 vs. T2) may generally be masked by the combined effect of other basal nutrients applied according to Table 23. For instance, the highly significant treatment effect (T1 vs. T2) at Magadu and Msimba in the first season may be interpreted as a regular N effect as no other factor than N differentiate the two treatments, whereas the significant treatment effect (T1 vs. T2) at Ukiriguru, Suluti, Lubonde, Mpangala and Nkundi may represent an additional effect of Cu and Zn. Looking at the leaf contents of Cu and Zn during the first season at the five sites (Table 43), such an effect cannot be excluded although the data do not allow for a statistical evaluation due to the lack of replicates and proper controls.

Table 41. Significance level[1] for differences between treatments for the first three seasons (effect of N, P and other nutrients on maize grain yield).

		Site									
Harvest	Comparison[2]	Ig	Uk	Ml	Ma	Ms	Su	Lu	Mp	Sa	Nk
1998/1999 (1st season)	T1 vs. T2		*		***	***	***	*	**		***
	T3 vs. T10				***	***	***	***		*	***
	T1 vs. T3			**							
	T2 vs. T10	*[3]								***	*
1999/2000 (2nd season)	T1 vs. T2	***				***	***				***
	T3 vs. T10	***				***	***			***	***
	T1 vs. T3	***								***	
	T2 vs. T10									***	***
2000/2001 (3rd season)	T1 vs. T2	***	***		**		***				***
	T3 vs. T10	**	*	*	***		***	*	***	***	***
	T1 vs. T3	*	**							***	
	T2 vs. T10			*					***	***	***

[1] Non-significant (blank), *p<0.05, **p<0.01, ***p<0.001.

[2] The first named treatment being significantly lower than the treatment for which the comparison is made.

T1 = Absolute control (no nutrient application).
T2 = P control (N and additional macro and micronutrients but no P).
T3 = N control (P and additional macro and micronutrients but no N).
T10 = All nutrients (N, P and additional macro and micronutrients).
Treatment comparisons:
T1 vs. T2 corresponds to the combined effect of N and other nutrients without any P.
T3 vs. T10 corresponds to the effect of N with 40 kg ha^{-1} MPR-P.
T1 vs. T3 corresponds to the combined effect of 40 kg ha^{-1} MPR-P and other nutrients without any N.
T2 vs. T10 corresponds to the effect of 40 kg ha^{-1} MPR-P with N.

[3] T10 is significantly lower than T2.

Table 42. Least square means of maize grain yield (t ha^{-1}) for the first three seasons (effect of N, P and other nutrients on maize grain yield).

		Site									
Harvest	Treatment	Ig	Uk	Ml	Ma	Ms	Su	Lu	Mp	Sa	Nk
1998/1999	T1	5.19	0.50	1.23	0.64	0.54	2.11	5.65	1.03	0.11	1.89
(1st season)	T2	5.45	1.13	1.82	2.45	2.13	5.52	6.50	2.42	0.04	4.22
	T3	4.63	0.87	2.69	1.06	1.08	2.12	5.07	1.40	0.48	2.36
	T10	4.50	0.91	2.19	2.37	2.51	5.62	6.66	2.17	1.20	4.99
1999/2000	T1	1.58	1.49	0.97	0.32	0.94	1.44	2.94	0.07	0.18	1.18
(2nd season)	T2	4.62	1.65	0.97	0.49	2.53	3.86	3.42	0.13	0.01	2.28
	T3	3.55	1.28	1.25	0.54	0.56	1.49	2.82	0.13	1.39	1.52
	T10	5.30	1.23	1.37	0.69	2.44	4.28	3.31	0.27	2.55	4.83
2000/2001	T1	1.36	1.48	1.28	0.40	2.87	1.41	2.23	0.42	0.33	1.65
(3rd season)	T2	3.88	3.01	1.76	1.33	3.17	3.90	2.68	0.89	0.09	3.89
	T3	2.44	2.42	1.95	0.42	2.99	1.26	2.03	1.16	1.46	1.67
	T10	3.60	3.18	2.87	1.82	2.97	4.24	2.99	2.71	2.51	5.30
Least significant difference (95%)		0.81	0.59	0.89	0.59	0.59	0.75	0.82	0.82	0.59	0.66

The lack of N response (T1 vs. T2) at Mlingano and Sasanda during the first season is most likely caused by the very strong P deficiency as indicated by the low leaf P contents (0.09-0.16% P) (Table 43). In fact, N application without P (T1 vs. T2) at Sasanda led to yield decreases in all seasons due to extreme nutrient imbalances and P, Ca and Mg deficiency induced by the N application. The significant and positive N effect after P application (T3 vs. T10) at Sasanda indicates a strong N and P interaction.

The lack of N effect (T1 vs. T2) at Igabiro during the first season may be ascribed to a strong K deficiency indicated by very low leaf K uptake, a very high N/K ratio and low N/Ca and N/Mg ratios (Table 43-Table 45). The absolute levels of N uptake indicate that the site is strongly N deficient. After K application, the N effect becomes highly significant both with and without P application and N/K ratios of the treated plots are significantly reduced. The effect of K is also supported by the lack of significant difference between T2 and T10 during the second and third seasons and the significant difference between T1 and T3 as the former indicate that the difference between T1 and T3 is due to K and not P. Although soil analyses indicated low availability of Zn at Igabiro (Table 29 and Table 34), leaf analyses did not indicate such deficiency. Similarly, significant differences between T1 and T2, T1 and T3, T3 and T10 but not T2 and T10 at Ukiriguru in the third season indicate that P is not limiting yields significantly. Instead, N along with other nutrients added (Zn, Cu and B) may explain the differences.

The effect of P presented in Table 36, can also be derived from Table 41 by comparison of T2 and T10. However, only the 40 kg MPR-P ha^{-1} was used in the analysis in contrast to all P levels of a particular P sources in Table 36. At Sasanda and Nkundi, 40 kg MPR-P ha^{-1} was able to significantly increase yields in all seasons whereas a yields were only increased at Mlingano and Mpangala in the third season.

The leaf element contents and ratios between elements (Table 43-Table 45) generally reveal several nutrient constraints and imbalances among the sites. Except maybe Mpangala in the first season, the control treatments (T1) indicate very strong N deficiency at all sites with levels substantially less than a critical level of 3% N {99}. N application generally increases N uptake substantially although not all levels reach the sufficient level despite relatively high levels of N (80-120 kg N ha^{-1}) indicating that the efficiency of N is low either due to leaching or other nutrient constraints, which limit N uptake.

Based on leaf contents of P and the N/P ratio of the P control treatment (T2), phosphorus seems to be strongly limiting during the first season at Mlingano, Sasanda and Nkundi in agreement with the significant effect of P on grain yields for those sites (Table 36 and Table 37). In the second and third seasons, also Ukiriguru and Magadu show deficient P uptake. Hence, despite Ukiriguru having sufficiently high availability of soil P, the strong moisture stress apparently limit the P uptake. Igabiro, Msimba, Suluti and Lubonde apparently have sufficient P uptake, which is also partly in agreement with the soil analyses (Table 35). In the third season, Lubonde may also start showing P deficiency indicating that the pool of easily available soil P is being exhausted.

Other important nutrient constraints include a very deficient K uptake at Igabiro (0.5-0.7% K) {99}, which lead to a very sharp decrease in yields of the control treatment (T1) from the first to later seasons (Table 42). As compensation for the reduced K uptake, the uptake of Ca and Mg is significantly higher than normal and cultivation on K deficient sites may therefore lead to a higher degree of Ca and Mg removal by the crop and hence depletion of the soil. The leaf and yield data show that the K deficiency is partly alleviated by addition of K. Apparently, K uptake at Ukiriguru and Mlingano are sufficient despite levels of exchangeable K being very low. Other sites, such as Suluti, Lubonde and Nkundi show clear signs of incipient K deficiency and without K application in order to replace what is removed by the crop, the K deficiency will eventually, also at sites such as Ukiriguru and Mlingano with small pools of exchangeable K, lead to yield decreases.

Table 43. Element content of selected leaf samples (1998/1999, 1st season).

Site	T	N	P	Ca	Mg	K	Zn	Cu	Mn	N/P	N/Ca	N/Mg	N/K
				%				mg kg^{-1}					
Ig	1	1.55	0.22	0.88	0.95	0.67	37	13	177	7	2	2	2
	2	1.76	0.27	0.95	1.04	0.53	39	15	251	7	2	2	3
	6	1.52	0.18	0.80	0.68	0.56	28	15	176	9	2	2	3
	9	1.83	0.24	0.90	0.90	0.46	25	14	243	8	2	2	4
	12	1.84	0.22	0.76	0.93	0.57	39	15	214	8	2	2	3
Uk	1	1.51	0.29	0.38	0.12	2.52	17	16	90	5	4	12	1
	2	1.48	0.28	0.50	0.12	2.58	20	15	160	5	3	12	1
	6	1.85	0.25	0.44	0.12	2.78	20	15	161	7	4	16	1
	9	1.67	0.27	0.47	0.16	2.88	23	11	163	6	4	11	1
	12	1.94	0.26	0.44	0.14	2.57	20	11	153	7	5	14	1
Ml	1	1.04	0.16	0.18	0.21	2.49	17	7	83	6	6	5	<1
	2	1.70	0.15	0.22	0.22	2.99	40	11	163	12	8	8	1
	6	1.74	0.23	0.25	0.23	3.17	28	12	121	8	7	8	1
	9	1.76	0.20	0.24	0.20	2.98	31	10	135	9	7	9	1
	12	1.74	0.22	0.25	0.22	3.35	27	11	118	8	7	8	1
Ma	1	1.16	0.17	0.19	0.08	2.33	15	11	123	7	6	14	1
	2	2.01	0.22	0.21	0.12	2.89	23	13	116	9	10	17	1
	6	1.80	0.25	0.22	0.10	2.77	15	11	126	7	8	18	1
	9	1.81	0.21	0.22	0.09	2.83	16	10	146	9	8	20	1
	12	1.74	0.22	0.24	0.11	2.47	16	10	97	8	7	16	1
Ms	1	1.36	0.34	0.33	0.23	2.25	16	8	55	4	4	6	1
	2	1.88	0.27	0.37	0.16	2.38	16	10	108	7	5	11	1
	6	1.81	0.27	0.46	0.20	2.50	16	10	117	7	4	9	1
	9	1.99	0.23	0.41	0.19	2.42	16	10	100	9	5	10	1
	12	1.59	0.34	0.39	0.17	2.52	17	10	110	5	4	9	1
Su	1	0.95	0.19	0.36	0.22	1.83	10	8	80	5	3	4	1
	2	1.77	0.21	0.55	0.26	1.88	25	13	177	8	3	7	1
	6	1.49	0.23	0.53	0.17	2.01	15	10	107	7	3	9	1
	9	1.35	0.15	0.42	0.20	2.01	15	9	100	9	3	7	1
	12	1.39	0.16	0.48	0.19	1.91	14	9	106	9	3	7	1
Lu	1	1.34	0.21	0.55	0.18	1.79	13	8	57	7	2	7	1
	2	2.10	0.22	0.45	0.18	1.90	16	10	64	9	5	12	1
	6	2.16	0.26	0.44	0.15	2.13	13	15	82	8	5	14	1
	9	2.30	0.26	0.46	0.15	1.93	20	14	75	9	5	15	1
	12	2.15	0.24	0.51	0.16	1.76	17	11	83	9	4	14	1
Mp	1	2.30	0.19	0.40	0.23	2.76	18	7	55	12	6	10	1
	2	2.34	0.20	0.31	0.13	2.73	16	9	52	12	8	18	1
	6	2.38	0.22	0.38	0.17	2.52	23	9	82	11	6	14	1
	9	2.43	0.19	0.40	0.20	2.76	17	9	54	13	6	12	1
	12	2.46	0.22	0.36	0.18	2.47	17	10	41	11	7	14	1
Sa	1	1.65	0.09	0.21	0.15	2.47	11	9	35	17	8	11	1
	2	2.29	0.11	0.15	0.13	2.66	17	12	62	21	15	17	1
	6	2.20	0.20	0.23	0.16	2.29	14	13	50	11	10	13	1
	9	2.18	0.17	0.22	0.15	2.54	14	11	49	13	10	15	1
	12	2.28	0.18	0.26	0.14	2.02	15	13	45	13	9	16	1
Nk	1	1.60	0.26	0.25	0.43	1.45	23	11	54	6	6	4	1
	2	2.12	0.17	0.29	0.31	1.35	20	14	88	12	7	7	2
	6	1.88	0.23	0.31	0.28	1.81	27	12	90	8	6	7	1
	9	1.95	0.19	0.30	0.32	1.29	32	13	142	10	7	6	2
	12	2.02	0.19	0.38	0.31	1.27	25	14	131	11	5	7	2

Table 44. Element content of selected leaf samples (1999/2000, 2nd season).

Site	T	N	P	Ca	Mg	K	Zn	Cu	Mn	N/P	N/Ca	N/Mg	N/K
				%				mg kg^{-1}					
Ig	1	2.04	0.30	0.86	0.99	0.37	19	13	120	7	2	2	6
	2	2.35	0.26	0.68	0.69	1.13	35	13	145	9	4	3	2
	6	2.37	0.23	0.73	0.55	1.31	29	11	147	10	3	4	2
	9	2.39	0.26	0.81	0.71	0.91	26	13	127	9	3	3	3
	12	2.13	0.25	0.83	0.79	0.84	27	12	146	9	3	3	3
Uk	1	1.87	0.19	0.64	0.24	2.21	17	14	128	10	3	8	1
	2	1.65	0.15	0.69	0.19	2.48	36	30	231	11	2	9	1
	6	2.67	0.15	0.73	0.24	2.29	25	10	334	17	4	11	1
	9	1.96	0.17	0.60	0.25	2.41	35	9	265	12	3	8	1
	12	1.66	0.17	0.65	0.29	2.39	26	10	248	10	3	6	1
Ml	1	1.77	0.14	0.18	0.19	2.46	29	8	122	13	10	9	1
	2	1.84	0.14	0.16	0.19	2.36	32	10	126	14	11	10	1
	6	1.78	0.22	0.24	0.24	2.54	17	9	103	8	8	7	1
	9	1.91	0.22	0.23	0.18	2.39	28	10	163	9	8	11	1
	12	1.80	0.22	0.21	0.19	2.45	28	11	142	8	9	10	1
Ma	1	0.92	0.12	0.21	0.11	2.08	16	5	160	7	4	9	0
	2	1.50	0.14	0.18	0.13	2.74	25	7	188	11	8	11	1
	6	1.24	0.20	0.20	0.11	2.81	16	5	196	6	6	12	0
	9	1.10	0.16	0.22	0.11	2.54	21	5	190	7	5	10	0
	12	1.41	0.20	0.29	0.13	2.50	14	6	166	7	5	11	1
Ms	1	1.80	0.27	0.31	0.16	2.33	19	8	48	7	6	11	1
	2	2.49	0.30	0.29	0.17	2.39	37	11	76	8	9	15	1
	6	2.35	0.32	0.32	0.15	2.48	19	9	73	7	7	16	1
	9	2.22	0.30	0.34	0.18	2.48	21	10	67	8	7	12	1
	12	2.18	0.32	0.28	0.16	2.51	18	9	67	7	8	14	1
Su	1	1.32	0.20	0.40	0.18	2.29	26	7	98	7	3	8	1
	2	2.12	0.26	0.38	0.16	2.42	25	11	91	8	6	13	1
	6	2.03	0.32	0.45	0.20	2.45	22	10	123	6	5	10	1
	9	2.01	0.27	0.38	0.17	2.59	54	10	104	7	5	12	1
	12	2.10	0.29	0.43	0.17	2.45	29	11	108	7	5	13	1
Lu	1	1.75	0.24	0.37	0.11	2.11	12	8	54	7	5	16	1
	2	2.35	0.26	0.34	0.10	2.11	18	11	65	9	7	24	1
	6	2.26	0.27	0.40	0.09	1.90	13	9	86	8	6	25	1
	9	2.37	0.29	0.33	0.10	2.02	17	10	88	8	7	24	1
	12	2.25	0.26	0.46	0.15	1.68	22	11	83	9	5	16	1
Mp	1	1.59	0.14	0.28	0.15	2.96	16	5	51	12	6	10	1
	2	1.54	0.15	0.35	0.16	3.30	24	9	58	10	4	10	1
	6	1.78	0.25	0.33	0.13	3.08	19	8	62	7	5	14	1
	9	1.88	0.24	0.35	0.16	2.85	20	10	57	8	5	12	1
	12	1.70	0.23	0.32	0.15	2.61	18	7	49	8	5	11	1
Sa	1	1.81	0.11	0.23	0.18	2.61	24	9	66	16	8	10	1
	2	1.91	0.10	0.15	0.14	2.57	39	8	88	20	13	13	1
	6	1.77	0.19	0.27	0.18	2.15	22	8	53	10	6	10	1
	9	1.86	0.16	0.26	0.15	2.28	13	8	42	11	7	12	1
	12	1.90	0.17	0.28	0.18	2.15	29	8	45	11	7	11	1
Nk	1	1.14	0.18	0.20	0.24	1.78	19	6	37	6	6	5	1
	2	1.73	0.17	0.25	0.25	2.11	31	10	68	10	7	7	1
	6	1.69	0.30	0.33	0.21	2.10	29	10	136	6	5	8	1
	9	1.84	0.27	0.32	0.21	2.01	27	11	105	7	6	9	1
	12	1.75	0.26	0.34	0.22	2.00	26	11	90	7	5	8	1

Table 45. Element content of selected leaf samples (2000/2001, 3rd season, dash=not determined).

Site	T	N	P	Ca	Mg	K	Zn	Cu	Mn	N/P	N/Ca	N/Mg	N/K
		%					mg kg^{-1}						
Ig	1	1.77	0.30	1.09	1.02	0.43	24	13	102	6	2	2	4
	2	2.14	0.26	0.65	0.49	1.37	38	13	100	8	3	4	2
	6	2.11	0.26	0.76	0.50	1.53	32	12	108	8	3	4	1
	9	2.11	0.27	0.76	0.55	1.28	33	12	112	8	3	4	2
	12	2.18	0.29	0.74	0.52	1.31	37	12	98	8	3	4	2
Uk	1	-	-	-	-	-	-	-	-	-	-	-	-
	2	-	-	-	-	-	-	-	-	-	-	-	-
	6	-	-	-	-	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-	-	-	-	-
	12	-	-	-	-	-	-	-	-	-	-	-	-
Ml	1	-	-	-	-	-	-	-	-	-	-	-	-
	2	1.59	0.16	0.16	0.14	2.46	40	9	160	10	10	12	1
	6	2.20	0.33	0.26	0.20	2.48	19	11	107	7	8	11	1
	9	-	-	-	-	-	-	-	-	-	-	-	-
	12	-	0.24	0.28	0.17	2.61	24	9	113	-	-	-	-
Ma	1	1.36	0.15	0.18	0.08	2.45	20	6	105	9	8	17	1
	2	2.08	0.18	0.17	0.09	2.75	23	9	151	12	13	23	1
	6	2.33	0.20	0.21	0.08	2.55	19	8	164	12	11	30	1
	9	2.10	0.22	0.26	0.09	2.72	25	8	187	10	8	24	1
	12	2.45	0.27	0.26	0.11	2.96	34	8	103	9	9	23	1
Ms	1	2.23	0.22	0.50	0.26	2.25	15	14	55	10	5	9	1
	2	2.47	0.22	0.38	0.22	2.51	24	15	91	11	7	11	1
	6	2.36	0.25	0.42	0.20	2.48	11	12	90	10	6	12	1
	9	2.25	0.22	0.38	0.23	2.50	19	13	69	10	6	10	1
	12	2.23	0.27	0.47	0.23	2.42	17	13	87	8	5	10	1
Su	1	1.62	0.25	0.39	0.20	2.00	15	8	59	7	4	8	1
	2	2.17	0.26	0.38	0.12	2.26	32	11	93	8	6	18	1
	6	2.11	0.32	0.44	0.15	2.28	39	10	115	7	5	14	1
	9	1.99	0.27	0.41	0.12	2.17	24	10	77	7	5	17	1
	12	2.05	0.28	0.42	0.11	2.19	27	10	82	7	5	18	1
Lu	1	1.70	0.10	0.44	0.19	1.50	12	6	39	17	4	9	1
	2	2.93	0.26	0.42	0.10	1.69	14	10	66	11	7	30	2
	6	2.45	0.24	0.43	0.11	1.65	12	8	70	10	6	22	2
	9	2.63	0.27	0.48	0.14	1.54	16	9	77	10	6	19	2
	12	2.56	0.23	0.62	0.19	1.24	13	8	74	11	4	13	2
Mp	1	2.47	0.21	0.35	0.18	1.75	14	6	39	12	7	13	1
	2	2.69	0.22	0.39	0.18	1.82	18	11	49	12	7	15	2
	6	1.96	0.22	0.33	0.12	1.83	11	8	36	9	6	16	1
	9	2.19	0.23	0.40	0.19	1.67	13	9	33	10	5	11	1
	12	1.70	0.20	0.27	0.09	1.62	14	8	32	9	6	19	1
Sa	1	1.69	0.12	0.23	0.16	2.00	13	9	82	15	7	11	1
	2	1.89	0.12	0.18	0.09	2.15	16	10	81	16	11	20	1
	6	2.49	0.20	0.27	0.14	2.03	12	11	40	12	9	18	1
	9	2.29	0.22	0.22	0.16	2.07	10	10	40	11	11	14	1
	12	1.87	0.20	0.26	0.15	1.98	12	10	37	10	7	12	1
Nk	1	1.34	0.23	0.18	0.22	1.65	20	7	37	6	7	6	1
	2	2.58	0.23	0.21	0.13	2.25	35	15	76	11	12	20	1
	6	1.54	0.22	0.33	0.17	1.66	22	9	93	7	5	9	1
	9	1.67	0.28	0.30	0.14	1.84	16	10	88	6	6	12	1
	12	1.98	0.26	0.29	0.11	1.67	16	10	87	8	7	19	1

Ca uptake of the P control treatment (T2) is at a deficient level (<0.4% Ca) {99, 138} at Mlingano, Magadu, Sasanda and Nkundi. Except at Magadu the low Ca uptake is in agreement with very low levels of soil Ca. Apparently, application of TSP or PR seems to significantly increase Ca uptake on the Ca deficient sites.

Several sites are showing deficient Mg levels and highly variable N/Mg ratios. Most severe Mg deficiency is seen at Magadu and Sasanda but also Ukiriguru, Suluti, Lubonde and Mpangala show deficient levels in some seasons. It seems that both Ca and Mg uptake at Magadu may be limited by strong soil acidity and high Al saturation as both soil exchangeable Ca and Mg is relatively high. At Sasanda low Ca and Mg uptake may be a result of high $K/(Ca+Mg)^{0.5}$ ratio, which lead to imbalanced Ca and Mg uptake. Apparently, addition of 25 kg Mg ha^{-1} and 50 kg Mg ha^{-1} in the second and third season respectively is not able to increase the Mg uptake at Sasanda indicating that something else limit Mg uptake.

Uptake of Zn seems to be at a deficient level at Magadu, Suluti, Lubonde and Sasanda whereas Cu uptake is low at Mlingano, Magadu, Suluti, Lubonde, Mpangala, Sasanda and Nkundi. At Mlingano soil indices of Cu availability do not apply well with the levels of Cu uptake. Application of Zn and Cu generally seems to increase Zn and Cu uptake slightly. Uptake of Mn is generally above the critical level of 15 mg Mn kg^{-1} and below the toxic level of 225 mg Mn kg^{-1} {99, 272}. High uptake of Mn may be associated with periods of waterlogging due to heavy rainfall although no clear pattern is seen from the data.

Other essential macro and micronutrients, which have not been estimated such as S, Fe, B and Mo, may or may not be deficient. Based on soil analyses especially B is suspected to be deficient at most of the sites (Table 34) whereas S is likely to be deficient at most inland sites as a result of prolonged leaching, low input through precipitation and low plant availability {196}. Comparison of T1 and T2 may include an effect of S along with N as N was applied as sulphate of ammonia. The significant difference between T1 and T2 at Ukiriguru and Mpangala during the first season may possibly be an S effect along with the effect of the micronutrients applied. Fe is like Mn not likely to be deficient and toxicity is mainly a question of strong waterlogging, which was not a problem for any of the sites.

The calculation of the soil moisture balance during the growing seasons reveal that large differences exist between the sites and between harvests. Actual precipitation during the growing season vary from 258 mm at Ukiriguru in the first season to more than 2000 mm at Nkundi in the third season. The estimated actual evapotranspiration during the growing season vary from 258 mm to 738 mm. In few cases (Igabiro, Ukiriguru in all seasons, and Mpangala in the third season) all moisture entering the soil through precipitation is removed by evapotranspiration leaving the soil at the wilting point at harvest. These sites generally showed severe moisture stress during the critical period after tasseling and any measure to increase the available soil moisture capacity is expected to increase yields. At Ukiriguru all seasons and Mpangala in the third season, yields were very strongly affected by moisture stress as also observed in the field, whereas at Igabiro, the yield reduction due to low moisture content was not very obvious despite MDG being low in the first two seasons. A remarkable finding as also the K uptake at Igabiro was deficient suggesting that the physiological water management by the maize plants should be poor. Other sites have also dried up to the wilting point at harvest but have at the same time experienced severe leaching sometime during the growing season. Hence, bad distribution of the precipitation in relation to water consumption of the plants has reduced the efficiency of the precipitation. It is a paradox that sites such as Magadu and Msimba show severe moisture stress in the critical period with yields strongly reduced by water shortage and at the same time experience moisture losses up to 430 mm through leaching or runoff. As a direct consequence of moisture stresses, several sites experienced severe termite attack during dry spells leading to highly reduced yields. The figures emphasize the importance of water management through water harvesting, increased water holding capacities of the soils and larger effective root depth. Sites such as Mlingano, Suluti and Nkundi are also at the wilting point at harvest and they also dry up fast due to low water holding capacities but here the distribution between precipitation and consumption is better and so water shortage is not an important issue except in years with erratic rainfall. However, with leaching volumes of more than a few hundreds of millimetres a substantial amount of nutrients is expected to be lost from the system, which is particularly harmful in a low fertility, and non-resilient system.

Table 46. Soil moisture characteristics at the various sites during the three first seasons.

Site	Harvest	RD	AWC	50% T	H	CP	P	AET	L	MH	MCG
		cm	mm m^{-1}	days after planting	days		mm			%	%
1	1	150	115	80	160	40	476	470	-	<5	38
	2	150	115	80	160	40	506	506	-	<5	20
	3	150	115	80	160	40	501	501	-	<5	51
2	1	150	61	80	160	40	258	258	-	<5	15
	2	150	61	80	160	40	295	295	-	<5	1
	3	150	61	80	160	40	331	331	-	<5	16
3	1	150	86	70	150	40	562	479	83	<5	72
	2	150	86	70	150	40	598	470	128	<5	60
	3	150	86	70	150	40	482	393	89	<5	68
4	1	75	123	70	150	40	489	336	153	<5	32
	2	75	123	70	150	40	322	322	-	<5	20
	3	75	123	70	150	40	446	331	115	<5	41
5	1	90	88	70	150	40	708	277	431	<5	5
	2	90	88	70	150	40	379	379	-	<5	31
	3	90	88	70	150	40	943	412	531	<5	62
6	1	150	81	70	150	40	1225	506	719	<5	94
	2	150	81	70	150	40	904	532	370	<5	91
	3	150	81	70	150	40	1124	506	618	<5	90
7	1	150	181	130	260	65	820	658	128	13	92
	2	150	181	130	260	65	1172	652	436	31	95
	3	150	181	130	260	65	1006	692	285	11	82
8	1	150	231	150	280	65	890	688	114	26	88
	2	150	231	150	280	65	880	738	142	<5	69
	3	150	231	150	280	65	552	552	-	<5	33
9	1	150	236	110	210	50	1147	637	318	54	97
	2	150	236	110	210	50	806	595	15	55	98
	3	150	236	110	210	50	1288	645	433	59	97
10	1	75	130	110	210	50	832	512	321	<5	84
	2	75	130	110	210	50	968	544	424	<5	83
	3	75	130	110	210	50	2017	689	1328	<5	81

Column headings: RD = Estimated effective root depth, AWC = available water content at pF=2.5 tension, 50% T = 50% tasseling, H = harvest, CP = critical period of moisture supply used in calculation of MDG (days after 50% tasseling), P = precipitation monitored in the field, AET = actual evapotranspiration estimated on the basis of potential evapotranspiration at nearest meteorological station and availability of soil moisture, L = leaching (soil water in excess of AWC at estimated effective root depth), MH = soil moisture at harvest, MCG = (1-MDG) = average moisture content in CP as % of potential AWC at the effective soil moisture wetting depth).

6.3 Discussion

The ten experimental sites represent a more or less random selection of soils of the humid to sub-humid parts of Tanzania, and the site and soil characteristics found here are expected to represent at least a part of the large range of agro-ecological conditions under which the Tanzanian agriculture operates. Except maybe Msimba, the soils were, on the basis of an evaluation of the general soil fertility prior to initiation of the field experiments, expected to be suitable for application of phosphate rocks. Most of the sites are characterized by having highly weathered and leached soils with low natural fertility and low capability of sustaining intensive agricultural production without addition of fertilizers and/or manure. Also the resilience properties, i.e. the capability of restoring soil fertility after prolonged periods of low-input agriculture is low due to the highly weathered nature dominated by low activity clay minerals with limited capability of storing nutrients in plant available form, especially in the subsoil. The content of weatherable minerals from which base cations and micronutrients could be released is generally low and initially a number of soil fertility constraints are expected. Even the much younger soils developed on volcanic ash, represent soils with highly limiting soil fertility problems due to the particular composition of the parent material and pedogenetic development stage. In contrast to the more weathered soils, the Msimba site may represent a more fertile soil due to the continuous influx of soil and water from the adjacent weathering crystalline rocks and due to the contents of weatherable minerals and 2:1 layer silicates. However, soil physical and climatical characteristics are also influencing the site productivity potential and thereby modifying the role of soil fertility. For instance, rainfall distribution during the growing season with few very heavy rainfall events along with limited root depth and low water holding capacity lead to low productivity at Msimba despite the relatively high soil fertility. On the other hand, Suluti and Nkundi are examples of sites, which due to the favourable climatical conditions are giving high maize yields despite their low soil fertility. However, the latter sites are also examples of sites where yields are expected to decline rapidly if not supplied with a balanced nutrient input through fertilizers.

The results of the general characterization of the sites and the field experimental results suggest that a number of productivity constraints exist, which must be dealt with before any sustainable increases in yields can be expected. In other words, N, which is normally receiving the major interest by farmers in the tropics, is obviously not the only constraint for crop production. The field experiments strongly emphasize the need of looking at all possible constraints to high crop production. Soil analyses were generally indicative of possible soil fertility problems but they do not give the full explanation of the results from the field experiments. Instead a number of parameters including nutrient availability as evaluated by leaf analyses and the effect of climate and large field variability must be considered in order to explain the behaviour of the applied plant nutrients {13}.

From the data in Table 41 and Table 42 it is seen that N is a major constraint for maize yields at all sites, at least after the first season. This is in agreement with findings from previous field experiments in Tanzania and with the general knowledge of the cycling of N in tropical soil systems {2}. The lack of N response at some sites during the first season was explained either as a result of other nutrient deficiencies or drought preventing the expression of the N effect or due to residual N from previous fertilizers or from mineralization of the previous crop or fallow vegetation during the growing period. However, the pool of easily available N from mineralization is normally low, which is also demonstrated from the field experiments by the decreasing yields of the N control and an increasing N response with time. Hence, input of N through fertilizers, manure or crop residues or through inter-cultivation or fallowing with leguminous crops seems to be a prerequisite of sustainable agriculture in the humid to sub-humid parts of Tanzania. However, the N application must always be accompanied by other essential nutrients at amounts, which at least correspond to the amounts removed by the crop or else the effect of N may be absent or vanish with time. The strong interaction between N, P and other plant nutrients observed at Sasanda is an example of such mutual dependency between N and other nutrients. As addition of nutrients through non-fertilizer based materials may not always add sufficient amounts of all essential nutrients, availability of compound fertilizers is an important step in managing the soil fertility.

Based on soil analyses, P seems to be deficient at a number of sites in agreement with the assessment of the general soil fertility properties. However, a clear, significant P response was only experienced at two sites, e.g. Sasanda and Nkundi. The other strongly deficient sites where a P response was expected (Mlingano, Magadu, Mpangala) only showed inconsistent P response in some years (Table 36). This lack of P response at sites, which are assessed as P deficient has also been observed previously (Figure 26). In similarity with N, the results indicate that the absence of clear P response at these three sites can be explained by other factors such as strong soil acidity, deficient uptake of macro (K, Ca, Mg) and micronutrients (B, Zn, Cu), erratic rainfall and low AWC.

Igabiro, Ukiriguru, Msimba, Suluti and Lubonde apparently have sufficient levels of plant available P as no P response were indicated in any season. However, based on P adsorption properties it seems that sites such as Ukiriguru, Msimba and Suluti all possess low P buffering capacity and a P response would be expected after a few years of cultivation. Igabiro and Lubonde have probably, due to their high P adsorption capacity and relatively intensive management, been supplied with P fertilizers through a number of years leaving a larger reserve of P available for plant uptake. A significant P response at these sites may not be likely within the timespan of these field experiments although leaf P content at Lubonde during the third season indicated a deficient level. At Igabiro, a significant P effect would possibly remain absent until the strong K deficiency is relieved.

High variability in the yield data may also explain the lack of significant treatment effects at some sites. From the LSD/average yield (Table 37) it is seen that differences up to approximately 50% of average yield are required at Mpangala before any significant treatment effects are observed. On the other hand relatively low residual error at Igabiro, Suluti, Lubonde and Nkundi makes the interpretations firmer. High residual error at Mpangala may be attributed to the strong B deficiency, which apparently had a varying effect across the experimental area. Also at Mlingano an effect of old termite mounds and at Magadu a generally high field variability, which is observed during the growing season seems to cause high within block variation. At Ukiriguru severe moisture stress may be the reason for the high residual error. Hence, the detrimental effect of moisture stress, nutrient deficiencies and general soil variation on the statistical interpretation is evident. Apparently blocking, which was done without much respect to field variation, was not sufficiently effective at all sites. Use of other statistical techniques such as the Post-Mortem Residual Analysis and Nearest Neighbour Means could possibly improve the interpretations {164}.

K deficiency seems to be widespread among the non-volcanic sites indicating that more attention should be put on incorporating K in future fertilizer recommendations. Igabiro could be an example of a site where K deficiency problems have risen due to a one-sided fertilization strategy applying only N and P. Removal of K by the crop without replacement together with the relatively low amounts of weatherable minerals and the low cation exchange capacity are probably the primary reasons for the generally low K availability among the soils. Other macronutrients such as Ca and Mg also show deficient levels in some of the soils due to the same processes as for K. From the analyses of soil B, Zn and Cu and from leaf analyses of Zn and Cu it seems that deficiency of all three nutrients is also widespread.

Hence, the general characterization of the soils and the field experiments strongly indicate that soils of the humid to sub-humid parts of Tanzania often suffer from multinutritional problems partly due to their inherent low natural fertility and resilience caused by weathering and leaching through time and partly due to management strategies with only little replacement of the nutrients removed by crop harvest and leaching. They strongly emphasize the need for applying a balanced compound fertilizer type containing all required nutrients in plant available form. The situation at Sasanda with low uptake of Ca and Mg due to high $K/(Ca+Mg)^{0.5}$ ratio even indicate that different types of compound fertilizers with varying nutrient ratios such as those available in most Western countries are required depending on specific conditions. Each specific application requirement must be based on crop species and variety, crop rotation, soil conditions and other management practices such as addition of manure, crop residues or other agro-minerals.

The field experiments support the previous findings that MPR is a suitable substitute for TSP on acid soils, which respond to TSP application. In the first season after application the relative agronomic effectiveness is around 75% increasing in the second and third season to values around 90-100% indicating that the pool of plant available P derived from MPR after the first season is comparable with P made available through soluble P fertilizers. These figures agree well with the figures derived from the Minjingu PR database in

Chapter 5.2. The lower effect of MPR in the first year is presumably due to the smaller amount of P released from PR products compared to water-soluble P fertilizers immediately after application. Dissolution studies of MPR and other PRs have revealed that dissolution of PR is fast and happens within days or weeks after application {89, 92, 106, 248}. After the initial fast release of P, dissolution reaches a certain level depending on soil properties followed by a much lower dissolution rate, which continues until the entire mineral have dissolved. Hence, the reason for the lower RAE in the first season is primarily that only a fraction of the P available from TSP is available from MPR. In the second season the MPR continues to release P through dissolution from the PR mineral whereas the effectiveness of P released from TSP may decrease due to irreversible adsorption {214, 269}. Alternatively the amount of plant available P released from MPR reaches during the second season a threshold value comparable with what was released by TSP during the first season and beyond which an increase in adsorbed P do not lead to a further increase in yields.

However, the RAE derived from most PR studies including those presented in Table 40 is normally overestimated if both TSP and MPR is broadcasted. If TSP was banded as is the normal practice in order to increase the efficiency of TSP by reducing the contact between soil particles and P, the difference between the two sources may have been larger resulting in a lower RAE {123}. In fact, such an effect was indicated by a study conducted at Sasanda and Magadu comparing placement or broadcasting of TSP and MPR at two different P levels (E.M, Kadogholo, personal communication 2000). At Sasanda, banding of high P rates resulted in a marked decrease and increase in yields for MPR and TSP respectively indicating that high rates of MPR should always be broadcasted and TSP always placed at sites with high P adsorption capacity. When comparing PR and water-soluble P sources in the field, broadcasting and banding respectively seems to be the application strategy, which most correctly estimates the relative agronomic effectiveness.

Granulation of the MPR seemed to reduce the RAE in the first season compared with the powder product. This is most likely explained by reduced dissolution of the PR particles due to the smaller specific surface area of the granules and hence less contact between soil particles and the apatite minerals {78}. A reduced dissolution of GPR compared to MPR was in fact observed in both laboratory and field dissolution studies (Chapter 7). Other studies have also indicated a reduction in the short-term P availability due to granulation of PR materials {45, 78}. In the second and third seasons the difference between the two sources either became smaller or vanished indicating that the amount of plant available P exceeded the threshold value in similarity with the difference between MPR and TSP. Alternatively the difference between GPR and MPR in the first season could be explained by the fact that the granule size were much coarser in the first season compared with the second and third seasons due to differences in the method of granulation (Figure 29). In any way, mini-granulation does not seem to reduce the effectiveness of MPR except maybe in the first season after application. This is an important finding as it was previously stated that some sort of mini-granulation is important in order to reduce the dust problem and hence the health risk caused by inhalation of the radioactive PR particles during application. On the other hand, the lower RAE during the first season may have a negative influence on the acceptance by farmers of the MPR product as part of their economic returns is postponed a year or two.

Both the problems of RAE of MPR less than 100% and the difference between MPR and GPR during the first season may be alleviated by direct application of PR some weeks before planting. Assuming that the soil is moist, the initial fast dissolution may then have completed at the time of planting and thereby enhancing the “starter effect”, which is normally an important characteristic of the water-soluble P fertilizers. However, pot experiments have indicated that application of reactive phosphate rocks to soils characterized by large P adsorption capacity six weeks before planting reduced the RAE compared to application at planting due to the increased P fixation {48}. PR application some time before planting may therefore not be the optimum practice on soils with high P adsorption capacity. Alternatively, a small amount of water-soluble P could be added along with the PR material in the first year in order to improve the starter effect {57}. A general compaction of MPR with water-soluble P sources such as TSP or partial acidulation may not be advisable due to the generally high reactivity of MPR and GPR after the first season in acid soils. However, on less acidic soils, an increase in the fraction of water-soluble P of MPR through partial acidulation could possibly extend the use of MPR to areas less suitable for direct application. In order to improve the long-term utilization of the residual PR under such conditions simultaneous use of other management techniques such as the use of crop species capable of acidifying the root zone or mixing with compost are required {164}.

P levels around 40 kg PR-P ha^{-1} seems to be sufficient to reach maximum yield response at Mlingano, Magadu, Mpangala and Nkundi. At Sasanda, agronomically optimum P levels may go beyond 120 kg PR-P ha^{-1} due to the very low amounts of plant available P and very strong P adsorption capacity. However, the economic optimum may not be as high as the marginal return of adding more PR could be questionable. A similar higher optimum level would also be expected at Mpangala if macro and micronutrient stresses were alleviated and climatical conditions became more favourable. The yield potential at Mpangala should be considerably higher than what is seen during the first three seasons. A better utilization of the precipitation through improved infiltration along with subsoil liming in order to increase the effective root depth could possibly also lead to higher yields at Magadu.

6.4 Conclusion

The field experiments under the Phosphate Rock Utilization Project were conducted at sites representing a range of agro-ecological conditions in important maize growing areas of Tanzania. The sites are characterized by either highly weathered and leached soils with low natural soil fertility and low resilience properties or by slightly developed soils on volcanic ash. Prior to initiation of the field experiments, all sites were considered as suitable for direct application of MPR. The sites are influenced by more or less important productivity constraints affecting the yield potential. Soil fertility problems include low soil pH, high subsoil acidity, low CEC, macro and micronutrient deficiencies, sub-optimum ratios between exchangeable macronutrients, strong P adsorption capacity and low organic carbon contents. Physical and climatical constraints include poor workability, surface crusting, low available water holding capacity, erosion caused by very heavy rainfall events and soil moisture stress due to erratic rainfall pattern. The poor water efficiency at some sites also resulted in severe termite attack during dry spells leading to highly reduced yields. Most of these constraints must be considered and alleviated before sustainable yield increases due to fertilizer application can be expected.

Nitrogen proved to be a major constraint at all sites although the observed yield increases due to the experimental design may have contained effects of other applied macro and micronutrients. Two of the ten sites showed a clear and highly significant response to P in all seasons, whereas for three sites it was only the case in some seasons. Five sites did not show any significant yield increase due to P application. Sufficient soil P levels, moisture stress, other nutritional constraints and high field variability were used to explain the lack of P response at the sites, which did not show any significant yield increases due to P application.

For those sites with P response, the field experiments showed that MPR and GPR were inferior to TSP only in the first season. From the second season onwards RAE was around 100% indicating that both PR sources are effective substitutes for TSP on soils comparable with the soils found at the experimental sites. Granulation apparently reduced the RAE compared with the ground product but the difference was only pronounced in the first season. Application of PR to the moist soil some weeks prior to planting or addition of small amounts of water-soluble P along with PR at planting may circumvent the problem of the delayed effect of PR due to the time dependent mineral dissolution.

Under the conditions present at the experimental sites, 40 kg PR-P ha^{-1} resulted in near maximum yields at all sites except Sasanda. However, as other productivity constraints are alleviated, higher maximum yields and higher optimum PR rates could be expected. Higher rates were generally required at Sasanda, which is characterized by a very high P adsorption capacity.

The water balance study revealed that moisture stress is a major factor influencing the maize yields between the sites. A number of sites experienced severe moisture stress during the critical grain filling period either due to insufficient precipitation during the growing season or due to low water efficiency despite the precipitation exceeding the potential evapotranspiration. Low water holding capacity of the soils and uneven distribution of the rainfall events resulted in severe water losses through leaching and runoff at most of the sites. A few sites did not show any moisture stress due to favourable climatic conditions. The strong leaching environment and runoff observed at several sites may lead to extensive leaching of nutrients. Generally, management strategies are urgently required in order to reduce soil and nutrient losses and to improve the water efficiency.

7 Dissolution of PR in soils and the effect of PR dissolution on soil properties

A fundamental prerequisite of a phosphate rock (PR) being efficient for direct application is that it readily dissolves during the growing season and thereby releases phosphate ions to the soil solution, which then can be taken up by the plants or adsorbed by soil constituents in a more or less exchangeable form {88}. Phosphate rock, soil and plant properties as well as application rate and method, and climate affect the rate and degree of dissolution, and an understanding of the influence of these factors is important for the efficient use of phosphate rocks as P source in agricultural production. By estimation of the degree and rate of dissolution either by relating the increase in reaction products over an un-treated control with the amount added, or by determining the non-dissolved residues, it is possible to estimate the potential agronomic effectiveness of various phosphate rocks in a given soil-plant system. As measurement of PR dissolution under field conditions is laborious and only gives an estimate of dissolution due to fluxes of reaction products and difficulties in sampling and estimation of the amount of PR added, dissolution studies in closed systems are sometimes preferred when screening or evaluating phosphate rocks for direct application (Chapter 2.3). In this study both laboratory dissolution experiments as well as studies of PR dissolution under field conditions are carried out in order to evaluate the dissolution under more controlled conditions as well as under more natural field conditions. Knowledge about phosphate rock characteristics and measurement of soil properties before and after application enables identification of the most important factors affecting the PR dissolution and the evaluation of the effect of PR dissolution on soil properties.

In connection with the agronomic evaluation of the soft Minjingu PR as P source for maize in the sub-humid to humid parts of Tanzania (Chapter 6), soil samples were collected from the ten experimental fields in order to:

1) Evaluate the effect of soil and PR properties on the dissolution of various PR materials in soils (laboratory) and of Minjingu PR in soils under field conditions (field).
2) Compare the dissolution of mini-granulated and non-granulated Minjingu PR in soils (laboratory and field)
3) Evaluate the effect of PR dissolution on soil solution chemistry (laboratory).
4) Compare the dissolution of Minjingu PR with two widely used phosphate rocks with varying reactivity (laboratory).
5) Evaluate the effect of PR dissolution on soil properties, including availability of P after PR application (laboratory and field).
6) Evaluate the relation between dissolution, availability of P, and the relative agronomic effectiveness of the MPR (field).

7.1 Materials and methods

7.1.1 Laboratory dissolution study

Soils

Surface soil material was collected from each of the ten experimental fields used in the evaluation of the Minjingu phosphate rock as P source for maize (see Chapter 6.1.1). In addition, surface soil material from another location in the Southern Highlands (Ihanda) was included in the laboratory experiment as previous field experiments indicated a remarkably high agronomic effectiveness of an igneous non-reactive Tanzanian phosphate rock (Panda Hill) at this site indicating that this site is particularly suitable for PR application {270}.

The soils were air dried, sieved to pass a 2 mm sieve and mixed before further analysis. In addition to the properties already described in Chapter 6.2.1, the following soil chemical properties were determined: H^+ buffer capacity (H_b) as described by Kanabo and Gilkes {107}, i.e. end over end shaking (40 r.p.m.) of seven batches of 1 g soil with 10 cm^3 0.1 M KCl for 20 min., followed by 20 min. shaking with 0.1 cm^3 of KOH solution giving additions of 0-3 cmol OH^- kg^{-1}, and twelve hours equilibration before pH measurement. The H buffer capacity was calculated as the reciprocal of the slope of pH plotted as a function of the added OH^- corresponding to the amount of OH^- required to change pH of the soil by one unit.

P sorption isotherms were determined using the following procedure: Duplicate samples of 10 g surface soil were mixed with 1 dm^3 0.01 M $CaCl_2$ in a reciprocal shaker. After 48 hours, shaking was suspended for a few minutes allowing the larger particles to settle, and 10 cm^3 of the clear supernatant solution were withdrawn from the bottle followed by replacement with 10 cm^3 fresh P solution containing 50 mg P dm^{-3}. Shaking, withdrawal of equilibrium solution and replacement with fresh P solution were repeated at 48-hour intervals until adsorption levelled off and the equilibrium concentration reached approximately 1 - 2 mg P dm^{-3}. Phosphate adsorption P_{ads} (mg P kg^{-1}) at addition *t* was calculated as:

$$P_{ads(t)} = \frac{\left(P_{eq(t-1)} + 0.5\ \text{mg P dm}^{-3} - P_{eq(t)}\right)}{10\,\text{g soil}} 1000\,\text{g kg}^{-1} \qquad (12)$$

where $P_{eq(t)}$ and $P_{eq(t-1)}$ were the equilibrium P concentrations (mg P dm^{-3}) at addition *t* and (*t-1*) respectively. The adsorption data were fitted to the Langmuir equation and the sorption maximum (P_{max}), and affinity parameter (K) were calculated using a least squares non-linear method.

All phosphorus measurements were done using the molybdenum blue method adopted to flow injection analysis {96}.

All analyses were carried out in duplo.

Phosphate sources

A water-soluble triple superphosphate (TSP), MPR and two sedimentary reference carbonate fluorapatites, representing high and medium reactive PRs, were used in the laboratory dissolution experiment.

The beneficiated Tanzanian phosphate rock from the Minjingu soft ore, was used both as a mini-granulated material (GMPR) with a particle size range between 0.5-1 mm and as a finely ground material (MPR) with 98.6% of the material having a particle size of less than 0.5 mm (Figure 29 in Chapter 6.1.5). The mini-granulated MPR was made by drying, crushing and sieving a 1:1 mixture of water and ground MPR. The two standard PR materials supplied by the International Fertilizer Development Centre (IFDC) were the ungrounded beneficiated and highly reactive North Carolina phosphate rock (NCPR) (IFDC stock no. R232,48), and the ground beneficiated medium reactive Central Florida phosphate rock (CFPR) (IFDC stock no. R231,77). Crystallographic characteristics and elemental composition of the phosphate sources is given in Table 7, Table 10 and Table 49 (the corresponding legends are: MPR and GMPR = S8, NCPR = R1, CFPR = R2).

The water-soluble triple superphosphate, obtained by the Tanzanian Fertilizer Company, was crushed and sieved to obtain the same particle size range as the mini-granulated MPR.

Solubility of the phosphate rock sources in neutral ammonium citrate at pH 7 (second extraction) was determined according to the method of AOAC {10} except that only 0.5 g P material was used and that extraction was done twice at 70 °C using a reciprocating shaker mounted on a water bath. The PR samples were ground to less than 250 µm before extraction.

Total P (P_{total}) was determined by digestion with conc. HNO_3 and conc. HCl {10} using the molybdenum blue method. All analyses were carried out in duplo.

Dissolution procedure

Five samples of each soil material were thoroughly mixed with one of each of the five different P sources at a rate of 300 mg total P kg^{-1} soil. The amount of soil used was 300 g per pot except for the two volcanic soils (Mpangala and Sasanda) where only 200 g per pot was used. The soil-P mixtures were stored in 350 cm^3 plastic containers, brought to field capacity with distilled water, capped loosely and left at 25-30 °C for 120 days. Distilled water was added whenever the moisture loss exceeded 5%. The moisture content at field capacity was prior to initiation estimated by equilibrating a loosely packed sample of 100 cm^3 of each soil material for 48 hours on a sand bath held at a tension of –100 cm water column (pF 2). One blank sample with no P addition was included for all soils. At the end of the dissolution period the soils were transferred to a centrifuge tube specifically designed for withdrawal of soil solution and centrifuged for 30 min. The soil solution was analysed for pH, total P, Ca, Mg, K and Na using the molybdenum blue method for P, AAS for Ca and Mg and FES for K and Na.

After centrifugation the soils were air dried, crushed and thoroughly mixed before duplicate sub-samples of each treatment were analysed for the following chemical properties: pH in water (pH_w) and 1 M KCl (pH_K) at a soil:solution ratio of 1:2.5. Cation exchange capacity at pH 7 (CEC_7) and exchangeable base cations (Ca, Mg, K and Na) by NH_4-acetete method with determination of CEC by Kjeldahl distillation and measurement of Ca and Mg using AAS, and FES for K and Na {29, 257}. Exchangeable aluminium (Al) and total extractable acidity (Al+H) by extraction of 10 g of soil with 25 cm^3 1 M KCl followed by filtration and measurement of exchangeable aluminium by AAS and total extractable acidity by titration with NaOH {257}. Sodium bicarbonate extractable P (P_{Olsen}) as described in Chapter 6.1.3 and available P (P_i) using the following iron-oxide impregnated filter paper (Fe-O strip) method: 1 g of soil and one Fe-O strip (20 cm^2) were extracted with 50 cm^3 0.02 M KCl for 16 hours in a reciprocating shaker (60 c.p.m.) followed by gently rinsing with water in order to remove adhered soil particles. The filter paper strips were dried before extraction with 50 cm^3 0.1 M H_2SO_4 for 1 hour in a reciprocating shaker (100 c.p.m.). Preparation of Fe-O strips was done according Myers et al. {178}.

P fractionation including the following steps carried out on the same soil sample:

1) NaCl extractable P (P_{NaCl}) and exchangeable Ca (Ca_{ex}) by end over end shaking (40 r.p.m.) of 2 g of soil with 50 cm^3 1 M NaCl solution buffered to pH 7.8 with 0.1 M H_3BO_4/0.016 M NaOH for 30 min. followed by centrifugation (4000 r.p.m., 15 min.), and measurement of P and Ca in the supernatant using the molybdenum blue method and AAS respectively {197}. The primary objective of this step was removal of exchangeable Ca, which could cause precipitation of calcium phosphate, or adsorption of phosphate by precipitated $CaCO_3$ during the subsequent extraction with NaOH (Chapter 2.3.1). Buffering of the extract was done in order to prevent additional dissolution of phosphate rock during extraction in the case where the soils have appreciable amounts of exchangeable acidity (Chapter 2.3.1). As the extracting agent can be considered relatively mild this fraction is thought to represent very weakly adsorbed and hence immediately plant available P.

2) NaOH extractable P (P_{NaOH}) by end over end shaking (40 r.p.m.) with 50 cm^3 0.5 M NaOH for 16 hours, followed by centrifugation (4000 r.p.m., 15 min.), and measurement of P in the supernatant {135}. This fraction is thought to represent adsorbed and exchangeable P.

3) Dithionite-citrate-bicarbonate extractable P (P_{DCB}) by extraction with 5 cm^3 1 M $NaHCO_3$, 40 cm^3 0.3 M $Na_3C_6H_5O_7$ (Na-citrate) and 1 g $Na_2S_2O_4$ (Na-dithionite) at 70 °C with frequent stirring for 15 min., followed by centrifugation (4000 r.p.m. 15 min.), and measurement of P in the supernatant {148}. This fraction is thought to represent adsorbed but non-exchangeable P (occluded P).

4) Sulphuric acid extractable P (P_{resid}) by extraction with 50 cm^3 6 M H_2SO_4 at 70 °C with frequent stirring for 15 min. followed by centrifugation (4000 r.p.m. 15 min.), and measurement of P in the supernatant {158}. This fraction is thought to represent residual soil P and includes in case of P treated samples the non-dissolved residual P from the P source.

Between each of the fractionation steps the soil was washed with 50 cm^3 water, followed by centrifugation and discarding of the supernatant. All P measurements were performed using the molybdenum blue method adopted to flow injection analysis {96}. $NaHCO_3$ extracts were acidified and shaken in order to remove CO_2 before P measurement. Dissolution of the P sources during each P fractionation step was estimated by extraction of 0.1 g of each P source mixed with 1 g of non-treated surface soil from Igabiro using the same method as described above. All analyses were carried out in duplo.

The fraction of the phosphate sources, which had dissolved in the soils during the 120 days, was estimated by four approximations, which under optimal conditions should lead to the same estimates of PR dissolution:

1) Adsorbed P to P added (ΔP_{add}-method):

$$\mathrm{Diss}_{\Delta P_{add}} = \frac{(P_{NaCl} + P_{NaOH} + P_{DCB})_{(+P)} - (P_{NaCl} + P_{NaOH} + P_{DCB})_{(-P)}}{P_{added}} \qquad (13)$$

where P_{NaCl}, P_{NaOH} and P_{DCB} are the amounts of P extracted by each of the first three steps in the P-fractionation scheme, P_{added} is the total amount of P added, and (+P) and (-P) indicate the treatments with and without P addition respectively. This approximation assumes that: a) the P released upon dissolution of the P-containing minerals forms complexes with soil constituents such as organic matter or iron and aluminium oxides from which the P is completely extracted by the three first steps in the fractionation scheme (NaCl, NaOH and DCB), and b) negligible amounts of non-dissolved PR dissolves during each of the first three extraction steps.

2) Adsorbed P to P sum (ΔP_{sum}-method):

$$\mathrm{Diss}_{\Delta P_{sum}} = \frac{(P_{NaCl} + P_{NaOH} + P_{DCB})_{(+P)} - (P_{NaCl} + P_{NaOH} + P_{DCB})_{(-P)}}{(P_{NaCl} + P_{NaOH} + P_{DCB} + P_{resid})_{(+P)} - (P_{NaCl} + P_{NaOH} + P_{DCB} + P_{resid})_{(-P)}} \qquad (14)$$

or

$$\mathrm{Diss}_{\Delta P_{sum}} = \left(1 - \frac{P_{resid(+P)} - P_{resid(-P)}}{P_{sum(+P)} - P_{sum(-P)}}\right) \qquad (15)$$

where P_{NaCl}, P_{NaOH}, P_{DCB} and P_{resid} are the amounts of P extracted by each of the four steps in the P-fractionation scheme, and where (+P) and (-P) refer to treatments with or without P addition respectively. The assumptions are: a) the P released upon dissolution of the P-containing minerals forms complexes with soil constituents such as organic matter or iron and aluminium oxides from which the P is completely extracted by the three first steps in the fractionation scheme (NaCl, NaOH and DCB), b) total inorganic P of the soils in both P treated and non-treated soils is the sum of the four fractionation steps, and c) negligible amounts of non-dissolved PR dissolves during each of the first three extraction steps.

3) Residual P to P added (ΔP_{resid}-method):

$$\mathrm{Diss}_{\Delta P_{resid}} = 1 - \frac{P_{resid(+P)} - P_{resid(-P)}}{P_{added}} \tag{16}$$

where P_{resid} is the amount of P extracted by the last step in the P fractionation scheme, P_{added} is the total amount of P in the P material added, and (+P) and (-P) indicate the treatments with and without P addition respectively. This approximation assumes: a) that the forth step extracts all native inorganic P as well as all remaining non-dissolved PR and b) that negligible amounts of non-dissolved PR have dissolved during the previous extraction steps.

4) Exchangeable Ca (ΔCa_{ex}-method):

$$\mathrm{Diss}_{\Delta Caex} = \frac{Ca_{ex(+P)} - Ca_{ex(-P)}}{Ca_{added}} \tag{17}$$

where Ca_{ex} is the amount of extractable Ca during the first step (buffered NaCl). Ca_{added} is the total amount of Ca in the P material added including other accessory Ca-containing minerals, and (+P) and (-P) indicate the treatments with and without P addition respectively. This approximation assumes: a) that there is no preferential dissolution between the Ca-P minerals and other Ca-containing minerals such as calcite or dolomite in the P material added, b) that the dissolution is congruent for all Ca-containing minerals, c) that the Ca released upon dissolution accumulates in the soil as exchangeable Ca and is extracted by the NH_4-acetate, and d) that negligible amounts of non-dissolved PR dissolves during extraction.

Statistical analysis

The effect of PR dissolution on soil properties was evaluated using the following model {128}:

$$Y_{ij} = \mu + \alpha_i + u_j + v_{ij} + \varepsilon_{ij} \tag{18}$$

where

Y_{ij} = soil property (pH, extr. P etc. as duplicate value) for the i^{th} treatment and j^{th} soiltype 1..132
α_i = effect of the i^{th} treatment (fixed) 1..6
u_j = random effect of the j^{th} soiltype (j=1..11) $N(0, \sigma_u^2)$
v_{ij} = random effect of the ij^{th} soiltype*treatment interaction $N(0, \sigma_v^2)$
ε_{ij} = random residual error $N(0, \sigma^2)$

If either logarithm or square root transformation of data yielded a better distribution of residuals the analysis was done on the transformed data.

The effect of soil properties on PR dissolution was evaluated using a similar model but with addition of continuous soil parameters as covariates. A model with one covariate is presented below:

$$Y_{ij} = \mu + \alpha_i + \beta x_j + u_j + v_{ij} + \varepsilon_{ij} \tag{19}$$

where

Y_{ij} = PR dissolution ($Diss_{\Delta Padd}$) for the i^{th} PR treatment and j^{th} soiltype 1..55
α_i = effect of the i^{th} PR treatment (fixed) 1..5
βx_j = effect of the j^{th} soil property 1..11
u_j = random effect of the j^{th} soiltype (j=1..11) $N(0, \sigma_u^2)$
v_{ij} = random effect of the ij^{th} soiltype*treatment interaction $N(0, \sigma_v^2)$
ε_{ij} = random residual error $N(0, \sigma^2)$

The soil parameters tested as covariates were soil pH (pH_{KCl} or pH_w), P adsorption parameters (Langmuir P_{max} or K), soil P (P_{NaCl} or P_i), H^+ buffer capacity (H_b), exchangeable acidity (Al+H) or Al saturation (Al_{sat}), and Ca saturation (Ca_{sat}).

7.1.2 Field dissolution study

Soils

One block, randomly selected at each experimental field, consisting of all the twelve treatments tested, were sampled before and after treatments were applied to the experimental plots. A total of three samplings were carried out, i.e. one before initiation of the experiment and one after each of the first two growing seasons. At each sampling a composite soil sample was collected from each 25 m^2 plot by systematic sampling of nine 200 cm^3 subsamples from the 0-10 cm layer. The composite samples were air dried, crushed to less than 2 mm and mixed before further analysis.

Samples from treatment no. 2 (P control), 6 (TSP120), 9 (GPR120) and 12 (MPR120) (see Table 22) were analysed for the following properties: pH in 1 M KCl (pH_K) at a soil:solution ratio of 1:2.5. Total exchangeable acidity (Al+H) by titration, and exchangeable aluminium (Al_{ex}) by measurement of Al using AAS {257}. P fractionation using the same procedure as described for the laboratory dissolution experiment (Chapter 7.1.1) with the following modifications:

a) The DCB step was omitted as the results from the laboratory experiment indicated only a small increase in P_{DCB} after P addition and dissolution.
b) Washings between each step were done using 0.1 M NaCl instead of water in order to facilitate sedimentation and reduce loss of solids.
c) Replacement of the procedure for residual P extraction by 17 hours of shaking with 50 ml 0.5 M H_2SO_4 followed by centrifugation (5 min., 5000 r.p.m.).
d) In addition to measurement of inorganic P in the strongly coloured NaOH extract (P_{NaOH}), total P ($P_{NaOH(total)}$) was determined after removal of the dissolved organic matter by oxidation using the following procedure: An aliquot of 0.25 cm^3 of the NaOH extract were added 0.5 cm^3 0.5 M H_2SO_4 and 0.25 cm^3 concentrated H_2O_2 and heated to 70 °C on sand bath until dryness, followed by dissolution of the residue in 10 cm^3 0.02 M H_2SO_4 and measurement of P. Quadruplicate blank samples were digested using the same procedure and their mean P content was subtracted from all non-blank samples. The difference between $P_{NaOH(total)}$ and P_{NaOH} is considered to represent the NaOH extractable organic P ($P_{org(NaOH)}$).

Soil samples from the first sampling were also analysed for total organic carbon (C) {55}, and P adsorption index (P_{ads}) by 16 hour equilibration with 120 mg P dm^{-3} at a soil:solution ratio of 1:25 followed by calculation of P adsorption (mg P kg^{-1}) on the basis of the difference between initial P concentration and equilibrium P concentration. All phosphorus measurements were done using the molybdenum blue method adopted to flow injection analysis {96}. All analyses were carried out in duplo.

The degree of dissolution of the P sources was estimated as described above according to Eq. (14) ($Diss_{\Delta Psum}$).

Phosphate sources

For the field study the phosphate sources were those described in Chapter 6.1.5, i.e. MPR in mini-granulated and non-granulated forms and a TSP.

Statistical analysis

The effect of PR dissolution on soil properties was evaluated using the following split-plot model, which regards site (soiltype) as blocks, treatments as whole-plot factor and sampling time as sub-plot factor {128}:

$$Y_{ijk} = \mu + r_k + \alpha_i + w_{ik} + u_{jk} + \beta_j + (\alpha\beta)_{ij} + \varepsilon_{ijk} \qquad (20)$$

where

Y_{ijk} = soil property (pH, extr. P etc.) for the i^{th} treatment, j^{th} sampling time and k^{th} site 1..120
r_k = random effect of the k^{th} site (block) (k=1..10) $N(0, \sigma_r^2)$
α_i = effect of the i^{th} treatment (fixed) i = 1..4
β_j = effect of the j^{th} sampling time (fixed) j = 1..3
$\alpha\beta_{ij}$ = effect of the ij^{th} treatment*sampling time interaction (fixed)
w_{ik} = random whole-plot error effect of the ik^{th} site*treatment interaction $N(0, \sigma_w^2)$
u_{jk} = random error effect of the jk^{th} site*sampling time interaction $N(0, \sigma_u^2)$
ε_{ijk} = random split-plot error effect (residual error) $N(0, \sigma^2)$

If either logarithm or square root transformation of data yielded a better distribution of residuals, the analysis was done on the transformed data. The effect of soil pH, exchangeable soil acidity, P adsorption, exchangeable Ca, easily extractable P and soil organic matter on PR dissolution was evaluated using the same model with inclusion of either pH_K, H+Al, P_{ads}, Ca_{ex}, P_{NaCl} or C as covariate. The covariate soil properties were those estimated for each of the soil samples collected except P_{ads} and C, which were only determined on the soil samples collected before initiation of the experiment, i.e. sampling no. 0.

7.2 Results

Laboratory dissolution study

Table 47 and Table 48 list the main soil characteristics of the selected surface soil samples (refer to Chapter 6.2.1 for description of the basic characteristics). The additional Ihanda soil is provisionally classified as a Thermic, very fine, kaolinitic, Rhodic Kandiustult and is in comparison with the other non-volcanic surface soils characterised by relatively high content of organic matter, high CEC_7, high levels of exchangeable acidity, high P adsorption capacity and high contents of oxalate extractable Fe, Al, Si and P. Calcium saturation percentage among the sites varies from 29 to 70% for Mlingano and Msimba respectively, indicating a relatively large variation in the soils ability to act as sinks for the Ca^{2+} released during dissolution. However, BS_e is generally high and the amount of exchangeable acidity is generally lower than required for complete PR dissolution. Addition of 300 mg PR-P kg^{-1} soil requires approximately 2.3 cmol(+) H^+ kg^{-1} soil for complete dissolution of the PR alone. As dolomite was identified as accessory mineral in the MPR (Chapter 4.2) a slightly larger proton requirement would be expected for the MPR and GPR treatments. Hence, from the amounts of exchangeable acidity it seems that proton supply will be limiting for complete dissolution in all soils. As soil pH increases during dissolution additional cation exchange capacity and proton supply may be provided from the variable charge components, which is also indicated by CEC_7 and H^+ buffer capacity (H_b).

Table 47. Soil chemical characteristics.

Origin	pH_w	pH_{KCl}	Exchange capacity and exchangeable cations										
			Ca	Mg	K	Na	H+Al	CEC_e	CEC_7	Al_{sat}	Ca_{sat}	BS_e	BS_7
			cmol(+) kg^{-1}							%	%	%	%
Igabiro	5.55	4.21	1.78	1.10	0.04	0.04	0.37	3.32	6.83	10	54	89	43
Ukiriguru	5.34	4.12	0.86	0.23	0.14	0.00	0.31	1.53	2.46	19	56	80	50
Mlingano	5.32	4.10	0.68	0.87	0.20	0.03	0.61	2.38	7.27	25	29	74	24
Magadu	4.86	3.76	2.91	1.70	0.57	0.07	1.41	6.65	11.63	21	44	79	45
Msimba	6.47	5.23	9.69	2.67	1.30	0.08	0.02	13.75	16.27	0	70	100	84
Suluti	6.22	4.78	1.47	0.59	0.21	0.04	0.03	2.33	4.67	1	63	99	49
Lubonde	5.66	4.40	3.84	0.92	0.57	0.02	0.12	5.46	10.73	2	70	98	50
Mpangala	6.03	4.81	5.85	1.62	0.96	0.04	0.05	8.51	12.50	0	69	99	68
Sasanda	5.53	4.57	1.21	0.60	0.47	0.03	0.21	2.51	10.13	6	48	92	23
Nkundi	5.91	4.72	2.13	1.47	0.22	0.01	0.04	3.86	6.38	1	55	99	60
Ihanda	6.20	4.76	2.95	2.40	1.39	0.31	1.60	8.65	13.59	n.d.	34	82	52

n.d. = not determined.

Table 48. Clay content, acid buffer capacity, organic carbon, P adsorption characteristics and extractable elements.

	Clay	H_b	C	Total P		Extr. P			P_{max}	K
				P_{inorg}	P_{org}	P_{olsen}	P_i	P_{NaCl}		
	%	cmol OH$^-$ (kg^{-1} pH^{-1})	mg C g^{-1}	mg P kg^{-1}						dm^3 mg^{-1} P
Igabiro	26	1.35	15.4	152	181	4.5	0.7	1.2	514	2.332
Ukiriguru	9	0.73	3.3	139	72	18.9	5.3	9.5	203	1.004
Mlingano	54	1.02	11.7	88	94	1.6	1.4	0.4	469	3.083
Magadu	55	1.62	12.0	256	164	31.4	2.5	3.3	532	1.865
Msimba	27	2.90	22.8	208	230	10.3	3.8	3.6	200	1.991
Suluti	24	2.18	9.8	259	213	12.3	4.2	6.2	200	1.727
Lubonde	43	1.71	25.8	388	362	9.2	1.0	1.7	986	2.486
Mpangala	30	2.76	28.5	237	409	3.9	1.3	0.8	1020	4.042
Sasanda	35	2.47	34.5	188	238	0.9	1.7	0.4	1863	18.185
Nkundi	18	2.64	20.2	102	117	4.2	1.4	1.4	185	1.799
Ihanda	52	2.55	27.4	348	250	n.d.	2.2	0.9	987	2.303

n.d. = not determined.

The characteristics of the P sources are presented in Table 49. As discussed in Chapter 4.3, *a*-cell dimension of the MPR do not conform to the high solubility in neutral ammonium citrate (NAC), which indicate that the MPR is slightly less reactive than ground NCPR and slightly more reactive than CFPR. Based on *a*-cell dimensions and NAC, NCPR and CFPR represent highly and medium reactive PRs respectively. Due to the fine grinding (<250 µm) of the unground NCPR before extraction, the NAC solubility was determined to be slightly higher than indicated by IFDC (Table 7).

The recovery of P after P fractionation of a fresh mixture of dry soil and each of the P sources is presented in Table 50. On average less than 5 % of the P originating from the PR sources is extracted during the three first steps confirming the selectivity of the extracting agents in the P fractionation scheme. For TSP, more than 94% of the P is released during the first and second step confirming the high solubility of TSP in aqueous solutions. However, total P recovery is generally lower than expected. This may partly be attributed to small losses of solids during each of the washings between each fractionation step and partly to the inability of the final acid step to sufficiently extract all residual PR. This seems to be most pronounced for NCPR as this material was unground leading to a large time dependency for dissolution of residual PR at short extraction times. Apparently 15 min. extraction with 6 M H_2SO_4 while heating was not enough to dissolve all residual PR. The lower P recovery than expected is also seen in the dissolution experiment, although the difference is smaller (Table 51). On average 78% of the P was recovered during the P fractionation in the laboratory dissolution experiment.

Table 49. Mineralogy, and total content of P, Ca and CO_2 in the phosphate sources used.

Material	*a*-cell dimension[1]	P		Ca^2	Total $CO_2{}^2$
		P_{total}	P_{NAC}	Ca_{total}	
	(Å)	%	%	%	%
Minjingu PR	9.362	13.1	2.7	31.0	3.9
North Carolina PR	9.328	12.9	3.5	35.2	6.0
Central Florida PR	9.356	14.0	2.1	33.8	3.5
TSP	n.d.	20.4	n.d.	n.d.	n.d.

n.d. = not determined.

[1]From Table 10.

[2]From Table 7.

Table 50. Absolute and relative solubility of the different P sources during P fractionation.

Material	Sum (Step 1-4)	P_{NaCl} (Step 1)	P_{NaOH} (Step 2)	P_{DCB} (Step 3)	P_{resid} (Step 4)
	% P (absolute)		% (relative)		
Minjingu PR	8.6	0.1	-1.9	2.5	99.3
North Carolina PR	2.6	0.0	-4.8	4.3	100.5
Central Florida PR	9.7	0.0	2.7	1.8	95.4
TSP	18.2	82.2	12.3	2.8	2.7

Table 51 presents the results of the statistical analysis using model (18). The analysis was carried out on two data sets, i.e. with or without inclusion of the TSP treatment. The first analysis evaluates the effect of the P sources (TSP and PRs) on the various P fractions and estimates of P source dissolution whereas the latter evaluates the effect of PR addition only. In general, inclusion of the TSP treatment increased the coefficient of variation significantly and reduced the ability to identify any significant differences and as one of the objectives of the analysis was to evaluate the relative reactivity of the various PRs it was decided to leave TSP out in the latter analysis.

For all P fractions and estimates of dissolution, the treatment effect (PR source) was highly significant ($p<1\%$). PR addition resulted in a significant ($p<5\%$) increase of easily available P (P_{NaCl}), adsorbed P (P_{NaOH}), and residual P (P_{Resid}) compared to the control treatment. For the MPR and GPR treatments a small but significant increase in the occluded P fraction (P_{DCB}) were also observed. The sum of P extracted by P fractionation was significantly higher than the untreated control irrespective of P source but apparently the P_{sum} was significantly lower for NCPR than for the other P sources. This may in agreement with the observations on total P recovery be attributed to the larger particle size of NCPR and hence lower recovery of residual PR-P in the final acid extraction. TSP resulted in a significantly larger increase in P_{NaCl} and P_{NaOH} compared to any of the PRs.

Although the four estimates of PR dissolution were highly correlated (Table 52) their absolute values were relatively different. Best agreement between the estimates were found between $Diss_{\Delta Padd}$ and $Diss_{\Delta Caex}$ indicating that on average 35-39%, 22-28%, 33-38% and 26-29% of the MPR, GPR, NCPR and CFPR respectively dissolved during the 120 day period. The general trend in the relative PR dissolution was similar among the sites (Figure 34). However, large differences in the absolute values of PR dissolution among the sites were observed. A fact, which was also confirmed by a highly significant random effect of soiltype on the dependent variables according to model 18 (data not shown).

Table 51. Average values for extractable P in the various P-fractions and the estimated dissolution ($Diss_{\Delta Padd}$, $Diss_{\Delta Psum}$, $Diss_{\Delta Presid}$, $Diss_{\Delta Caex}$) after 120 days.

Treatment	P_{NaCl}	P_{NaOH}	P_{DCB}	P_{Resid}	P_{Sum}	$Diss_{\Delta Padd}$	$Diss_{\Delta Psum}$	$Diss_{\Delta Presid}$	$Diss_{\Delta Caex}$
			mg P kg^{-1}			%	%	%	%
Control	2.7^{a}	108^{a}	62.6^{a}	43^{a}	216^{a}	-	-	-	-
MPR	9.5^{bc}	195^{b}	73.1^{b}	164^{b}	442^{b}	35^{a}	47^{a}	60^{a}	39^{a}
GPR	7.8^{b}	165^{c}	68.1^{bc}	215^{c}	455^{b}	22^{b}	28^{b}	43^{b}	28^{b}
NCPR	10.4^{c}	195^{b}	67.8^{ab}	136^{d}	409^{c}	33^{a}	51^{a}	69^{c}	38^{a}
CFPR	7.7^{b}	176^{c}	67.1^{ac}	210^{c}	461^{b}	26^{c}	32^{b}	44^{b}	29^{b}
TSP	32.4	317	73.0	56	478	83	95	96	n.d.
p>F (PR)	***	***	**	**	***	***	***	***	***
$LSD_{0.05}$ (PR)	2.0	14	5.4	22	21	3	5	8	4
$LSD_{0.05}$ (All)	8.9	18	5.2	21	21	6	7	7	n.d.

Treatments (control and PRs) with same letter down through the columns are not significantly different at 5% level.
p>F indicates the probability of an F value greater than the one calculated from the data (NS = non significant, *<5%, **<1%, ***<0.1%).
$LSD_{0.05}$ is the least significant difference at 5% level, (PR) = control and PR treatments, (All) = all treatments.
n.d. = not determined.

Table 52. Correlation matrix (r) for the estimates of PR dissolution.

	$Diss_{\Delta Padd}$	$Diss_{\Delta Psum}$	$Diss_{\Delta Presid}$	$Diss_{\Delta Caex}$
$Diss_{\Delta Padd}$	1	0.95	0.88	0.98
$Diss_{\Delta Psum}$	-	1	0.98	0.97
$Diss_{\Delta Presid}$	-	-	1	0.93
$Diss_{\Delta Caex}$	-	-	-	1

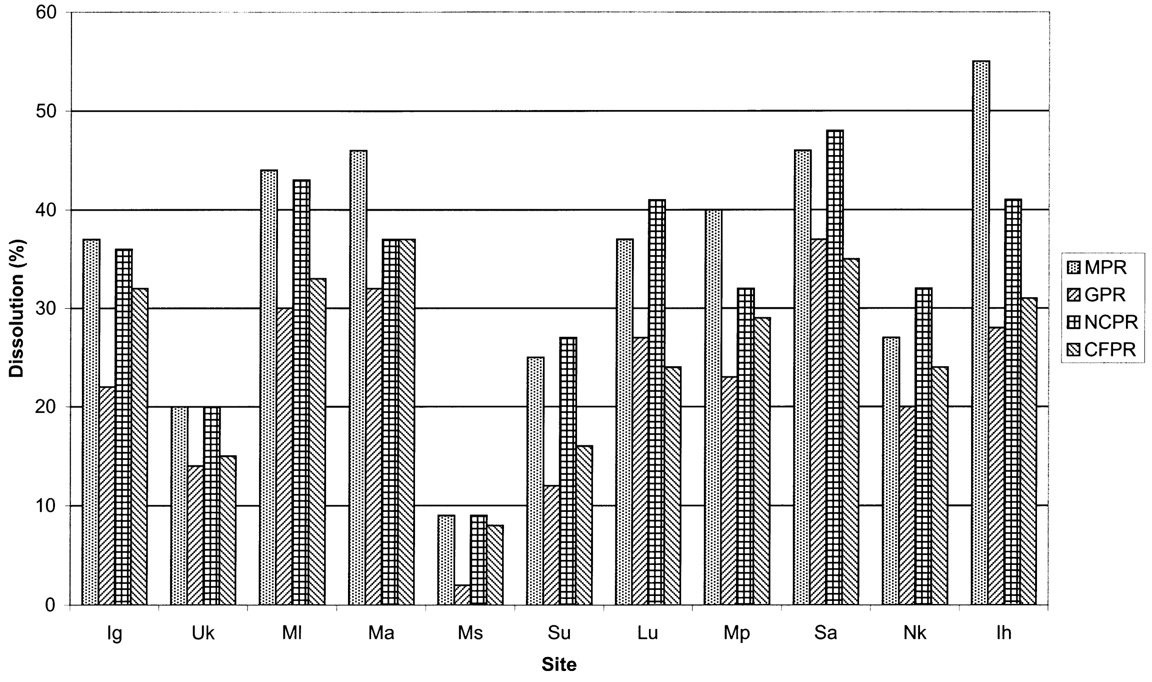


Figure 34. Dissolution ($Diss_{\Delta Padd}$) (%) of the various PR materials among the 11 sites.

Table 53 presents the effect of P addition on soil solution chemistry. Due to the generally high variation in the data only few significant treatment effects were observed. For the MPR and NCPR treatments, solution P concentration were significantly increased compared with the control but when the TSP treatment was included in the analysis, treatment effects were not significant due to the increased residual error. Soil solution K^{+} significantly decreased after PR application whereas Na^{+} showed a highly significant treatment effect with most P treatments significantly increasing the concentration over the control.

Table 53. Average values for soil solution composition after 120 days.

Treatment	pH	P	Ca	Mg	K	Na
		mg dm^{-3}				
Blank	4.88	0.02a	57	28	37^{a}	12^{a}
MPR	5.34	0.14b[1]	78	25	30^{b}	24^{b}
GPR	5.24	0.11a	64	24	30^{b}	21^{b}
NCPR	5.16	0.19b	85	25	29^{b}	20^{b}
CFPR	5.09	0.10a	69	24	29^{b}	15^{a}
TSP	4.96	2.11	110	32	35	18
p>F (PR)	NS	*	NS	NS	*	***
$LSD_{0.05}$ (PR)	-	0.10	-	-	5	4
$LSD_{0.05}$ (All)	-	-	31	-	5	4

[1] Lubonde (site no. 7) excluded in analysis due to obvious experimental error.
See explanation in Table 51.

Table 54 show the average values of soil chemical properties following dissolution. A highly significant increase in soil pH, exchangeable Ca, Mg, Na, CEC_e, CEC_7, calcium saturation (Ca_{sat}), and both bicarbonate extractable P (P_{olsen}) and Fe-O paper extractable P (P_i) was observed for all P treatments. Similarly exchangeable acidity and aluminium saturation (Al_{sat}) were significantly reduced by PR application.

Table 54. Average values for soil chemical properties after 120 days.

Treatment	pH_w	Exchange capacity and exchangeable cations							Al_{sat}	Ca_{sat}	P_i	P_{olsen}
		Ca	Mg	K	Na	H+Al	CEC_e	CEC_7				
		cmol(+) kg^{-1}							%		mg P kg^{-1}	
Blank	5.43^{a}	3.17^{a}	1.33^{a}	0.67	0.04^{a}	0.29^{a}	5.49^{a}	8.62^{a}	7.8^{a}	54^{a}	2.3^{a}	8.8^{a}
MPR	5.76^{b}	4.59^{b}	1.39^{b}	0.68	0.05^{b}	0.09^{b}	6.80^{b}	9.21^{b}	1.0^{bc}	69^{b}	8.1^{b}	26.5^{b}
GPR	5.75^{b}	4.19^{c}	1.41^{c}	0.68	0.05^{b}	0.11^{b}	6.44^{c}	9.01^{bc}	1.5^{b}	66^{b}	7.2^{b}	23.1^{c}
NCPR	5.83^{b}	4.74^{b}	1.36^{d}	0.67	0.05^{b}	0.09^{b}	6.90^{b}	9.09^{bc}	0.7^{c}	70^{b}	8.1^{b}	28.9^{b}
CFPR	5.77^{b}	4.22^{c}	1.35^{d}	0.67	0.05^{b}	0.11^{b}	6.40^{c}	8.94^{c}	1.4^{bc}	67^{b}	6.8^{b}	22.9^{c}
TSP	5.45	4.20	1.36	0.68	0.04	0.16	6.45	9.21	2.5	65	26.3	63.7
p>F (PR)	***	***	***	NS	**	***	***	***	***	***	***	***
$LSD_{0.05}$ (PR)	0.08	0.24	0.02	-	0.008	n.a.	0.24	0.21	n.a.	5	1.6	3.2
$LSD_{0.05}$ (All)	0.09	0.25	0.02	-	0.008	n.a.[1]	0.25	0.21	n.a.	4	8.3	10.4

n.a. = not available due to log transformation of data.
[1] Using all data indicate significant difference between PR treated samples, blank and TSP respectively).
See explanation in Table 51.

The effect of initial soil properties on the PR dissolution was evaluated by covariance analysis according to model (19) with $Diss_{\Delta Padd}$ as dependent variable. Before running the analysis, the PR materials were divided into three groups according to the findings in Table 51, i.e. MPR+NCPR, GPR and CFPR respectively. Only soil properties, which are likely to influence PR dissolution, were tested in the model, which ended up with the results presented in Table 55. The analysis indicated no confounding effects among the factors and assumptions on constant variance were fulfilled. There were no outliers or strongly influential observations in the dataset. As PR group entered the analysis as a class variable, estimation of PR dissolution based on values of P_{max} and pH_w, must be corrected for the particular PR group by either subtraction or addition of the estimates in Table 55. Hence, it is seen that dissolution of CFPR on average is 8.4% (absolute) less, whereas dissolution of GPR is 11.8% (absolute) lower than calculated from the regression equation. The PR group containing MPR and NCPR is considered the reference level and therefore no correction is needed for this group. The predicted versus determined dissolution using the model is presented in Figure 35.

Table 55. Effect of P_{max} and soil pH on PR dissolution ($Diss_{\Delta Padd}$ as dependent variable)

Parameter		Estimate	+/- (95%)	Probability
Intercept		99.3	51.9	-
	PR group			
	MPR + NCPR	0	-	-
	CFPR	-8.4	2.8	-
	GPR	-11.8	2.8	-
P_{max}		0.0123	0.008	0.007^{**}
pH_w		-13.4	9.4	0.011^{*}

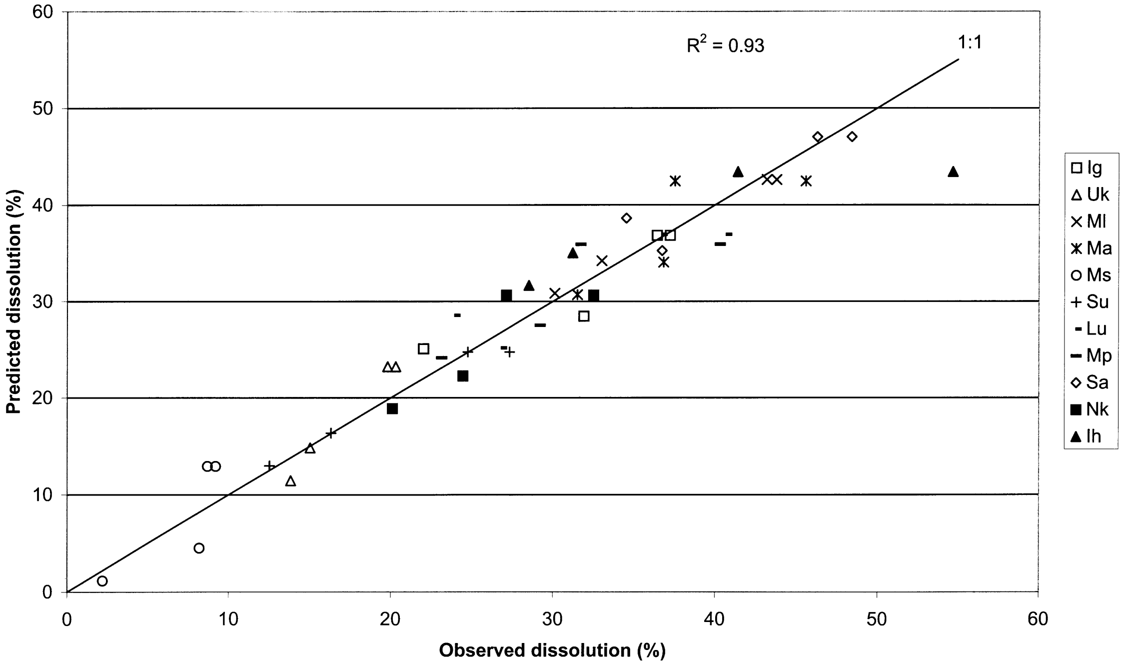


Figure 35. Predicted versus determined PR dissolution using the parameter estimates in Table 55.

The amount of available P (P_{NaCl}, P_i, or P_{olsen}) after PR dissolution was not found to be correlated with the amount of PR dissolved. Instead, it was found that 74% of the variation in bicarbonate extractable P (P_{olsen}) could be explained by the amount of PR dissolved (PR_{diss} = 300 mg PR-P $kg^{-1} \cdot Diss_{\Delta Padd}(\%)$), initial P level ($P_{olsen(init)}$) and P adsorption capacity (P_{max}) according to the following equation:

$$P_{olsen} = 0.15^{***} \cdot PR_{diss} + 1.06^{***} \cdot P_{olsen(init)} - 0.01^{***} \cdot P_{max} + 9.06^{**} \qquad (21)$$

Predicted versus determined P availability according to Eq. 21, and actual levels of P_{olsen} among the various sites are shown in Figure 36 and Figure 37 respectively.

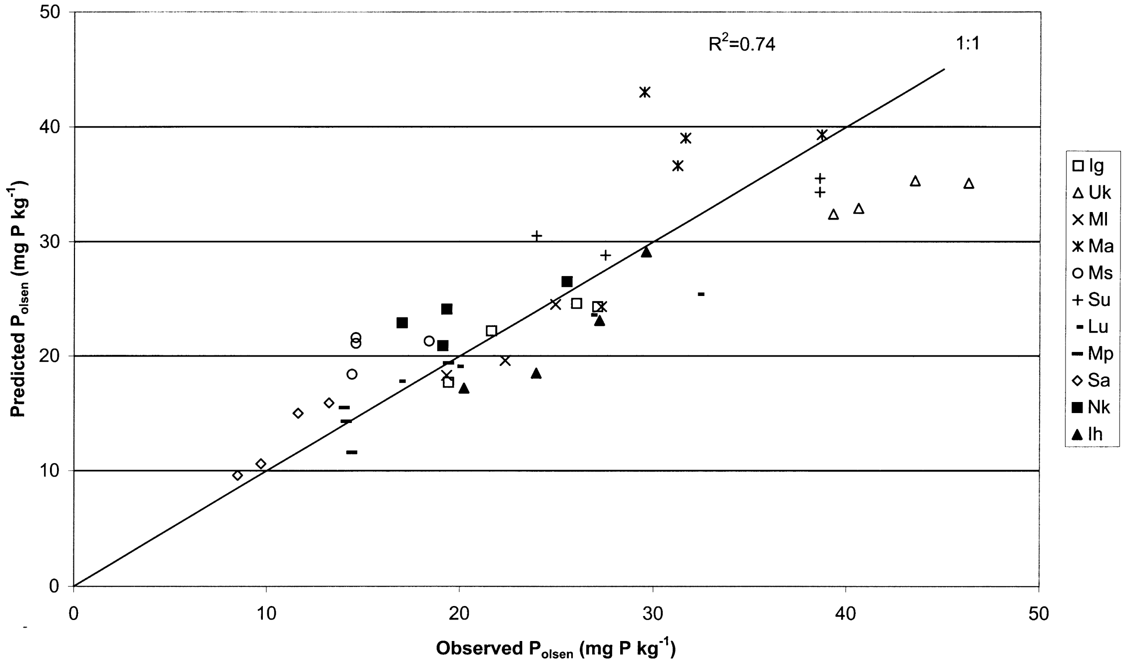


Figure 36. Predicted versus determined P availability (P_{olsen}) using the parameter estimates in Eq. 21.

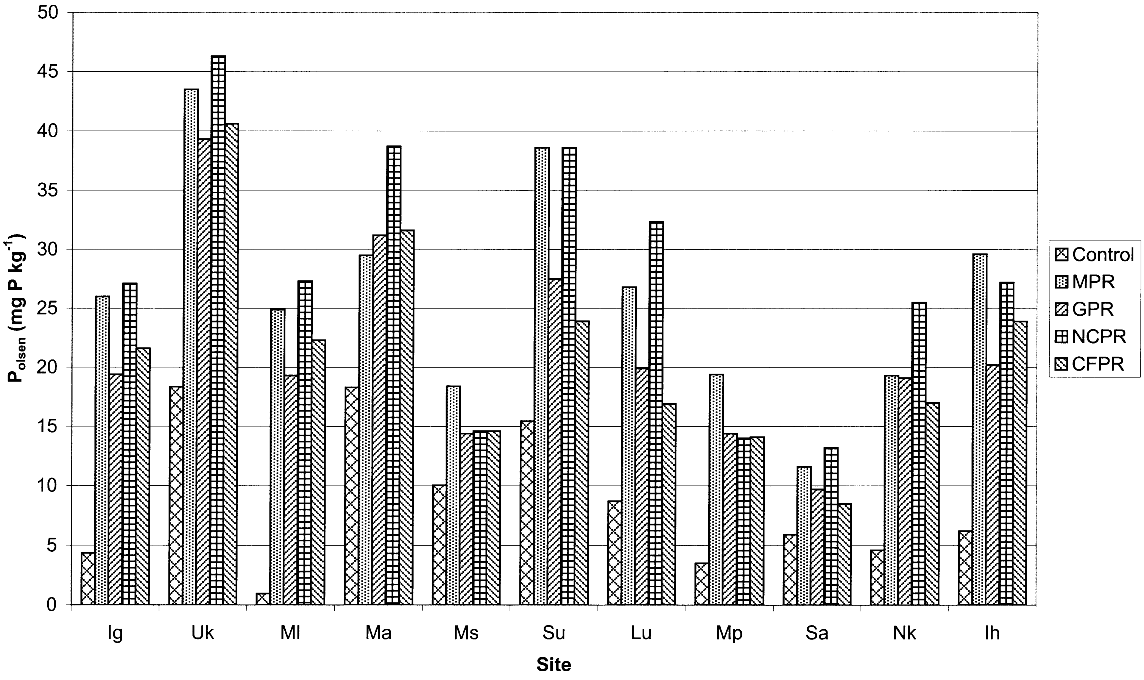


Figure 37. Availability of P (P_{olsen}) among the various sites according to treatment.

Field study

Table 56 show the result of the statistical analysis of the effect of sampling time and treatment on various soil parameters and the estimated P dissolution. For all except three analyses, the interaction term (sampling time*treatment) according to model (19) were highly significant ($p<0.1\%$) indicating that each combination of sampling time and treatment must be viewed separately. The estimation of the effect on P dissolution ($Diss_{\Delta Psum}$) were significant at 5% level only, whereas $P_{org(NaOH)}$ and P dissolution based on total P ($Diss_{\Delta Psum(total)}$) only showed significant treatment effects. The residual variation in the various tests was generally low and even small differences in the effect of sampling time and treatment were observable. The sites showed similar values across the different treatments at the initial sampling indicating relatively homogenous experimental fields. The significantly higher average soil pH of the control plot was apparently caused by a high soil pH of the control plot at Ukiriguru. Sites showing less than 20% increase in total P due to P application were excluded before running the statistical analysis with $\mathrm{Diss}_{\Delta\mathrm{Psum}}$ or $\mathrm{Diss}_{\Delta\mathrm{Psum(total)}}$ as dependent variables, as a small P increase made the estimation of PR dissolution highly uncertain. P increases less than 20% were attributed to the erroneous sampling between the ridges instead of the preferred sampling on the ridges in the treated plots leading to soil samples consisting mainly of raw unfertilised subsoil. Five out of the total of sixty observations were excluded in the analysis (the full data set is obtainable from the web, see Appendix 1.4).

The effect of soil properties on PR dissolution under field conditions was evaluated in a similar fashion as with the laboratory dissolution experiment. The results are seen in Table 57 and Figure 38.

7.3 Discussion

The laboratory dissolution study shows that PR reactivity has a primary influence on PR dissolution. The relative reactivity estimated by their dissolution during 120 days were: MPR=NCPR>CFPR>GPR. Hence, the results show both the effect of the mineralogical properties of the PR material, i.e. the degree of carbonate substitution, and the effect of physical properties, i.e. the particle size, on PR reactivity. Granulation of MPR reduces the PR reactivity from being a highly reactive PR to being a medium reactive PR in a way, which is comparable to the effect of PR mineralogy, i.e. from MPR to CFPR. As NCPR is normally ranked among the most reactive PRs found worldwide the previous suggestions that MPR is also highly reactive are now confirmed by the dissolution study. Hence, application of MPR is generally expected to have a comparable effect on PR dissolution, extractable P and agronomic effectiveness as the highly reactive NCPR. On the other hand, mini-granulation of the MPR material reduces the reactivity in a way that makes it comparable with phosphate rocks of medium reactivity such as CFPR.

The easily available P content (P_{NaCl}) and adsorbed P (P_{NaOH}) of the soil will generally increase significantly by addition MPR or GPR although the effect is significantly lower than the effect of TSP. Application of either TSP or PR generally had little effect on the amount of occluded P. Occlusion of added P may be regarded as a long term process under conditions where a significant part of the soil iron oxides periodically dissolve and reprecipitate due to redox processes caused by conditions such as heavy rainfall and poor soil drainage. This way, adsorbed P may slowly become occluded as continued build up of iron oxides eventually cover up previously adsorbed P. Alternatively, P may become occluded due to slow reactions involving diffusion of P into structurally porous iron oxides {213}. The results of the laboratory dissolution study do not indicate such processes, which is primarily attributed to the short time of observation and to the fact that the moisture content never exceeded the field capacity. However, under field conditions such processes exist as also indicated by the fact that on average approximately 30% of total inorganic P is present as occluded P (P_{DCB}).

Table 56. Least squares means for soil chemical properties before fertilizer application and after the 1st and 2nd growing season.

Sampling^1	Dependent variable^2	Treatment				
		Control	TSP	GPR	MPR	$LSD_{horisontal}$
0	pH_{KCl}	4.80	4.64	4.65	4.68	
1		4.54	4.50	4.53	4.64	0.17
2		4.39	4.31	4.55	4.59	
$p<0.001$	$LSD_{vertical}$		0.13			
0	Ca_{ex}	2.44	2.34	2.17	2.02	
1	(cmol(+) kg^{-1})	2.18	2.35	2.12	2.18	0.30
2		1.98	2.29	2.36	2.43	
$p<0.001$	$LSD_{vertical}$		0.18			
0	Al+H	0.17	0.17	0.22	0.14	
1	(cmol(+) kg^{-1})	0.28	0.22	0.27	0.15	0.13
2		0.37	0.28	0.23	0.16	
$p<0.001$	$LSD_{vertical}$		0.09			
0	Al	0.12	0.13	0.17	0.08	
1	(cmol(+) kg^{-1})	0.24	0.17	0.21	0.10	0.13
2		0.32	0.22	0.18	0.11	
$p<0.001$	$LSD_{vertical}$		0.09			
0	P_{NaCl}	2.7	2.3	2.7	2.7	
1	(mg P kg^{-1})	2.5	7.8	3.2	3.9	2.5
2		2.6	16.7	5.2	6.2	
$p<0.001$	$LSD_{vertical}$		2.2			
0	P_{NaOH}	104	101	118	118	
1	(mg P kg^{-1})	106	184	133	151	23
2		108	251	166	188	
$p<0.001$	$LSD_{vertical}$		15			
0	$P_{NaOH(total)}$	205	210	232	238	
1	(mg P kg^{-1})	211	296	249	271	31
2		213	371	285	311	
$p<0.001$	$LSD_{vertical}$		18			
0	$P_{org(NaOH)}$					
1	(mg P kg^{-1})	104	114	116	121	11
2						
$p=0.018$	$LSD_{vertical}$		NS			
0	P_{resid}	35	34	35	37	
1	(mg P kg^{-1})	34	42	99	91	26
2		34	51	182	202	
$p<0.001$	$LSD_{vertical}$		24			
0	P_{sum}	142	137	155	158	
1	(mg P kg^{-1})	142	233	236	245	35
2		144	318	353	396	
$p<0.001$	$LSD_{vertical}$		30			
0	$P_{sum(total)}{}^3$	243	246	270	278	
1	(mg P kg^{-1})	247	345	351	366	40
2		250	439	472	519	
$p<0.001$	$LSD_{vertical}$		30			
0	$Diss_{\Delta Psum}$	-	-	-	-	
1	(%)	-	92	24	41	9
2		-	91	27	33	
$p=0.026$	$LSD_{vertical}$			6		
0	$Diss_{\Delta Psum(total)}{}^3$	-	-	-	-	
1	(%)	-	92	27	37	9
2		-				
$p<0.001$	$LSD_{vertical}$	-		NS		

^{1}Sampling no.: 0 = before application, 1 = after 1st season, 2 = after 2nd season.

The "p" value is the probability of an F value greater than the one calculated from the data for the (sampling time*treatment) interaction effect. For the dependent variables $P_{org(NaOH)}$ and $Diss_{\Delta Psum(total)}$, "p" values are for the treatment effect only.

$^2LSD_{vertical}$ and $LSD_{horisontal}$ = Least significant difference when comparing means within the same column or row respectively.

^{3}Based on total P using $P_{NaOH(total)}$.

NS = non significant.

Table 57. Effect of soil pH and P adsorption index on PR dissolution ($Diss_{\Delta Psum}$ as dependent variable)

Parameter			Estimate	+/- (95%)	Probability
Intercept			139.5	43	-
	Season	PR source			
	1st season	GPR	-11.9	7	-
		MPR	10.0	6	-
	2nd season	GPR	-7.7	5	-
		MPR	0	-	-
P_{ads}			0.00935	0.0043	0.0002^{***}
pH_{KCl}			-24.9	9	0.002^{**}

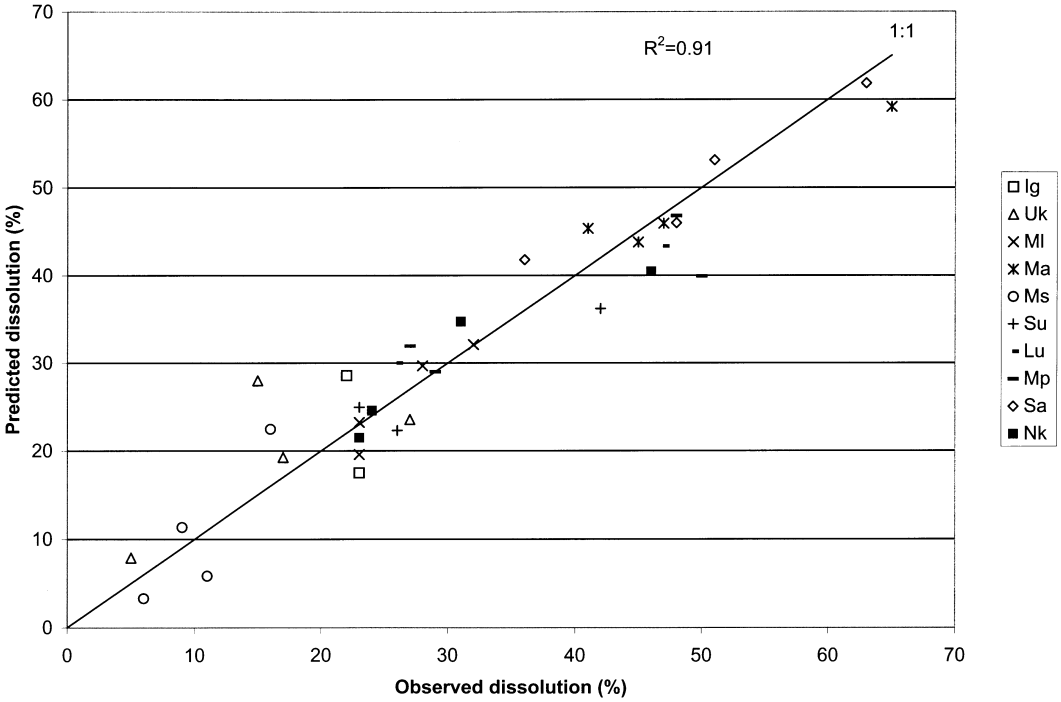


Figure 38. Predicted versus determined PR dissolution using the parameter estimates in Table 57.

The dissolution study shows that PR application results in an increase in residual PR in the soil. On average around 35 % of the added MPR dissolved during the 120 days leaving around 65% of added PR undissolved. It seems that dissolution of PR in this study was limited by proton supply but under field conditions acidifying processes due to plant or fertilizer effects may continuously provide protons, which can contribute to the continuing dissolution of the residual PR. Hence, any residual PR present in the soil will act as a potential source of P until all have dissolved. In contrast, soluble P sources such as TSP dissolves almost completely during a short period of time with the released P being mainly retained by adsorption. The advantage in the short term is that more P will be available to plant uptake but on the other hand risk of leaching, occlusion and fixation increases, which in the long term renders it less available for plant uptake. A higher residual effect of PRs compared to soluble P sources is normally depending on the rate at which the soluble P source becomes non-available and the rate of dissolution of residual PR {202}. A lower relative agronomic effectiveness of PRs in the first season after application can normally be attributed to the smaller amount of released P compared to water-soluble sources as also indicated by the dissolution study.

The low P recovery due to the inefficient extraction of residual PR or TSP in the last P fractionation step have lead to obvious erroneous estimates of dissolution based on either the sum of extractable P ($Diss_{\Delta Psum}$) or residual P ($Diss_{\Delta Presid}$). The problem could probably be confirmed and solved by estimation of residual P by extraction with 0.5 M H_2SO_4 at a soil:solution ratio of 1:200 for 16 hours {21} followed by subtraction of the sum of extractable P during the three first steps of the P fractionation scheme. However, as the degree of dissolution was estimable on the basis of the amount added and the sum of extractable P during the three first steps ($Diss_{\Delta Padd}$) no such additional extraction was done. Hence, it seems that the assumptions listed under the ΔP_{add}-method (Eq. 13) were fulfilled whereas assumptions of total extraction of residual P using the described method were not fulfilled. In future dissolution experiments, the capability of the final acid extraction step to extract total residual P must always be evaluated by appropriate analytical methods.

The agreement between $Diss_{\Delta Padd}$ and $Diss_{\Delta Caex}$ indicate that dissolution of MPR can also be estimated from the change in exchangeable Ca despite the content of dolomite. However, as calcite has also been identified as a common accessory mineral in MPR, the method seems to be less attractive as the assumption that MPR is the only Ca containing mineral dissolving hardly can be fulfilled.

The effect of PR dissolution on soil solution composition did not show as straightforward results as the effect on extractable P due to large residual error in the data set. Unfortunately the most likely reason for this may be problems of unclean labware in connection with the centrifugation and collection of the soil solution as also indicated by an extremely high P content in one of the samples. As the analysis could not be repeated unless the whole dissolution experiment was repeated too much emphasis should not be put on the data. However, it seems that on average, P solution concentration was increased with P addition, which also agrees well with the increased levels of extractable P. The small decrease in exchangeable Mg and K may be a result of the increased CEC of the soil due to increases in soil pH during PR dissolution, whereas the increase in solution Na may be the result of exchange by Ca released from the P sources.

Table 54 show some important effects of PR dissolution on soil properties. Soil pH, exchangeable Ca, Mg and Na increased significantly whereas exchangeable acidity significantly decreased. A similar pattern has been found previously {92}. The increase in exchangeable Ca followed the pattern of PR reactivity corresponding to a higher Ca release with increasing dissolution. Exchangeable Mg followed a slightly different pattern where the Minjingu treatments apparently released a significantly higher amount of Mg than both the control and the two other PRs. It is likely that dolomite present as accessory mineral in the Minjingu materials have contributed to the higher Mg release. The increase in exchangeable Mg and Na due to PR dissolution was generally small compared with the increase in exchangeable Ca corresponding to much lower amounts of these two elements in the PR materials (Table 7). Exchangeable K did not show any change corresponding to low amount of soluble K in the P materials. Exchangeable acidity decreased in agreement with the neutralising, proton consuming effect of PR dissolution (Chapter 2.3.3). However, although the amount of exchangeable acidity were calculated to be limiting for complete dissolution of the added PR, exchangeable acidity was not eradicated completely indicating that other factors such as diffusion of Ca and P away from the PR particle could have been more important for the rate and degree of PR dissolution in the present study.

An increase in CEC_e was expected from the increase in pH following PR dissolution whereas the increase in CEC_7 is more difficult to explain. Even though the exchange solution was buffered for the CEC_7 measurement, the control treatment may, due to more exchangeable acidity, have had a slightly lower pH than the treated samples leading to a slightly higher exchange capacity for the latter. After all the increases are small (<0.6 cmol(+) kg^{-1}). Al saturation and Ca saturation decreased and increased respectively following PR dissolution in accordance with the decrease and increase of exchangeable acidity and Ca respectively. Hence, the beneficial effect of PR addition on Al saturation is clearly demonstrated by the data. Most important is probably the clear and highly significant increases in the indices of plant available P (P_i and P_{olsen}). The levels of increase in average P_{olsen} values result in a shift in P availability range from deficient to sufficient. Compared with addition of TSP the increases in available P were generally substantially lower for the PR treatments indicating that the immediate effect on soil P following application of water-soluble P sources is much larger than would be expected by PR addition. However, as the PR materials continue to dissolve with time, P_{Olsen} may actually underestimate the P availability following PR application compared with addition of soluble P sources {198}. In addition, the beneficial effect of PR application on soil properties such as soil pH, exchangeable Ca, exchangeable acidity and Al saturation seems to be higher compared with TSP due to the larger neutralizing power of PR.

Equation 21 is not intended for operational use. However, it suggests that the absolute level of available P in the soil after PR application depends on both the amount dissolved, the initial P level and the P adsorption capacity. Hence, despite a similar amount of MPR dissolved at Magadu and Sasanda, levels of P_{olsen} are lower at Sasanda primarily due to the lower initial P levels and large P affinity. From the few sites showing significant P response (Chapter 6.2.2) there are indications that high PR dissolution also results in a correspondingly high RAE. For instance, RAE is consistently higher at Magadu and Sasanda than at Nkundi corresponding to a higher degree of PR dissolution. As strong P adsorption also affects P released from water-soluble P sources, the relative effect of PRs may primarily be a question of the amount dissolved indicating that soils characterized by high PR dissolution, such as highly P fixing soils, are the most suitable for direct PR application.

The covariance analysis revealed that soil pH and P_{max} were the only soil properties, which together had a significant influence on PR dissolution. From the parameter estimates in Table 55 it is seen that high P adsorption capacity and low soil pH increases PR dissolution. Neither soil P level, H^+ buffer capacity, exchangeable acidity, Al saturation nor Ca saturation showed any improvement in the prediction of PR dissolution. Other soil properties, such as content of organic matter, clay and sesquioxides, CEC etc. may have shown a significant effect on PR dissolution but those were not tested due to the possible correlation with the former properties. Hence, diffusion of P away from the dissolving PR particle together with the availability of protons may have been determining for PR dissolution in the present study. Whereas H^+ and OH^- diffusion is not likely to limit PR dissolution, the small flux of P by diffusion has previously be found to be an effective limitation for PR dissolution {89, 105, 248}. As P_{max} is normally related to the soils ability to remove soil solution P by adsorption, it influences the concentration gradient of P from the mineral surface to the soil solution and thereby the effective diffusion rate of P.

If diffusion of P is considered the limiting step in this experiment, it explains why the exchangeable acidity was not completely consumed despite the deficiency of protons. Even though protons were available at the rate required for dissolution, too slow removal of reaction products, i.e. P, from the mineral surface prevented further dissolution. Another possibility, which cannot explicitly be evaluated, is the effect of Ca diffusion, which has also been found to limit PR dissolution {133, 135}. Considering Ca diffusion as the limiting step implies that the exchangeable acidity would only be available for PR dissolution at the rate at which Ca released from the PR is able to exchange with the exchangeable acidity. The absence of significant effect of Ca saturation indicate however, that Ca diffusion is not limiting in this case although a better estimate of the soils Ca exchange capacity and the ability to release acidity at increased Ca concentrations would be valuable. A generally small range in Ca saturation and low amounts of exchangeable Ca of the soils may also explain the insignificant effect of Ca. The significant effect of pH is probably due to its strong driving force for dissolution and the fact that the soils exhibit a large range in exchangeable acidity and pH. Especially under conditions where the amount of protons is insufficient for complete dissolution the differences may become determining {89}. Looking at the values in Figure 35 it is seen that neutral soil pH together with a low P adsorption capacity (e.g. Msimba) lead to very limited PR dissolution whereas very high P adsorption capacity can lead to high dissolution despite soil pH being not very low (e.g. Sasanda). The figure also show that low soil pH is not enough if P_{max} is low (e.g. Ukiriguru). As a rough estimate it can be seen that in soils having low P_{max} (<200 mg P kg^{-1}) less than 30% of the PR have dissolved whereas in soils having high P_{max} (>200 mg P kg^{-1}) more than 30% dissolved. Within each group soil pH will then act as a modifying property for dissolution.

The effects of P application under field conditions generally follow the trends from the laboratory dissolution study (Table 56). The beneficial effect of PR addition on soil pH is also clearly demonstrated. Whereas the soil pH of the control plot decreases with time due to removal of nutrients and acidifying fertilisers (sulphate of ammonia), the pH of the PR plots is more or less constant due to the acid buffering effect of PR dissolution. Addition of TSP does not increase soil acidity beyond that created by normal cultivation, i.e. compared with the control plot, but apparently the increased release of Ca does not provide any significant acid buffering effect. A decrease of 0.4 pH units of the control plot during two seasons is relatively dramatic and represent a substantial decrease in soil fertility corresponding to a lower CEC_e and base saturation, higher Al saturation and lower availability of nutrients such as P, micronutrients and base cations. It seems that application of high levels of PR such as those evaluated here (1000 kg PR ha^{-1} yr^{-1} corresponding to 120 kg P ha^{-1} yr^{-1}) is able to maintain the soil acidity level more or less constant whereas substantially higher liming requirements are needed when not using PRs or when PRs are applied at lower rates. The figures clearly indicate the need for controlling soil acidity through liming in order to maintain the soil fertility of tropical soils. The decrease in soil fertility of the control plot is also seen from the highly significant decrease in exchangeable Ca, which may be attributed to plant uptake and increased leaching due to the decreased CEC_e and increased soil acidity. In contrast, application of PR effectively increases exchangeable Ca levels with time whereas TSP is only able to maintain them at the present level. As was also discussed in Chapter 6.2.1, levels of exchangeable Ca were like the other base cations generally low among the ten experimental sites and any improvement in the levels of exchangeable base cations must be regarded as an important step towards sustaining soil fertility.

The effect of P application on extractable P also agrees with the laboratory dissolution experiment. Application of TSP resulted on average in a large, significant increase in easily extractable P (P_{NaCl}) in the first season whereas the increase in P_{NaCl} following PR were smaller and only significantly higher than the control in the second season corresponding to the fast and slow release respectively. PR application more than doubled the amount P_{NaCl} with MPR being slightly, but not significantly, higher than GPR. Hence, it seems that although GPR may be less reactive as also indicated by the laboratory dissolution experiment it might not have a very significant effect under field conditions, which could be attributed to the increased disintegration and dispersal of granules during incorporation, cultivation, weeding and ridging and due to the stronger influence of leaching rainfall.

None of the extractable P fractions in the control plot showed any signs of P depletion with time. However, such changes may not be visible during two years as the amount of P participating in exchange reactions may exceed the amounts removed annually by plant uptake. On the other hand, P application generally resulted in significantly higher levels of soil P. On average, application of 120 kg P ha^{-1} yr^{-1} resulted in an increase in total P of 80-100 mg P kg^{-1} yr^{-1} corresponding to approximately 70% increase in soil P per year. The levels of P increase corresponds well with an estimated cultivation depth of approximately 10 cm and an average bulk density of 1.25 t m^{-3} indicating that total P recovery during the modified P fractionation procedure were higher compared with total P recovery in the laboratory dissolution experiment.

The average NaOH extractable organic P ($P_{org(NaOH)}$) more or less equals a constant fraction of P of approximately 115 mg P kg^{-1} irrespective of sampling time and treatment. However, among the sites, $P_{org(NaOH)}$ showed highly different values according to the content of organic matter and P_{org} given in Table 48. Apparently the fraction does not change significantly after two years of P application. The significant treatment effect and the lack of significant (sampling time*treatment) interaction indicate that the treatment effect is rather due to inherent differences in $P_{org(NaOH)}$ between the plots than due to an actual effect of the P source. However, with longer sampling periods, significant changes in the organic P fraction due to different P sources are more likely.

From the estimates of PR dissolution it is seen that MPR dissolution is significantly larger than GPR dissolution corresponding to the higher reactivity of the former. However, although significant, the difference is not dramatic and apparently they tend to approach each other with time. From $Diss_{\Delta Psum}$ two trends are observable, i.e. one of GPR showing increasing dissolution with time and one of MPR showing decreasing dissolution with time. The increased dissolution of GPR may be explained by the decrease in average granule size of the PR material used from year 1 to year 2 (Chapter 6.1.5) whereas the decrease in MPR dissolution may be a result of an increased influence of neighbouring particles, and effect of partial acid neutralisation after the first year application. Although some deviations are seen for the individual sites (Figure 39), the average MPR and GPR dissolution of 27% and 37% respectively are in agreement with the estimates of average dissolution measured in the laboratory experiment, i.e. 22% and 35%.

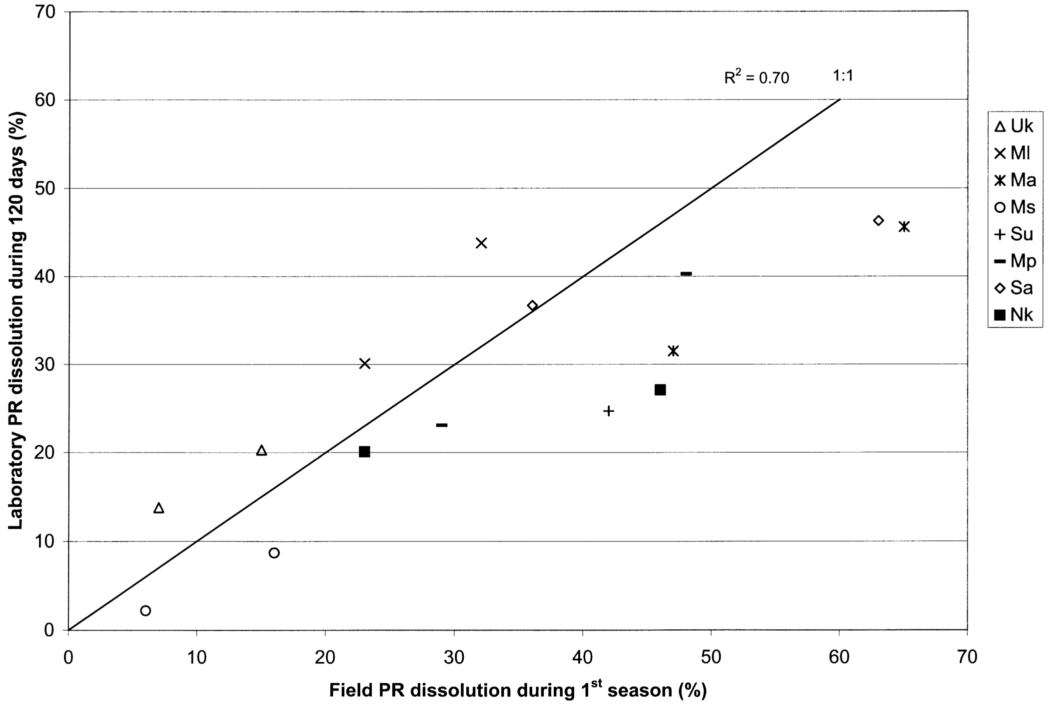


Figure 39. Comparison of laboratory dissolution ($Diss_{\Delta Psum}$) during 120 days and field dissolution during the 1st growing season of MPR and GPR.

The effect of soil properties on PR dissolution agrees with the findings from the laboratory dissolution experiment. Soil pH and P adsorption index were the only soil properties among those investigated, which had a significant effect on PR dissolution. Hence, it supports the previous suggestions that diffusion of P from the PR particles together with the soils ability to supply protons are determining for the degree of PR dissolution of the Minjingu products at the experimental sites both under laboratory and field conditions. The effect of Ca saturation, estimated using Ca saturation of the surface horizon of the soil profile, did not show any significant effect on PR dissolution (data not shown) indicating in agreement with the laboratory dissolution experiment that Ca diffusion apparently is not limiting PR dissolution among the experimental fields. This could be explained by the generally low content of exchangeable Ca and presumably low soil solution concentrations of Ca due to the highly weathered and leached nature of the soils.

7.4 Conclusion

Both the laboratory dissolution study and the evaluation of PR dissolution under field conditions showed a significant effect of PR reactivity on PR dissolution. Both mineralogical and physical properties affect the PR reactivity as estimated by PR dissolution when comparing a highly carbonate substituted PR (NCPR or MPR) and medium carbonate substituted PR (CFPR) or when comparing mini-granulated and non-granulated forms of MPR. On average, mini-granulation of MPR reduces the PR dissolution both under laboratory and field conditions by 25-35% compared to the non-granulated MPR product corresponding to a reduction in reactivity class from a highly reactive to a medium reactive PR. Non-granulated MPR was found to be as reactive as unground NCPR, which is normally classified as one of the most reactive PRs worldwide. Hence, based on the reactivity estimations presented here, application of MPR is expected to have a similar agronomic effectiveness as unground NCPR whereas mini-granulated MPR is expected to be similar to CFPR.

Direct application of PR materials to soils significantly reduces levels of exchangeable acidity and Al saturation through the acid buffering effect of PR dissolution and soil pH levels are either maintained at a constant level or increased by PR application with the following beneficial effects on general soil fertility parameters such as CEC_e, base saturation and availability of plant nutrients. Release of Ca and P through dissolution of the apatite mineral increases the amount of exchangeable Ca and plant available P of the soil. PR dissolution is a relatively slow process and continues, depending on the removal of reaction products and supply of protons, as long as any non-dissolved PR remains in the soil. Hence, the release of P from PR materials and the following increase in labile inorganic P fractions are generally significantly smaller compared to the release of P from soluble P sources but the residual effect of PR on available P may go beyond the effect of soluble P sources due to the continued release of PR-P with time and due to a higher risk of P occlusion following the rapid and extensive P release from the soluble source.

Among soil properties, which are expected to influence PR dissolution, i.e. soil acidity, acid buffer capacity, P adsorption capacity, P level and Ca saturation, only P adsorption capacity and soil pH were found to have a significant effect on PR dissolution indicating that proton supply as well as P diffusion, i.e. provision of reactants and removal of reaction products, are the most determining factors affecting PR dissolution. Apparently Ca diffusion did not seem to limit PR dissolution compared to P diffusion as inclusion of Ca saturation as covariate in the statistical analysis proved non-significant, probably due to the generally low soil solution concentration and low amounts of exchangeable Ca of the soils.

MPR dissolution ranged from less than 10% during 120 days in the laboratory or during 1 year in the field for Msimba to more than 50% at Sasanda representing a nearly neutral soil with low P adsorption capacity to a slightly acid soil with very high P adsorption capacity respectively. 91% of the variation in MPR or GPR dissolution under field conditions was described by PR type, sampling time, soil pH and P adsorption capacity whereas 93% of the variation was described by PR type, soil pH and P adsorption in the dissolution experiment.

8 Final discussion and conclusion

The need for increased and balanced nutrient input in Tanzanian agriculture is unquestionable. These studies, as well as many previous studies of soil fertility in Tanzania, have uncovered moderate to severe multinutritional deficiencies in many areas of Tanzania. Fertilizer based solutions, in addition to other approaches such as improved fallows, hedgerows, N-fixation, manuring and application of crop residues or agro-minerals, seems inevitable. Availability of compound fertilizers or various single nutrient fertilizers are required in order to alleviate the serious nutrient deficit in Tanzanian agriculture. However, the fertilizer materials must be incorporated into general soil productivity and soil conservation strategies, which considers and alleviates all possible productivity constraints and increases the long-term production sustainability.

Regarding P, a number of possibilities and limitations exist in relation to utilization of MPR as directly applied P source. Considering the previous experiences and the present situation, the future prospects for the MPR mine might seem brighter than first assumed due to the following reasons:

1a) The presence of a beneficiation plant in working condition at Minjingu (Chapter 3.4). Relatively small additional investments are required for rehabilitation of the mining equipment, for the very important measures required to improve the working environment up to international standards, and for a granulation unit.

1b) The presence of approximately 4.8 Mt and 2.4 Mt of remaining hard and soft ore respectively, most of which can be mined and beneficiated using the present or slightly modified techniques, and indications of another potential deposit of similar kind, which is yet to be more thoroughly surveyed, nearby at Mwembe Hill (Chapter 3.3). In addition, the interlayering bentonitic clays, which are estimated to 5-8 Mt may also be utilized as a by-product and thereby contribute to the future profitability.

1c) A mine location directly on The Great North road on which transport on tarmac road towards Arusha in the north or on gravel road towards Dodoma in the south is facilitated. In addition, warehouse facilities including railway tracks connected to the central railway system exist in Arusha enabling a possible future transport via rail.

1d) A large group of potential buyers among large and small-scale farmers in Tanzania and surrounding East African countries. Application of inorganic phosphorus through fertilizers has so far been very limited in Tanzanian agriculture, and average crop yields are normally very low reflecting the combined effect of widespread soils with low fertility and sub-optimum management practices, including inputs in general, during several decades. Effective P replenishment in tropical farming systems generally necessitates fertilizer based P applications.

1e) The improved investment climate and high economic growth potential in Tanzania.

However, the previous problems and considerations suggest that the merits of the Minjingu phosphate concentrate would be more promising if used as a directly applied phosphate source instead of being raw material for the production of soluble fertilizers. The reasoning behind this is that:

2a) The MPR has medium to high reactivity and is comparable with the most soluble phosphate rocks found world wide (Chapter 3.5.2 and 7.3), indicating that it is suitable for direct application to moderately acid and acid, phosphorus deficient soils in sub-humid to humid areas, which are widespread in Tanzania and neighbouring countries (Chapter 5.3). The agronomic effectiveness of directly applied MPR derived from the soft ore is comparable with water-soluble P fertilizers from the second season (Chapter 5.1 and 6.3), indicating that from an agronomic point of view there is no technical reason why the product could not substitute imported soluble P fertilizers in certain key areas suitable for direct MPR application (Chapter 5.3).

2b) The selected method of dry beneficiation at the mine is not able to produce high quality concentrates suitable for production of phosphoric acid (Chapter 3.5.2). The beneficiation process, however, increases the P content by 20-60% depending on the ore grade, which significantly improves the economic competitiveness as most soils suitable for direct application are located more than 500 km away from the mine (Chapter 5.3). The impurities of the beneficiated material, which are mainly feldspar, quartz, colloidal silica, calcite and dolomite, do not at all result in any harmful or detrimental effects when applied directly to soils. Both quartz and feldspars are among the more inert primary minerals and weather relatively slowly with the feldspars releasing base cations. Finely ground colloidal silica weather faster than quartz when applied to soils and the silicic acid released could result in a beneficial competition for adsorption sites increasing the availability of the dissolved phosphate. Accessory calcite ($CaCO_3$) and dolomite ($MgCa(CO_3)_2$) would in most cases have a beneficial effect as it slowly raises soil pH and simultaneously releases bases although it at the same time reduces the amount of soil acidity available for phosphate rock dissolution.

2c) If applied directly, production of a slightly beneficiated concentrate from the hard ore would also be possible using the present mining and processing techniques. An impact crusher and a ball mill designed for initial and later crushing has already been installed at the mine for processing the hard ore if required (Chapter 3.4). The dry process beneficiation of the hard ore however, has proved to be more difficult than the soft ore due to similar granulometric composition of the phosphate and accessory minerals. The final concentrate might therefore be of lower grade and quality and hence not be suitable for further processing or long transport. However, inclusion of the hard ore in the workable reserve increases the tonnage of suitable ore with about 4.8 Mt increasing the potential economic viability and mine life considerably. Recently conducted agronomic pot and field experiments using ground hard ore have shown comparable responses as with the soft ore (M.M. Msolla, personal communication, 2001).

2d) The use of indigenous resources for agricultural needs saves foreign currency used for importation of fertilizers to the country. If the phosphate concentrate was meant for the production of soluble phosphate fertilizers it presently had to be exported and re-imported, as there are no domestic processing possibilities. Transport of the ore to the Ocean has previously proven to be both difficult and expensive and the relatively small size of the deposit can probably not support construction of an economically viable processing plant. Direct application result in a lower production price per kg P as the input cost for production is lower compared with transport and processing the ore at a phosphate factory. This means that a phosphate fertilizer would be available at a lower cost in Tanzania, which due to the high cost:output ratio is a very important prerequisite if a large number of resource poor farmers should start using phosphate inputs. Accessibility of a low cost P fertilizer in Tanzania would therefore increase the group of potential buyers considerably.

2e) The production of the beneficiated concentrate is likely to have less impact on the environment compared to the production of soluble phosphates due to the waste water effluents and problems of treatment and control. Previously when the fertilizer factory in Tanga still produced soluble phosphates the phosphogypsum by-product was discharged directly into the Indian Ocean causing environmental concerns due to high levels of radioactive ^{226}Ra. Also the detrimental effect on the aquatic environment of directly applied MPR may be lower as the material dissolves slowly and does not cause high soil solution concentrations of phosphate, which on some soil types could be lost by leaching.

2f) Improved effects on soil properties such as soil pH, exchangeable acidity and Ca after direct MPR application compared with TSP. The liming effect of MPR must also be included when calculating the production economics for P application.

However, the implementation of direct application of Minjingu phosphate rock also has some limitations, which has to be considered before a PR adventure could turn out successfully:

3a) High transportation costs due to poor infrastructure and long distances are likely to affect the economic viability of MPR harder than soluble sources such as triple superphosphate. For instance assuming same price for the bulk transport of TSP and beneficiated MPR respectively the transport costs would be 54% higher per unit P for MPR (13.1% P) as compared with TSP (20.1%) due to the lower concentration of P in MPR. The profitability of MPR far away from the source such as in Rukwa and Ruvuma Region in the Southern Highlands of Tanzania have been shown to be questionable as the distance from the mine to the potential areas exceed 1000 km (Chapter 5.3). An estimate of today’s transportation cost to the regional town of Sumbawanga, and the ex-factory price of MPR of 750 USD t^{-1} P would result in an approximate price of 2130 USD t^{-1} P compared with a market price of 1750 USD t^{-1} P for TSP. In this example transportation costs of MPR constitute 65% of the estimated price compared to less than 40% for TSP. Options such as subsidising the MPR product may not be an optimum solution from a socio-economic view. However, development of a better infrastructure is an important component for lowering the transportation costs for agricultural inputs and outputs, which then may increase the farmer’s revenue so that the economics of using fertilizers improves. The best alternative may be that the phosphate concentrates are used primarily in areas within a certain distance from the mine depending on the transport cost and production economics. This would be even more important in case of utilization of the hard ore or the deeper soft ore layers due to the lower grade.

3b) As the agronomic effectiveness of directly applied MPR and reactive phosphate rocks in general is much more sensitive to soil, plant, climatic and management effects compared to TSP, the risk of failure by implementing broad use of MPR is larger. It can be difficult to predict the agronomic effectiveness of MPR in a given plant-soil system, and the need of information on the agro-ecologic conditions is much larger. If farmers without appropriate advice try out direct application themselves, a failure in agronomic response could have a negative effect on the acceptance by farmers, as the reputation of the material would be disputed. This emphasizes the need for pinpointing prioritised target areas where the chance of success is greatest followed by training of extension staff and farmers as well as delineation of suitable soils on the basis of information on the socio-economic and agro-ecological conditions including soil and leaf analytical data. It must be strongly emphasized that all possible productivity constraints including, soil chemical and physical properties as well as climatical conditions are considered when developing fertilizer based recommendations for farmers. For this a national advisory and analytical service must be provided in order to support decisions at local level. In addition, a viable fertilizer sector must be developed so that compound fertilizers are available throughout the country.

3c) Large efforts in marketing of and information about the product, with respect to the limitations, are required. The tremendous task of marketing and information should not be ignored. An annual production of 100,000 tons of concentrate implies direct application of MPR on 6000-7000 km^2, which with the current farm structure involves several hundred thousand small-scale farmers. The number of large-scale farmers and the area involved would probably not suffice for the distribution of the potential annual MPR production. As the situation shows today, it has so far been very difficult to promote the use of even soluble P fertilizers to any significant extent mainly due to the poor economic returns.

3d) The beneficiated powder product is composed of fine and very fine particles, which makes the product very dusty and inconvenient to handle and apply. Reducing the particle size and hence the specific surface area of the phosphate particles increases dissolution and hence agronomic effectiveness but also increases the problems of dustiness and fluidity of the product. Some kind of mini-granulation, which has shown not decrease dissolution and RAE significantly (Chapter 6.2), is required in order to make the product marketable and attractive to customers. Granulation on the other hand also opens up the possibility for co-granulation with other nutrients or even TSP so that production of compound fertilizers would be possible.

3e) The high content of natural long-lived radionuclides in the phosphates is another concern, which can turn out to be very crucial for the future of the mine. The concerns are both related to the health implications for the mineworkers and inhabitants of Minjingu and to the possible environmental effects following the utilization of the phosphates either as raw material in the phosphate or feedstuff industry or as directly applied phosphorus source in agriculture. Utilization of the phosphates inevitably lead to dispersal of radioactive matter into the environment, which in the case of Minjingu is aggravated by the very high levels of radionuclides, compared to other phosphate rocks. The issue of radiation is very sensitive and could have negative influence on the acceptance of the product by farmers if the wrong information is spreading. Several investigations have looked into the possible detrimental effects of mining and utilization of the Minjingu phosphates (Chapter 3.6). However, presently there is still a need to further investigate the effect of direct MPR application on levels of radiation in various plant species and plant parts in order to assess the public health risks relative to other sources of radiation. In addition, the long-term environmental effects of increased levels of radionuclides and their mobility in tropical soils are not well known. Recommendation of widespread use of MPR in agriculture may only be advisable if the estimated annual effective dose equivalents received by persons involved in the utilization of MPR and calculated from annual rates of; a) direct ambient exposure, b) inhalation of radioactive gases and dust, and c) intake of food (animal and plant products) and water, are less than the norms stipulated by international agencies.

3f) Problems of sustaining the product quality and supply. The beneficiated concentrate is relatively sensitive to the ore grade and quality and differences in the reactivity and grade of the end product might result. As the total reserves are not very large compared to the area suitable for direct application, the mine life and therefore product supply is not lasting more than a few decades, which could lead to confusion among farmers if the product suddenly became unavailable or changed in properties.

3g) Direct application of MPR is probably not very suitable for high intensity farming using crops with high P demand such as many annual cash crops, and it is mainly limited to be used on acid soils of low fertility in the more humid areas. Perennial farming systems using crops such as coffee, tea, banana and sisal are probably more appropriate. The less acidic soils, typical for the semi-arid areas of Tanzania and neighbouring countries, are also probably not very suitable for direct application of MPR, limiting the use of MPR to certain key areas and leaving other areas more dependent on soluble P fertilizers. However, on less acidic soils, other management practices including co-application with TSP, low technology partial acidulation, anaerobic composting or utilization of crop species with potential dissolution enhancing properties could be considered.

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Sammendrag

Det overordnede formål med dette studie har været at undersøge hvilke muligheder og begrænsninger, der eksisterer i forbindelse med anvendelsen af den tanzaniske råfosfat fra Minjingu som direkte tildelt fosforgødning i det tanzaniske landbrug. Studiet omfatter en gennemgang af tidligere litteratur på området, jordbundskemiske og mineralogiske undersøgelser, markforsøg samt opløsningsforsøg i laboratoriet.

På grundlag af tidligere potte- og markforsøg synes råfosfaten fra Minjingu at være yderst anvendelig som fosforgødning til en række etårige afgrøder på sure, fosforlidende jorde i de mere nedbørsrige egne af Tanzania. Men på trods af de mange tidligere forsøg, har der vist sig behov for at undersøge effekten af Minjingu råfosfaten under mere varierede agroøkologiske forhold end tidligere. Dette ønske ledte i 1998 til igangsættelsen af Råfosfatprojektet, som er en komponent under Danidas Landbrugssektorprogram for Tanzania. Centralt for Råfosfatprojektet er udførelse af markforsøg med Minjingu råfosfaten i ti forskellige egne af Tanzania. Projektet udføres i samarbejde mellem det tanzaniske jordbrugsuniversitet, det tanzaniske landbrugsministerium og Landbohøjskolen. To Ph.D. studerende, en fra Tanzania og en fra Danmark har været tilknyttet projektet, som strækker sig over perioden 1998-2003.

Resultaterne af den mineralogiske undersøgelse af den bløde Minjingu råfosfat, som præsenteres i denne afhandling, viser, at råfosfaten hovedsageligt består af et fluorfattigt karbonatfluorapatitmineral. I bjergarten findes ud over apaititen blandt andet mindre mængder af frit calciumkarbonat, dolomit, kvarts, feldspater samt lermineraler. Råfosfaten stammer oprindeligt fra store mængder fugleekskrementer, som blev aflejret på Minjingubjerget i en periode gennem Pleistocæn, hvor bjerget lå som en isoleret ø i den dengang meget større Manyarasø. Elektronmikroskopiske undersøgelser bekræfter tidligere tyndslibsundersøgelser, der viste, at apatiten hovedsageligt forekommer som fiskebensstumper og udfældede submikroskopiske apatitkrystaller. Opløseligheden af den bløde råfosfat er væsentligt højere end forventet ud fra den normale relation mellem de krystallografiske egenskaber og opløseligheden i neutral ammoniumcitrat. Årsagen til denne afvigelse synes at bero på et ekstraordinært højt krystalbundet karbonatindhold samt en fraktion af apatiten bestående af meget små krystaller. Den hårde Minjingu råfosfat består ligeledes af et fluorfattigt karbonatfluorapatitmineral, men såvel det krystalbundne karbonat som fluorindholdet er mindre end i den bløde type. Opløseligheden af den hårde type er lavere end den bløde, men følger til gengæld den forventede relation mellem de krystallografiske egenskaber og opløseligheden i neutral ammoniumcitrat. Forskellen mellem de to råfosfattyper synes at bero på forskelle i lagenes aflejringshistorie samt efterfølgende omdannelse. Råfosfatlejet, som indeholder omtrent 7 Mt af den bløde og hårde fosfatholdige bjergart, er med det nuværende og eventuelt stigende fosforforbrug i Tanzania istand til at forsyne det tanzaniske landbrug med fosfor i flere årtier. En opkoncentreringsfabrik beliggende ved minen har siden 1983 produceret et kommercielt tilgængeligt finmalet råfosfatpulver med 13,1% P. På grund af problemer med opkoncentrering af råfosfaten til et egnet produkt for produktion af vandopløselige fosforgødninger samt manglen på lokale produktionsfaciliteter, anbefales det udelukkende at bruge Minjingu råfosfaten som en direkte tildelt fosforgødning.

Både det kommercielt tilgængelige pulverprodukt samt et minigranuleret produkt af Minjingu råfosfaten bliver i øjeblikket sammenlignet over fem vækstsæsoner med tripelsuperfosfat på ti forskellige lokaliteter i de mere nedbørsrige egne af Tanzania. Tre fosforniveauer, baseret på total fosforindhold, blev sammenlignet (henholdsvis 40, 80 og 120 kg P ha^{-1}). Fosfor blev tilført hvert år i de fire første år af forsøgsperioden. Forsøgsafgrøden er majs. Kvælstof og andre makro- og mikronæringsstoffer, som vurderedes til at være mangelende blev tilført som grundgødskning. Resultaterne af de tre første vækstsæsoner viste, at der på lokaliteter med signifikant udbyttestigning som følge af fosfortildeling kunne opnås sammenlignelige udbytter fra og med anden vækstsæson uanset fosfortype. Råfosfaten medførte generelt lidt lavere udbytter i

første sæson sammenlignet med tripelsuperfosfat, hvilket sandsynligvis skyldes effekten af den langsommere opløsning af råfosfaten i jorden. Minigranulering nedsatte generelt den relative effekt af råfosfaten på grund af den ringere kontakt mellem råfosfatpartikler og jordpartikler, men forskellen var udelukkende udpræget i første sæson. På lokaliteter med favorable vilkår for opløsning af råfosfat som følge af lavt pH, lavt indhold af ombytteligt calcium og høj fosforadsorptionskapacitet, opnås derfor efter et år, tilsyneladende samme mængde plantetilgængeligt fosfor fra råfosfaten som fra mere vandopløselige fosfatgødninger. Udbyttestigningerne som følge af fosfortildeling lå i området 0,4 til 4,5 t ha^{-1} under forudsætning af samtidig tildeling af store mængder kvælstof (80-120 kg N ha^{-1}) samt andre manglende makro- og mikronæringsstoffer.

Den manglende signifikante fosforrespons på flertallet af forsøgslokaliteterne skyldtes dels tilstrækkelige mængder af plantetilgængeligt fosfor i jordbunden, klimatiske forhold eller andre næringsstofproblemer, som i nogle tilfælde var årsag til en høj variation i udbyttedataene. Generelt fandtes en række næringsstofproblemer på de stærkt forvitrede og udvaskede jorde. Også de yngre jorde, udviklet på vulkansk aske har næringsstofproblemer som følge af høj fosforadsorptionskapacitet, lavt indhold af visse mikronæringsstoffer, lav kationadsorptionskapacitet og ubalanceret forhold mellem omyttelige kationer. Bæredygtige udbyttestigninger vil således kun kunne forekomme, hvis fremtidige gødskningsanbefalinger indarbejder hele registeret af næringsstofbehov på basis af jordbunds- og planteanalyser samt en agronomisk evaluering af de agroøkologiske betingelser. For at kunne opnå dette, er en udbyggelse af den nationale laboratoriekapacitet samt det nationale landbrugsrådgivningssystem nødvendig. Ligeledes er tilgængelighed af udvalgte blandingsgødninger påkrævet. Vandbalancestudierne viste, at flere lokaliteter var udsat for alvorlig vandstress i den kritiske periode for kernefyldning, men på samme tid var udsat for alvorlig udvaskning og overfladeafstrømning af flere hundrede millimeter nedbør tidligere i vækstsæsonen. Den ufavorable fordeling af nedbør i forhold til fordampningen samt jordenes generelt lave vandholdende evne understreger således behovet for udvikling af strategier på vandhusholdningsområdet.

Resultaterne af undersøgelserne vedrørende opløsning af råfosfaten under markforhold viste, at mellem 6 og 65% af det tilførte råfosfat opløstes i løbet af de to første vækstsæsoner. Mere end 90% af variationen i graden af opløsning kunne forklares af råfosfattypen (pulver eller minigranuleret), jordens pH samt fosforadsorptionskapaciteten. Jo mere sur og jo højere fosforadsorptionskapacitet desto højere grad af opløsning. Inddragelse af andre jordbundsegenskaber som ombyttelig surhed og calcium, syrebufferkapacitet eller plantetilgængeligt fosforindhold i regressionanalysen forbedrede ikke regressionskoefficienten signifikant. Dette indikerer, at den umiddelbare protonforsyning til, og fjernelse af fosfat fra den opløsende råfosfat, er de mest afgørende processer, der kontrollerer graden af råfosfatopløsning i de undersøgte jorde. Den absolutte forskel i graden af opløsning mellem de to råfosfattyper var i gennemsnit over de to vækstsæsoner 9% lavere for det minigranulerede produkt. Den reducerede opløsning af det granulerede produkt skyldes sandsynligvis nedgangen i det specifikke overfladeareal af de fosforholdige partikler. Forsøgene indikerer, at en høj opløsningsgrad ligeledes medfører en høj relativ agronomisk effekt af råfosfaten.

Tildeling af Minjingu råfosfat i marken har signifikant effekt på jordbundsegenskaber som pH, plantetilgængeligt fosfor, adsorberet fosfor, ombyttelig surhed og aluminium i sammenligning med effekten af tripelsuperfosfat eller ingen fosfat. Ved tildeling af råfosfat opretholdtes jordens pH og mængden af ombyttelig surhed i samme niveau gennem perioden, mens der i jorde uden tilførsel af råfosfat henholdsvis skete et signifikant fald i pH og en signifikant stigning i ombyttelig surhed. Mængden af ombytteligt calcium steg signifikant efter tildeling af råfosfat i modsætning til et signifikant fald i kontroljorde samt et konstant niveau i tripelsuperfosfattildelte jorde. Begge fraktioner af plantetilgængeligt fosfor samt adsorberet fosfor steg ved fosfortildeling i forhold til et konstant niveau for kontroljorde.

I laboratorieopløsningsforsøget blev opløsningen af Minjingu råfosfaten sammenlignet med to kendte råfosfattyper fra henholdsvis North Carolina og Central Florida. Efter 120 dage var graden af opløsning følgende: pulverform af Minjingu råfosfat~North Carolina>Central Florida>granuleret Minjingu råfosfat. Heraf kan ses, at især de mineralogiske egenskaber samt partikelstørrelsen har afgørende betydning for graden af opløsning af råfosfat. Opløsningen af Minjingu råfosfaten var generelt sammenlignelig med den meget reaktive og letopløselige North Carolina råfosfat mens granulering af Minjingu råfosfaten nedsatte opløseligheden i en grad, der er sammenlignelig med nedgangen i opløselighed forårsaget af forskelle i mineralogiske egenskaber mellem North Carolina og Central Florida råfosfaterne. Både resultaterne af analyserne af sammenhængen mellem jordbundsegenskabernes effekt på graden af opløsning, samt effekten af opløsning af råfosfat på jordbundsegenskaberne var sammenlignelige med resultaterne fra markforsøget.

Den sundhedsmæssige strålingsrisiko fra indholdet af radioaktive isotoper i Minjingu råfosfaten synes primært at være relateret til en forhøjet baggrundsstråling omkring Minjingu minen samt til indånding af radioaktive støvpartikler under brydning, opkoncentrering, håndtering, transport og tildeling i marken. Indførelse af forbedrede foranstaltninger, som reducerer muligheden for indtag af støvpartikler i forbindelse med arbejdet med råfosfaten ved Minjingu minen, er yderst påkrævet. På baggrund af markforsøgene, der viser, at granulering kun marginalt nedsætter effektiviteten af råfosfaten, anbefales det, at foretage granulering af råfosfatkoncentratet for at nedsætte støvproblemerne i forbindelse med håndtering af råfosfaten. Granulering af råfosfaten muliggør endvidere produktion af blandingsgødninger med indhold af flere næringsstoffer, hvilket markforsøgene ligeledes indikerer et stort behov for. Der synes at være behov for yderligere undersøgelser af langtidseffekterne af brydning og tildeling af Minjingu råfosfaten på spredningsvejene for radioaktive isotoper fra bjergart til mennesker. Informationer vedrørende den relative strålingsrisiko fra Minjingu råfosfaten, i forhold til andre strålingskilder, er ligeledes påkrævet.

Resultaterne præsenteret i denne afhandling støtter de hidtidige resultater, som viser, at Minjingu råfosfaten kan benyttes som en effektiv fosforkilde til majs på fosforlidende, sure jorde i de mere nedbørsrige egne af Tanzania og sandsynligvis ligeledes under lignede vilkår i nabolandene omkring Tanzania. Det lavere fosforindhold i Minjingu råfosfaten i forhold til mere vandopløselige fosforgødninger udgør dog en væsentlig begrænsning for anvendelsen af råfosfaten i områder, der ligger langt væk fra minen. Under de nuværende forhold anbefales det, at anvendelsen foregår i en maksimal afstand på op til ca. 1000 km fra minen. Præcis hvor og hvordan Minjingu råfosfaten er anvendelig som erstatning for mere opløselige fosforgødninger må bero på detaljerede undersøgelser af strategisk udvalgte områder, hvor alle dyrkningsbegrænsninger inklusiv jordbundsfrugtbarhed, jordbundsfysiske samt klimatiske forhold evalueres gennem analyser og feltstudier. Lokale produktionsforhold samt samfundsøkonomiske betingelser må ligeledes inddrages førend endelige gødskningsanbefalinger kan udarbejdes.

Gennem dette arbejde er ny og ekstra viden opnået omkring:

a) kemiske og mineralogiske egenskaber af den bløde og hårde Minjingu råfosfat
b) fordelingen af områder i Tanzania, hvor direkte tildeling af Minjingu råfosfaten, ud fra et agronomisk synspunkt, vil være mulig
c) effekten af minigranulering på den relative agronomiske effektivitet
d) næringsstofstatus samt mineralogiske egenskaber af jordene på udvalgte lokaliteter i Tanzania
e) effekten af tildeling af Minjingu råfosfat på jordbundsegenskaber samt effekten af jordbundsegenskaberne på opløsningen af Minjingu råfosfaten.

Nøgleord: Tanzania, Minjingu råfosfat, mineralogi, guano, makronæringsstoffer, mikronæringsstoffer, tropiske jorde, granulering, jordbundsfrugtbarhed, vandbalance

1 Appendices

1.1 Soil profile descriptions

1.1.1 Igabiro

Site Description

Location	Igabiro Farmers' Training Centre, Muleba District, Kagera Region, Tanzania
Elevation	1508 m a.s.l
Topographic Map	Name: Muleba, Sheet No. 9/3 (1:50,000)
Grid Co-ordinates	S 01.81980° E 031.55270°, UTM 36 M 339012 9798811 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Isohyperthermic, fine loamy, kaolinitic Typic Haplustox WRBSR: Umbric Ferralsol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Isohyperthermic
Climate	Mean annual air temperature: 19.9 °C (mean range: 14.0-25.7 °C) Mean annual precipitation: 1400-2000 mm
Agro-ecological Zone[§]	W3. Medium altitude plains and plateau of the Western Highlands, often dissected and covered by sands and loams with low fertility; medium growing period with unreliable onset period; OP80[†]: Oct.-Feb.
Geomorphology[§]	W7. The soil profile is located on the upper part of a straight slope (10-15%) on the hilly dissected Kamachumu plateau formed by parallel ridges and intervening narrow valleys Gradient: 6-8% towards ENE (within each terrace)
Parent Material	Quartzite rich sandstone
Land Use	Under cultivation (2-3 rotations of maize followed by 2-3 years fallow), ridging
Vegetation	Grass and herbaceous weeds (Digitaria sp., Bidens pillosa), Maesopsis eminii (Muhumula in Haya vernacular) as a common tree species in surrounding areas
Erosion	Presently nil. 15-18 m wide terraces separated by approx. 3 m wide grassed erosion control lines
Drainage	Well drained
Depth to groundwater	Not known
Date of description	June 7 1998 by E. Semu, J.M.R. Semoka and C. Szilas
Remarks	The soil surface was considered as half the height of the ridges. TSP has been added prior to cultivation, except for the last growing season.

Profile Description

Ap	0-18 cm	Very dark brown (7.5 YR 2.5/3, moist); loam; moderate medium to coarse granular; sticky, plastic, soft; interstitial voids, few medium vughs, few fine channels, common fine planes, medium porosity; few medium and common very fine roots; few termite/ant channels and nests; clear smooth boundary
A	18-43 cm	Very dark brown (7.5 YR 2.5/3, moist) matrix with few distinct clear fine and medium reddish brown (5 YR 4/4, moist) rounded mottles; loam; porous massive; sticky, plastic, friable; few medium vughs, few fine channels, medium porosity; very few very fine and fine roots; few termite/ant channels and nests; diffuse smooth boundary
AB	43-65 cm	Very dark brown (7.5 YR 2.5/2, moist) matrix with few distinct clear medium reddish brown (5 YR 4/4, moist) rounded mottles; loam; porous massive; sticky, plastic, friable; very few fine channels, medium porosity; few very fine and fine roots; clear smooth boundary
Bo1	65-110 cm	Dark brown (7.5 YR 3/4, moist) matrix with common distinct diffuse medium reddish brown (5 YR 4/4, moist) and few prominent clear medium very dark brown (7.5 YR 2.5/2, moist) rounded mottles; loam; porous massive; sticky, plastic, friable; very few fine channels, medium porosity; very few very fine and fine roots; very few elongated moderately hard weathered stones with black interior and red Fe-oxide coatings; few infilled large burrows; diffuse smooth boundary
Bo2	110-180 cm	Reddish brown (5 YR 4/4, moist) matrix with few prominent clear medium very dark brown (7.5 YR 2.5/2, moist) rounded mottles; sandy clay loam; porous massive; sticky, plastic, friable; common fine channels, high porosity; common faint thin clay cutans in patches; few very fine and fine roots; very few fine red hard Fe-oxide concretions; very few coarse gravel (2-6 cm) of slightly hard Fe-oxide coated sandstone (quartz); few infilled large burrows

[§] {51}

[†] Rain onset period with 80% probability.

1.1.2 Ukiriguru

Site Description

Location	Agricultural Research Institute, Ukiriguru, Magu District, Mwanza Region, Tanzania
Elevation	1230 m a.s.l. (GPS estimate)
Topographic Map	Name: Ukiriguru, Sheet No. 34/1 (1:50,000)
Grid Co-ordinates	S 02.71778° E 033.03093°, UTM 36 M 503438 9699629 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Isohyperthermic, coarse loamy, kaolinitic Kanhaplic Haplustult WRBSR: Haplic Acrisol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Isohyperthermic
Climate	Mean annual air temperature: 22.4 °C (mean range: 17.6-27.2 °C) Mean annual precipitation: 800-1000 mm
Agro-ecological Zone[§]	P8. Medium altitude (1000-1200 m) plains with mainly hardpan soils and clays of moderate fertility in topographic depressions and sandy to medium-textured soils of low fertility developed on granites; short single (3-3.5 months) growing period with unreliable onset period; OP80[†]: Nov.-March
Geomorphology[§]	PPs3. The soil profile is located on the upper part of a straight footslope of an Inselberg on flat to gently undulating plains (0-3%) on the Central Plateau Gradient: 5-9% towards SE (within each terrace)
Parent Material	Granite
Land Use	Under cultivation (sweet potatoes, sorghum), ridging for potatoes
Vegetation	Grass, legume (Crotolaria sp.) in patches
Erosion	Presently nil. 20-25 m wide terraces separated by approx. 3 m wide grass vegetated erosion control lines
Drainage	Well drained
Depth to groundwater	Not known
Date of description	June 5 1998 by E. Semu and C. Szilas
Remarks	The soil surface was considered as half the height of the ridges. The site has according to local farmers never been fertilized.

Profile Description

Ap	0-28 cm	Dark brown (7.5 YR 3/3, moist); coarse sandy loam; weak fine sub-angular blocky; non-sticky, non-plastic, soft; interstitial voids, few medium vughs, common very fine and fine channels, few very fine planes, medium porosity; many very fine and fine and common medium roots; 6 vol-% fine gravel (2-4 mm) of angular non-weathered quartz; common termite/ant channels and nests; clear wavy boundary
AB	28-49 cm	Dark brown (7.5 YR 3/3, moist); coarse sandy loam; porous massive; non-sticky, non-plastic, friable; interstitial voids, few medium vughs, few fine channels, medium porosity; few fine and medium roots; 6 vol-% fine gravel (2-4 mm) of angular non-weathered quartz; few termite/ant channels and nests; clear smooth boundary
Bt1	49-75 cm	Dark brown (7.5 YR 3/4, moist) matrix with few faint diffuse medium yellowish red (5 YR 4/6, moist) rounded mottles; coarse sandy loam; porous massive; non-sticky, non-plastic, friable; interstitial voids, few coarse vughs, few fine and medium channels, medium porosity; slight bridging of sand grains by clay particles; few fine and medium roots; 8 vol-% fine gravel (2-4 mm) of angular non-weathered quartz; few termite/ant channels and nests; diffuse smooth boundary;
Bt2	75-132 cm	Dark brown (7.5 YR 3/4, moist) matrix with common faint diffuse medium yellowish red (5 YR 4/6, moist) rounded mottles; coarse loamy sand; porous massive; non-sticky, non-plastic, friable; interstitial voids, few medium vughs, few fine and medium channels, medium porosity; slight bridging of sand grains by clay particles; few fine and medium roots; 14 vol-% fine gravel (2-4 mm) of angular non-weathered quartz; few termite/ant channels and nests; diffuse smooth boundary
BC	132-180 cm	Dark brown (7.5 YR 3/4, moist) matrix with common faint diffuse medium yellowish red (5 YR 4/6, moist) rounded mottles; coarse loamy sand; porous massive; non-sticky, non-plastic, friable; interstitial voids, few medium vughs, few fine channels, medium porosity; fine and medium roots; 25 vol-% fine gravel (2-4 mm) of angular non-weathered quartz; few termite/ant channels and nests

[§] {51}

[†] Rain onset period with 80% probability.

1.1.3 Mlingano

Site Description

Location	Mlingano Experimental Farm, National Soil Service, Mlingano, Muheza District, Tanga Region, Tanzania
Elevation	160 m a.s.l.
Topographic Map	Name: Muheza, Sheet No. 130/2 (1:50,000)
Grid Co-ordinates	S 05.11471° E 038.86882°, UTM 37 M 485460 9434706 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Isohyperthermic, very fine, kaolinitic Rhodic Kandiustox WRBSR: Rhodic Ferralsol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Isohyperthermic
Climate	Mean annual air temperature: 26.5 °C (mean range: 21.7-31.3 °C) Mean annual precipitation: 1000-1400 mm
Agro-ecological Zone[§]	E6. Semi humid tropical lowlands, mainly plains with friable clays of low to moderate fertility; two short growing periods; Main: 4-4.5 months duration; OP80[†]: Feb.-Apr.; Secondary: 2.5-3 months; OP80: Jul.-Nov.
Geomorphology[§]	EPh1. The soil profile is located on the higher part of a straight slope on the undulating to rolling plains (< 750 m) of the Eastern Plateau Gradient: 1-2% towards NE
Parent Material	Intermediate metamorphic rocks
Land Use	Fallow
Vegetation	Forbland (more than 80% grass coverage)
Erosion	No signs of erosion
Drainage	Well drained
Depth to groundwater	Not known
Date of description	May 13 1998 by E. Semu and C. Szilas
Remarks	

Profile Description

Ap	0-25 cm	Dark reddish brown (2.5 YR 3/4, moist); sandy clay; weak medium granular; slightly sticky, slightly plastic, friable; interstitial voids, common fine channels and many very fine planes, high porosity; common fine, few medium and very few coarse roots; few termite/ants channels; gradual smooth boundary
Bto	25-52 cm	Dusky red (10 R 3/4, moist); sandy clay; porous massive; slightly sticky, slightly plastic, friable; interstitial voids, very few medium vughs, few medium channels, medium porosity; few faint cutans of clay and Fe-oxides in random patches; few fine and very few medium roots; few termite/ant channels and nests; diffuse smooth boundary
Bo1	52-105 cm	Dusky red (10 R 3/4, moist); sandy clay loam; porous massive; slightly sticky, slightly plastic, friable; interstitial voids, very few medium vughs, few fine channels, medium porosity; very few fine roots; few termite/ant channels and nests; diffuse smooth boundary
Bo2	105-180+ cm	Dusky red (10 R 3/4, moist); sandy clay loam; porous massive; slightly sticky, slightly plastic, friable; interstitial voids, very few medium vughs, few fine channels, medium porosity; very few fine roots; few termite/ant channels and nests

[§] {51}

[†] Rain onset period with 80% probability.

1.1.4 Magadu

Site Description

Location	Magadu Experimental Farm, Sokoine University of Agriculture, Morogoro District, Morogoro Region, Tanzania
Elevation	568 m a.s.l. (GPS estimate)
Topographic Map	Sheet No. 183/3 (1:50,000)
Grid Co-ordinates	S 06.85183° E 037.64165°, UTM 37 M 349906 9242488 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Isohyperthermic, very fine, kaolinitic Kanhaplic Haplustult WRBSR: Chromic Acrisol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Isohyperthermic
Climate	Mean annual air temperature: 24.0 °C (mean range: 18.8-29.1 °C) Mean annual precipitation: 800-1000 mm
Agro-ecological Zone[§]	E4. Semi humid tropical lowlands, mainly plains with predominantly friable clays of low to moderate fertility; one medium growing period of 4.5-6 months duration and with unreliable onset dates; OP80[†]: Dec.-Mar.; severely infested by tsetse fly
Geomorphology[§]	EPh1. The soil profile is located on the lower part of the alluvial fan of the Uluguru Mountains in the Ngerengere River Valley, which slightly dissects the undulating to rolling plains of the Eastern Plateau (< 750 m) Gradient: 1.5-2% slope towards NW
Parent Material	Alluvial material from intermediate metamorphic rocks from the Uluguru Mountains
Land Use	Cleared for recultivation after 4 years fallow
Vegetation	Grass and herbaceous plants (less than 40% coverage)
Erosion	No signs of erosion
Drainage	Moderately well drained
Depth to groundwater	Not known
Date of description	May 25 1998 by J.P. Møberg and C. Szilas
Remarks	The surface horizon was observed under dry conditions. The structure may be granular under moist conditions

Profile Description

Ap	0-10 cm	Dark brown (7.5 YR 3/4, moist); clay loam; porous massive; sticky, plastic, hard; interstitial voids, common fine channels, medium porosity; common very fine and fine roots; few termite/ants channels; clear smooth boundary
Bo	10-47 cm	Yellowish red (5 YR 4/6, moist); clay loam; porous massive; slightly sticky, slightly plastic, slightly hard; interstitial voids, few medium vughs and fine channels, medium porosity; few very fine and fine roots; few termite/ant channels and nests; diffuse smooth boundary
Bto1	47-125 cm	Yellowish red (5 YR 4/6, moist) matrix with very few fine distinct sharp yellowish brown (10 YR 5/6, moist) rounded mottles and streaks; clay loam; porous massive; slightly sticky, slightly plastic, friable; interstitial voids, few medium vughs, common fine channels, high porosity; very few faint cutans of clay and Fe-oxides in root channels and random patches; few fine and medium roots; few termite/ant channels and nests; diffuse smooth boundary
Bto2	125-180+ cm	Yellowish red (5 YR 4/6, moist) matrix with common fine distinct clear yellowish brown (10 YR 5/6, moist) rounded mottles; clay loam; porous massive; slightly sticky, slightly plastic, friable; interstitial voids, very few medium vughs, common very fine channels, high porosity; very few faint cutans of clay and Fe-oxides in root channels and random patches; few fine and medium roots; few termite/ant channels and nests

[§] {51}

[†] Rain onset period with 80% probability.

1.1.5 Msimba

Site Description

Location	Msimba Seed Farm, Kilosa District, Morogoro Region, Tanzania
Elevation	430 m a.s.l. (GPS estimate)
Topographic Map	Sheet No. 182/1 (1:50,000)
Grid Co-ordinates	S 06.74959° E 037.05107°, UTM 37 M 284582 9253571 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Isohyperthermic, fine, mixed Ultic Haplustalf WRBSR: Haplic Luvisol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Isohyperthermic
Climate	Mean annual air temperature: 26.7 °C (mean range: 21.9-31.5 °C) Mean annual precipitation: 1000-1400 mm
Agro-ecological Zone[§]	E9. Low altitude (400-500 m) flat alluvial plains with predominantly fertile clays bordering zone H7, which is mainly mountainous topography at higher altitude; medium growing period (4-6.5 months) and in lowland strongly influenced by rainfall ponding and runoff collection; severely infested by tsetse fly; unreliable onset period; OP80[†]: Dec.-Mar.
Geomorphology[§]	EM3. The soil profile is located on the lower part of the undulating to rolling (2-10%) footslopes of the Ukaguru Mountains bordering the flat alluvial Mkata plains (subsidence basin) on the Eastern Plateau Gradient: 4-8% towards E
Parent Material	Intermediate metamorphic rock (biotite, quartzite)
Land Use	Under cultivation (maize)
Vegetation	Grass and herbaceous weeds (<80% coverage)
Erosion	No signs of erosion
Drainage	Well drained
Depth to groundwater	Not known
Date of description	June 16 1998 by J.M.R. Semoka, E. Semu and C. Szilas
Remarks	Very poor maize crop showing clear signs of P deficiency. Lithic contact below 90 cm.

Profile Description

Ap	0-18 cm	Reddish black (2.5 YR 2.5/1, moist); sandy loam; moderate very fine angular blocky; slightly sticky, slightly plastic, hard; interstitial voids, common fine vughs and very fine and fine channels and planes, medium porosity; common very fine and fine roots; common termite/ant channels and nests; gradual smooth boundary
AB	18-33 cm	Dark reddish brown (5 YR 3/3, moist); sandy clay; porous massive; sticky, plastic, friable; interstitial voids, very few very coarse vughs, common very fine and fine channels, medium porosity; very few faint thin clay cutans in random patches; very few very fine roots; few rounded hard medium gravel (0.6-2 cm) of non-weathered quartzite; few termite/ant channels and nests; gradual smooth boundary
Bt	33-64 cm	Dark reddish brown (5 YR 3/4, moist) matrix with few fine distinct clear very dark brown (7.5 YR 2.5/2, moist) mottles (root remnants); sandy clay; moderate fine sub-angular blocky; sticky, plastic, friable; interstitial voids, common medium vughs, few fine and medium channels and very fine planes, medium porosity; few faint thin clay cutans on pedfaces; very few very fine roots; common rounded hard medium gravel (0.6-2 cm) of slightly weathered quartzite/biotite/feldspar; few termite/ant channels and nests; abrupt smooth boundary
BC	64-90 cm	Dark reddish brown (5 YR 3/4, moist); sandy clay; porous massive; sticky, plastic, friable; interstitial voids, few fine channels, medium porosity; very few very fine roots; approx. 33 vol-% rounded and irregular coarse gravel and stones (< 10 cm) of slightly weathered quartzite/biotite/feldspar; few termite channels

[§] {51}

[†] Rain onset period with 80% probability.

1.1.6 Suluti

Site Description

Location	Suluti Experimental Substation, Songea District, Ruvuma Region, Tanzania
Elevation	924 m a.s.l. (GPS estimate)
Topographic Map	Sheet No. 300/1 (1:50,000)
Grid Co-ordinates	S 10.54447° E 036.08035°, UTM 37 L 180430 8833003 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Isohyperthermic, very fine, kaolinitic Rhodic Kanhaplustalf WRBSR: Rhodic Acrisol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Isohyperthermic
Climate	Mean annual air temperature: 21.8 °C (mean range: 16.4-27.2 °C) Mean annual precipitation: 1000-1400 mm
Agro-ecological Zone[§]	E7. Semi humid medium altitude plains with predominantly friable clays of low to moderate fertility; one medium and reliable growing period of 5-7 months duration; severely infested by tsetse fly; OP80[†]: Nov.-Dec.
Geomorphology[§]	EPh6. The soil profile is located on an almost flat dissected plain at medium altitude (750-1300 m) on the Eastern Plateau Gradient: 2% towards E
Parent Material	Intermediate metamorphic rocks
Land Use	Fallow for the last 5 years, previously normal maize production
Vegetation	Grass (more than 80% coverage)
Erosion	Nil at present but probably interrill earlier
Drainage	Well drained
Depth to groundwater	Not known
Date of description	May 22 1998 by E. Semu and J.P. Møberg
Remarks	The surface horizon and the AB were observed under dry conditions. The structure may be granular in the Ap under moist conditions. Augering down to about 230 cm indicated that the soil was similar as at 180 cm depth.

Profile Description

Ap	0-15 cm	Dark reddish brown (2.5 YR 3/3, moist); sandy loam; porous massive; slightly sticky, slightly plastic, hard; interstitial voids, very few medium vughs and few fine channels, medium porosity; common very fine and fine roots; few termite/ant channels and nests; clear smooth boundary
AB	15-25 cm	Reddish brown (2.5 YR 4/4, moist); sandy loam; porous massive; slightly sticky, slightly plastic, very hard; interstitial voids, few medium vughs, many very fine channels, medium porosity; common very fine roots; common termite/ant channels and nests; gradual smooth boundary
Bo1	25-70 cm	Dark red (2.5 YR 3/6, moist); clay loam; porous massive; slightly sticky, slightly plastic, friable; interstitial voids, common fine to medium vughs and fine channels, high porosity; common very fine and few fine and medium roots; few very fine black nodules (Mn-oxides or organic matter); common termite/ant channels and nests; diffuse smooth boundary
Bo2	70-120 cm	Dark red (2.5 YR 3/6, moist) matrix with few fine distinct black rounded mottles; clay loam; porous massive; slightly sticky, slightly plastic, friable; interstitial voids, very few medium vughs, few fine channels, high porosity; few very fine and few fine roots; few very fine weathered black rock residues; few termite/ant channels and nests; diffuse smooth boundary
Bo3	120-180+ cm	Dark red (2.5 YR 3/6, moist); clay loam; porous massive; slightly sticky, slightly plastic, friable; interstitial voids; few fine channels, high porosity; few very fine and very few medium roots;

[§] {51}

[†] Rain onset period with 80% probability.

1.1.7 Lubonde

Site Description

Location	Lubonde near Ng'anda village, Njombe District, Iringa Region, Tanzania
Elevation	2131 m a.s.l. (GPS estimate)
Topographic Map	Sheet No. 261/3 (1:50,000)
Grid Co-ordinates	S 09.33577° E 034.57393°, UTM 36 L 672859 8967734 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Isothermic, fine, Humic Rhodic Haplustox WRBSR: Humic Ferralsol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Isothermic
Climate	Mean annual air temperature: 15.2 °C (mean range: 9.7-20.6 °C) Mean annual precipitation: 1000-1400 mm
Agro-ecological Zone[§]	H5. Volcanic highlands with plateau and strongly dissected landforms covered by volcanic ash soils (not at this particular location); long and often continuous growing periods of 6-12 months duration; OP80[†]: Nov.-Dec.
Geomorphology[§]	HP3. The soil profile is located in the Southern Highlands on the middle part of a straight slope on the undulating to rolling plains and plateau at high altitude (1800-2400 m) with mountainous ridges and steep-sided valleys Gradient: 6-7% towards NE
Parent Material	Basement complex rocks
Land Use	Under cultivation (potatoes, maize), ridging for potatoes
Vegetation	Originally highland tropical forest
Erosion	Potential splash, interrill and rill erosion
Drainage	Well drained
Depth to groundwater	Not known
Date of description	May 20 1998 by J.M.R. Semoka and C. Szilas
Remarks	Ridging has probably been done down to approx. 50 cm. The soil surface was considered as half the height of the ridges. The site has recently been fertilized with TSP. Apparently the soil is not covered by volcanic ash like some of the surrounding soils.

Profile Description

Ap1	0-25 cm	Very dusky red (2.5 YR 2.5/2, moist); sandy loam; very weak very fine granular and fine sub-angular blocky; slightly sticky, slightly plastic, friable; interstitial voids, common very fine channels, few very fine planes, high porosity; many very fine roots; few small to medium dark reddish brown (2.5 YR 3/4, moist) rounded soft iron concretions; few termite/ant channels; gradual smooth boundary
Ap2	25-55 cm	Very dusky red (2.5 YR 2.5/2, moist); sandy loam; weak medium sub-angular blocky; slightly sticky, slightly plastic, friable; interstitial voids, common very fine channels and planes, high porosity; few very fine and fine roots; few medium dusky red (2.5 YR 3/4, moist) rounded soft iron concretions; few termite/ant channels; clear wavy boundary
Bom	55-64 cm	Dark reddish brown (2.5 YR 3/4, moist); sandy clay loam; porous massive; sticky, plastic, firm; interstitial voids, common very fine channels, medium porosity; very few very fine roots; very few very fine Fe-oxide nodules (same colour as matrix); continuous compacted layer probably caused by cultivation; few termite/ant channels; clear smooth boundary
Bo1	64-125 cm	Dusky red (10 R 3/4, moist); sandy loam; porous massive; slightly sticky, slightly plastic, friable; interstitial voids, few very fine channels, high porosity; few very fine and fine roots; infilled large burrows or root remnants; gradual smooth boundary
Bo2	125-180+ cm	Dusky red (10 R 3/4, moist); sandy loam; porous massive; slightly sticky, slightly plastic, firm; interstitial voids, few very fine and fine channels, medium porosity; few very fine roots; continuous somewhat compacted layer; few termite/ant channels

[§] {51}

[†] Rain onset period with 80% probability.

1.1.8 Mpangala

Site Description

Location	Mpangala School near Matamba village, Makete District, Iringa Region, Tanzania
Elevation	2250 m a.s.l. (GPS estimate)
Topographic Map	Sheet No. 245/4 (1:50,000)
Grid Co-ordinates	S 08.98872° E 033.93526°, UTM 36 L 602808 9006355 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Thermic Andic Dystrustept WRBSR: Andic Cambisol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Thermic
Climate	Mean annual air temperature: 15.3 °C (mean range: 8.9-21.6 °C) Mean annual precipitation: 1000-1400 mm
Agro-ecological Zone[§]	H5. Volcanic highlands with plateau and strongly dissected landforms covered by volcanic ash soils; long and often continuous growing periods of 6-12 months duration; OP80[†]: Nov.-Dec.
Geomorphology[§]	HP3. The soil profile is located in the Southern Highlands on the lower part of a straight slope on the undulating to rolling plains and plateau at high altitude (1800-2400 m) with mountainous ridges and steep-sided valleys Gradient: 17% towards NE
Parent Material	Basement complex rocks covered by volcanic ashes
Land Use	Under cultivation (wheat, potatoes, maize)
Vegetation	Originally highland tropical forest
Erosion	Active interrill and rill erosion. 10-25% of area moderately affected
Drainage	Well drained
Depth to groundwater	Not known
Date of description	May 19 1998 by J.M.R. Semoka and J.P.Møberg
Remarks	Quite fresh pieces of pumice were observed in the Bw1 and Bw2 horizons, and more weathered pyroclastic material in the Bw2 horizon. More coarse material was present below 180 cm and sticky and plastic red clay (5 YR 3/3, moist) at about 250 cm. Bulk density of the volcanic ash is estimated to be less than 0.7 g cm^{-3}.

Profile Description

Ap	0-20 cm	Black (7.5 YR 2.5/1, moist); loamy sand; weak medium granular; non-sticky, non-plastic; friable; interstitial voids, few fine channels and fine planes, very high porosity; many very fine and fine roots; abrupt smooth boundary
A	20-55 cm	Very dark brown (7.5 YR 2.5/2, moist); sandy loam; weak medium sub-angular blocky; non-sticky, slightly plastic, friable; interstitial voids, common very fine channels and few very fine planes, very high porosity; common fine and few medium roots; few medium yellowish brown (10 YR 5/6, moist) rounded soft pieces of pumice; infilled large burrows (Krotovinas); gradual smooth boundary
Bw1	55-95 cm	Very dark brown (7.5 YR 2.5/3, moist); sandy loam; weak medium to coarse sub-angular blocky; slightly sticky, slightly plastic, friable; interstitial voids, common fine channels and few very fine planes, high porosity; common very fine and few fine roots; few fine yellowish brown (10 YR 5/6, moist) rounded and elongated soft pieces of pumice and few reddish rounded soft Fe-oxide nodules; infilled large burrows (Krotovinas); diffuse smooth boundary
Bw2	95-150 cm	Dark brown (7.5 YR 3/4, moist) matrix with dark yellowish brown (10 YR 4/6, moist) streaks of pyroclastic material; loam; porous massive; sticky, slightly plastic, friable; interstitial voids, common very fine channels, high porosity; very few very fine roots; few fine dark red (10 R 3/6, moist) rounded soft pieces of pumice; arbitrary boundary
Bw3	150-180 cm	Strong brown (7.5 YR 4/6, moist); otherwise as above

[§] {51}

[†] Rain onset period with 80% probability.

1.1.9 Sasanda

Site Description

Location	Sasanda near Mbimba Experimental Substation, Mbozi District, Mbeya Region, Tanzania
Elevation	1650 m a.s.l. (GPS estimate)
Topographic Map	Sheet No. 258/1 (1:50,000)
Grid Co-ordinates	S 09.16039° E 033.03262°, UTM 36 L 503584 8987508 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Isohyperthermic, medial, mixed Dystric Haplustand WRBSR: Umbric Andosol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Isohyperthermic
Climate	Mean annual air temperature: 19.0 °C (mean range: 13.0-24.9 °C) Mean annual precipitation: 1000-1400 mm
Agro-ecological Zone[§]	H5. Volcanic highlands with plateau and strongly dissected landforms covered by volcanic ash soils; long and often continuous growing periods of 6-12 months duration; OP80[†]: Nov.-Dec.
Geomorphology[§]	HP5. The soil profile is located on the lower part of a straight slope on the undulating medium to high altitude (1200-1600 m) plateau of the Southern Highlands Gradient: 2-5% towards S
Parent Material	Gneissic rocks covered by volcanic pumice and ash (from Mt. Rungwe)
Land Use	Fallow
Vegetation	Grasses and ferns (more than 80% coverage), originally highland tropical forest
Erosion	No signs of erosion
Drainage	Well drained
Depth to groundwater	Not known
Date of description	May 18 1998 by J.M.R. Semoka and C. Szilas
Remarks	Remnants of ridges used during previous cultivation. Bulk density of the volcanic ash is estimated to be less than 0.7 g cm^{-3}

Profile Description

Ap	0-32 cm	Very dark brown (7.5 YR 2.5/2, moist); loam to silt loam; weak medium granular and fine sub-angular blocky; non-sticky, non-plastic; friable; interstitial voids, common very fine channels and planes, very high porosity; common very fine and few fine roots; very few medium dark yellowish brown (10 YR 3/6, moist) rounded soft pieces of pumice; few open large burrows and termite/ant channels; clear wavy boundary
Bw1	32-65 cm	Dark brown (7.5 YR 3/4, moist); loam; weak medium granular and fine sub-angular blocky; sticky, slightly plastic, friable; interstitial voids, very few coarse vughs, few fine channels and very fine planes, very high porosity; few very fine and very few fine roots; very few fine dark yellowish brown (10 YR 3/4, moist) rounded soft pieces of pumice; few termite/ant channels and nests; diffuse smooth boundary
Bw2	65-125 cm	Dark brown (7.5 YR 3/4, moist); loam; weak medium to coarse sub-angular blocky; sticky, slightly plastic, friable; interstitial voids, very few coarse vughs, few fine channels and very fine planes, very high porosity; few very fine roots; very few fine very dark greyish brown (10 YR 3/2, moist) rounded soft pieces of pumice; few faint cutans of clay on ped faces; few termite/ant channels and nests; diffuse smooth boundary
Bw3	125-180 cm	Dark brown (7.5 YR 3/4, moist); loam; weak medium sub-angular blocky; sticky, slightly plastic, friable; interstitial voids, few fine vughs and channels, very high porosity; very few fine roots; very few fine yellowish brown (10 YR 5/8, moist) rounded soft pieces of pumice; few termite/ant channels and nests

[§] {51}

[†] Rain onset period with 80% probability.

1.1.10 Nkundi

Site Description

Location	Nkundi Experimental Substation, Nkansi District, Rukwa Region, Tanzania
Elevation	1927 m a.s.l. (GPS estimate)
Topographic Map	Sheet No. 206/4 (1:50,000)
Grid Co-ordinates	S 07.87022° E 031.42288°, UTM 36 M 326124 9129801 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Thermic, fine, kaolinitic Acruoxic Kandiustult WRBSR: Chromic Acrisol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Thermic
Climate	Mean annual air temperature: 17.2 °C (mean range: 11.1-23.3 °C) Mean annual precipitation: 1000-1400 mm
Agro-ecological Zone[§]	U, High altitude plains and plateau covered by sandy and loamy soils of low fertility; mainly one medium growing period of 5-6.5 months duration and with reliable onset dates; OP80[†]: Nov.-Dec.
Geomorphology[§]	U1, The soil profile is located on the middle part of a straight slope on the flat to very gently undulating high altitude plains (1400-2000 m) of the Ufipa Plateau Gradient: 4-5% towards S
Parent Material	Gneisses and schists
Land Use	10 years fallow following 5 years wheat
Vegetation	Grassland with scattered shrubs (more than 80% grass coverage)
Erosion	No signs of erosion
Drainage	Well drained
Depth to groundwater	Not known
Date of description	May 16 1998 by J.M.R. Semoka and C. Szilas
Remarks	Large abandoned and eroded termite mounds (approx. 2 pr. ha) and smaller active mounds less than 50 cm high (approx. 500 pr. ha)

Profile Description

Ap	0-8 cm	Very dark brown (7.5 YR 2.5/2, moist); loamy sand; moderate medium granular; slightly sticky, slightly plastic, slightly hard; interstitial voids, very few fine channels and common very fine planes, high porosity; common fine roots; few very fine and fine rounded hard red and black Fe/Mn nodules; few fine angular gravel of quartzite; few termite/ant channels; clear smooth boundary
A	8-29 cm	Dark brown (7.5 YR 3/4, moist); loamy sand; weak very fine to fine sub-angular blocky; slightly sticky; slightly plastic; slightly hard; interstitial voids; very few very fine channels and planes, medium porosity; few fine roots; few very fine and fine rounded hard red and black Fe/Mn nodules; few fine angular gravel of quartzite; few termite/ant channels; clear smooth boundary
AB	29-62 cm	Yellowish red (5 YR 4/6, moist) matrix with few fine sharp distinct black (10 YR 2/1, moist) streaks of old root remnants; loamy sand; very weak very fine sub-angular blocky; slightly sticky, slightly plastic, slightly hard; interstitial voids, very few very fine channels and planes, medium porosity; very few very fine roots; few very fine and fine rounded hard red and black Fe/Mn nodules; few fine angular gravel of quartzite; few termite/ant channels; diffuse smooth boundary
Bo1	62-135 cm	Yellowish red (5 YR 4/6, moist) matrix with few fine sharp distinct very dark brown (10 YR 2/2, moist) streaks of old root remnants; sandy loam; very weak fine sub-angular blocky; slightly sticky, slightly plastic, slightly hard; very few medium vughs, very few very fine channels and planes, medium porosity; very few very fine and medium roots; few very fine and fine rounded hard red and black Fe/Mn nodules; few fine angular gravel of quartzite; few termite/ant channels and nests
Bo2	135-180 cm	As above

[§] {51}

[†] Rain onset period with 80% probability.

1.1.11 Ihanda (soil only used in laboratory dissolution study).

Site Description

Location	Near Ihanda village, Mbozi District, Mbeya Region
Elevation	1895 m a.s.l. (GPS estimate)
Topographic Map	Sheet No. 257/2 (1:50,000)
Grid Co-ordinates	S 09.15749° E 032.87817°, UTM 36 L 486615 8987826 (map datum: Arc1950)
Soil Classification	Soil Taxonomy (8th ed. 1998): Thermic, very fine, kaolinitic Rhodic Kandiustult WRBSR: Chromic Acrisol
Soil Climate	Soil moisture regime: Ustic Soil temperature regime: Thermic
Climate	Mean annual air temperature: 17.4 °C (mean range: 11.3-23.5 °C) Mean annual precipitation: 1000-1400 mm
Agro-ecological Zone[§]	H5, Semi humid tropical highlands, mainly dark loamy soils of moderate natural fertility developed on volcanic ash and pumice or heavy textured soils with high organic matter content; one medium to long growing period of 6-12 months duration; OP80[†]: Nov.-Dec.
Geomorphology[§]	HU2, The soil profile is located on the lower part of a straight slope in the rolling to hilly rift benches, plateaux and plains of the Southern Highlands Gradient: 1-2 % towards NW
Parent Material	Basic crystalline rocks
Land Use	Permanent fallow as part of field boundary
Vegetation	Grasses, trees and shrubs
Erosion	No signs of erosion
Drainage	Well drained
Depth to groundwater	Not known
Date of description	March 27 1999 by O.K. Borggaard and C. Szilas
Remarks	

Profile Description

A	0-30 cm	Dark brown (7.5 YR 3/2, moist); clay; strong fine to medium granular; slightly sticky, slightly plastic, friable; interstitial voids, many fine channels, medium porosity; many fine and few coarse roots; very few fine rounded hard and soft iron concretions; few termite/ants channels; gradual smooth boundary
AB	30-40 cm	Dark reddish brown (5 YR 3/3, moist); clay; weak fine to medium sub-angular blocky; slightly sticky, slightly plastic, firm; interstitial voids, many very fine planes, medium porosity; few faint non-coherent cutans of clay on pedfaces; few fine and very few coarse roots; very few very fine rounded soft iron concretions; few termite/ant channels; diffuse wavy boundary
Bto1	40-80 cm	Dark reddish brown (2.5 YR 3/4, moist); clay; weak fine to medium sub-angular blocky; slightly sticky, slightly plastic, friable; interstitial voids, many very fine and fine and very few coarse planes, medium porosity; few faint non-coherent cutans of clay on pedfaces; few very fine and fine and very few coarse roots; many termite/ant channels; gradual smooth boundary
Bto2	80-130 cm	As Bto1 except that matrix colour is dusky red (10 R 3/4, moist) and that the horizon lacks biological features such as termite/ant channels

[§] {51}

[†] Rain onset period with 80% probability.

1.2 Agro-ecological zones

Soil types and moisture zones as defined by de Pauw {51} were given an index value corresponding to the assumed suitability for direct application of MPR (1=very good, 2=good, 3=moderate and 4=poor) (see table below and refer to de Pauw {51} for more information).

Soil index[1]

Soil Number	Index	Soil Number	Index
1	4	22	3
2	4	23	1
3	4	24	1
4	4	25	1
5	4	26	2
6	3	27	1
7	1	28	1
8	2	29	3
9	2	30	3
10	4	31	3
11	3	32	2
12	1	33	3
13	2	34	4
14	1	35	3
15	1	36	4
16	4	37	4
17	4	38	3
18	4	39	4
19	4	40	3
20	4	41	1
21	3		

[1] 1=very good, 2=good, 3=moderate, 4=poor.

Moisture index[1]

Moisture zone	Index	Moisture zone	Index
su1	4	sh5	1
su2	4	sc1	2
su3	3	sc2	1
su4	2	sc3	1
su5	1	sc4	1
sm1	3	sc5	1
sm2	3	sc6	1
sm3	2	sc7	1
sm4	1	sc8	1
sm5	1	dm1	1
sh1	2	dm2	1
sh2	1	dm3	3
sh3	1	du	4
sh4	1		

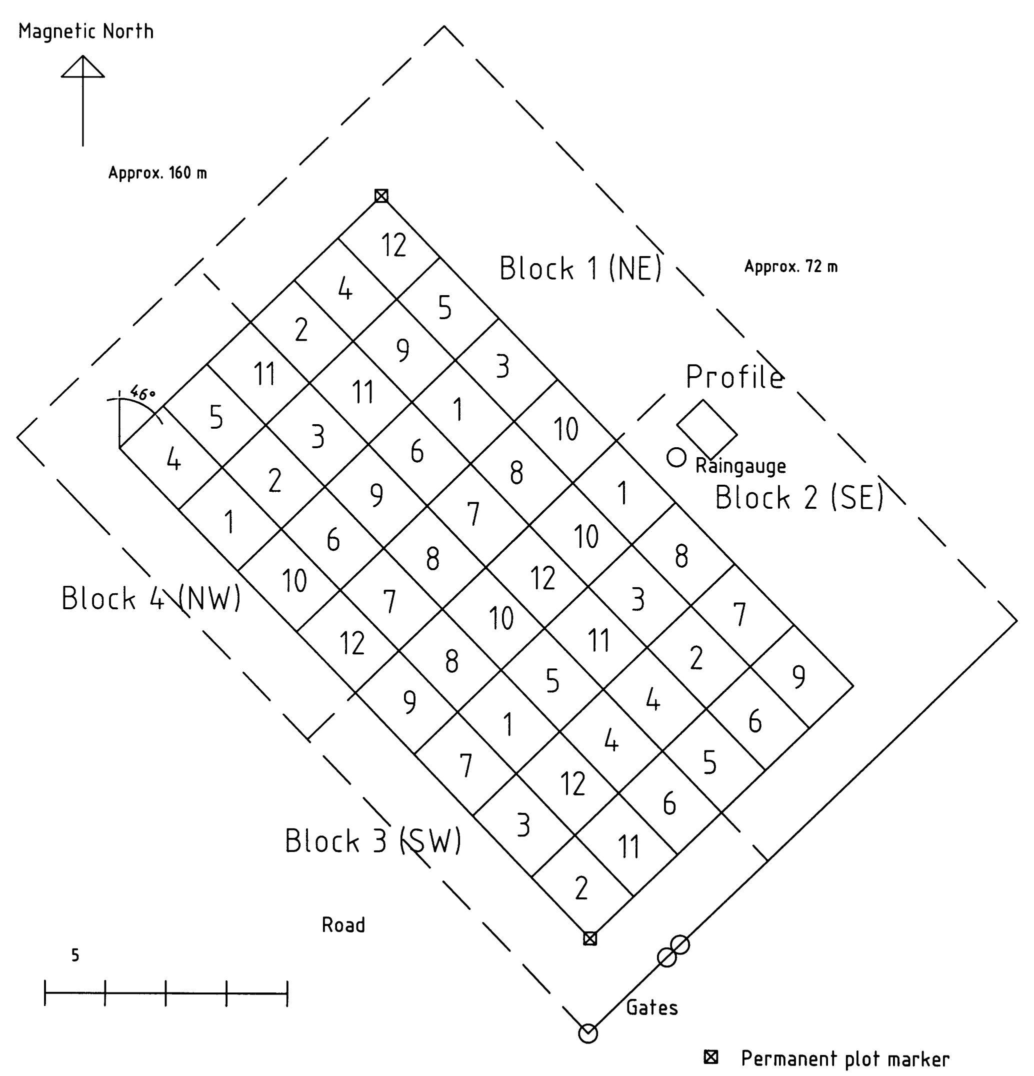
The combined effect of soil type and moisture characteristics was then used to classify the area of each agro-ecological zone into four MPR suitability classes as described in the table below.

MPR suitability class.

	Moisture index			
Soil index	1	2	3	4
1	Highly suitable	Highly suitable	Suitable	Moderately suitable
2	Highly suitable	Suitable	Suitable	Moderately suitable
3	Suitable	Suitable	Moderately suitable	Not suitable
4	Moderately suitable	Moderately suitable	Not suitable	Not suitable

1.3 Example of field experimental design

4. Magadu



Gross plot area: 5 x 7 m = 35 m2	Net plot area: 4.167 x 6 = 25 m2

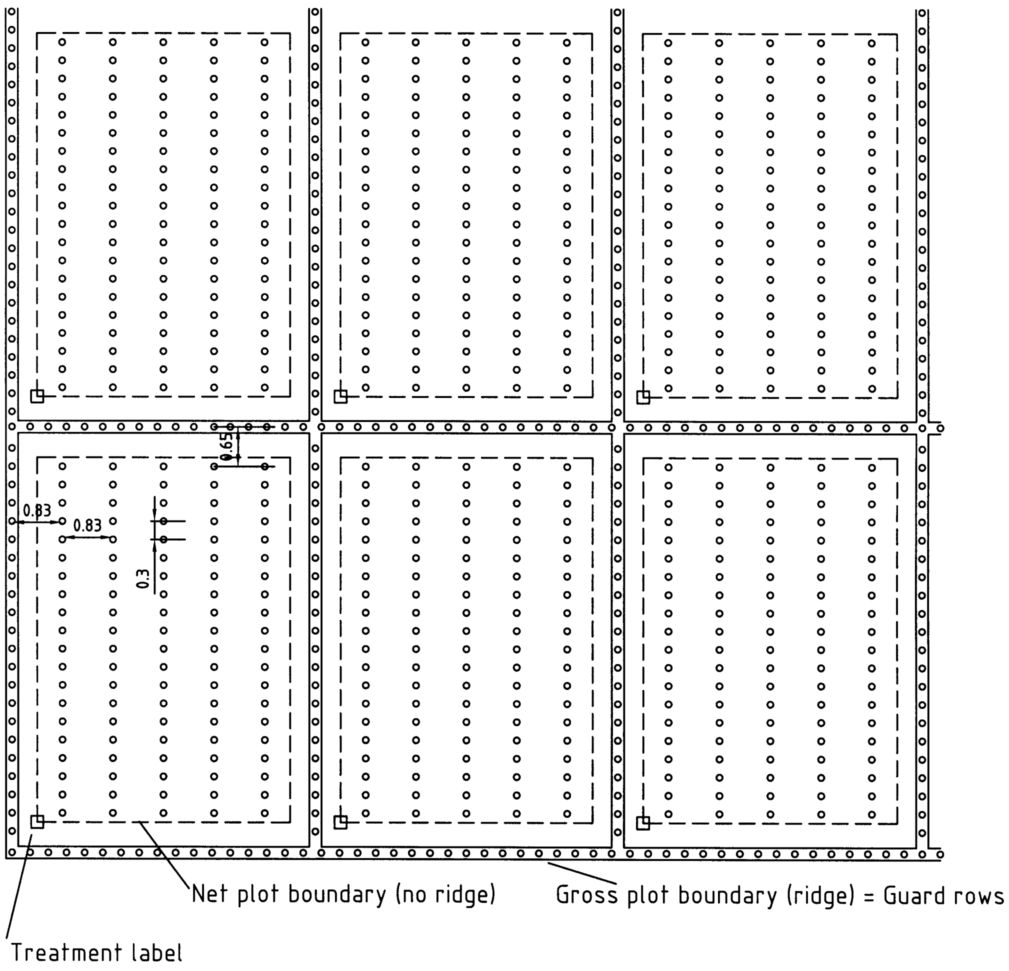
Basic nutrient application:
N: 40+40 kg N/ha as $(NH_4)_2SO_4$ (except for treatment no. 1 and 3)
Zn: 10 kg Zn/ha as Zn_2SO_4

Treatments:
1. Control (no N, P or any other nutrients)
2. Control for P (no P appl.), basic N appl. (80 kg N/ha)
3. Control for N (no N appl.), 40 kg P/ha as Minjingu PR
4. Triple super phosphate 40 kg P/ha
5. Triple super phosphate 80 kg P/ha
6. Triple super phosphate 120 kg P/ha
7. Granulated Minjingu phosphate rock 40 kg P/ha
8. Granulated Minjingu phosphate rock 80 kg P/ha
9. Granulated Minjingu phosphate rock 120 kg P/ha
10. Non-granulated Minjingu phosphate rock 40 kg P/ha
11. Non-granulated Minjingu phosphate rock 80 kg P/ha
12. Non-granulated Minjingu phosphate rock 120 kg P/ha

Location of profile: S 6.85183° E 037.64165°		Elevation: 568 m asl.	Morogoro District	Morogoro Region
Scale: 1:500	Latest revision: 2000/07/07	SUA-KVL Minjingu Phosphate Rock Project 1998-2003		

Appendix 1.3. Example of field experimental design

Plot Layout



Gross plot size = 5x7m = 35m2
Net plot size = 4.167x6m = 25 m2
Number of plants per net plot = 5 rows × 20 plants = 100
Row spacing within net plot = 83.3 cm
Row spacing between outer row and guard row = 83.3 cm
Plant spacing = 30 cm (both plot rows and guard rows), first plant is 65 cm from guard row.
Basal macro/micro nutrients and phosphorus are applied to the gross plot (35 m2).
Nitrogen for the net plot (5 rows x 20 plants = 25 m2) is applied from small preweighed bags, whereas nitrogen for the guard rows is applied from 50 kg bags of SA according to instructions.

Scale = 1:100	Latest revision: 2000/07/07

1.4 The PRUP and MPR database

Both the data collected during PRUP and the previous MPR related data described in Chapter 5.1 are compiled into Microsoft Excel workbook files. The structure of the databases is seen below.

Overview of the PRUP database structure.

Sheet name	**Content**	**No. of variables**
1. Site	Specific data regarding each experimental site	35
2. Horizon	Specific data regarding each identified horizon of the described soil profile at each experimental site	23
3. Chemist	Soil analytical data from each identified horizon	39
4. Physics	Soil physical data from each identified horizon	26
5. Mineral	Soil mineralogical data from each identified horizon	27
6. Fieldexp	Grain yield and element uptake from each experimental site	31
7. Precip	Precipitation data from each experimental site	4
8. Fieldvar	Analytical data from each of the four blocks at each experimental site	24
9. Incub	Analytical data from laboratory dissolution experiment	27
10. Dissol	Analytical data from the annual soil sampling at each experimental site	23

Overview of the MPR database structure.

Sheet name	**Content**	**No. of variables**
1. Mprsoil	Soil analytical data for soils used in MPR experiments (MPR database, Ch. 5.1)	26
2. Mprexp	Yield and nutrient uptake for pot and field experiments (MPR database, Ch. 5.1)	12
3. Mprdiss	Effects of P application on soil properties (MPR database, Ch. 5.1)	16

Both database files including detailed descriptions are available at: www.kemi.kvl.dk/~casz
or through direct inquiry to Casper Szilas: casz@bigfoot.com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