

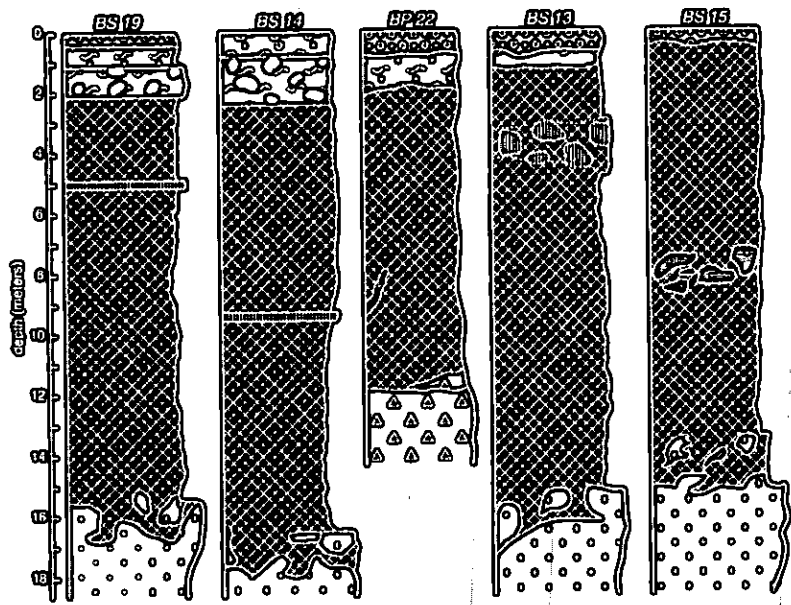
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GEOLOGICA ULTRAIECTINA

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Faculteit Aardwetenschappen
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No. 192

MINERALOGY AND GEOCHEMISTRY OF BAUXITE AND BENTONITE DEPOSITS FROM MOZAMBIQUE



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MOZAMBIQUE**

PROEFSCHRIFT

**TER VERKRIJGING VAN DE GRAAD VAN DOCTOR .
AAN DE UNIVERSITEIT UTRECHT
OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. H. O. VOORMA,
INGEVOLGE HET BESLUIT VAN HET COLLEGE VOOR PROMOTIES
IN HET OPENBAAR TE VERDEDIGEN
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DOOR

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GEBOREN OP 12 JANUARI 1960, TE MANICA, MOZAMBIQUE**

PROMOTOR: PROF. DR. R. D. SCHUILING

THE STUDIES CARRIED OUT AND DESCRIBED IN THIS THESIS HAVE BEEN CONDUCTED WITHIN THE FRAMEWORK OF A COOPERATION PROGRAM BETWEEN THE FACULTY OF EARTH SCIENCES OF UTRECHT UNIVERSITY, THE NETHERLANDS AND THE DEPARTMENT OF GEOLOGY OF THE EDUARDO MONDLANE UNIVERSITY, MAPUTO, MOZAMBIQUE. THE PROGRAM IS FINANCIALLY SUPPORTED BY NUFFIC

To my Parents,

and my Brothers and Sisters

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PREFACE & ACKNOWLEDGEMENTS

The present thesis is the result of geological research carried out in different stages on the subjects of bauxite and kaolinitic clays, as well as of bentonites in Mozambican territory. Initial data collection was carried out from 1986 till 1992, during the implementation of projects for mineral exploration and economic evaluation of their deposits undertaken by the National Directorate of Geology (DNG). During this period, all chemical data were limited to some major components of the mentioned mineral commodities, and to certain physical-chemical properties, which govern their immediate traditional applications. In 1992 a research project was initiated within the framework of a cooperation project between the Department of Geology, Eduardo Mondlane University and the Faculty of Earth Sciences of Utrecht University. The project aimed to study processes of weathering/low temperature alteration and their products, taking the bauxites, bentonites and laterites in Mozambique as the main subject. At the start of the research it was thought that, as a starting point for the systematic description of the deposits, it was best to compare two contrasting geological settings where deposits are being mined. For this purpose, in 1993/1994, chemical analysis was extended to include trace and Rare Earth Elements, and chemical characterization of waters, in order to bring out insight into processes of chemical and mineral weathering and alteration to bentonites, bauxites and kaolinitic clays.

It is thanks to several individuals and institutes that this work could be executed and for this I wish to address my gratefulness, particularly to: Professor Dr. R. D. Schuiling, Department of Geochemistry UU, my promotor in this work since the early stages of the research, for his attendance and recommendation, in the field in Mozambique and during my stay in Utrecht, and for the review of the thesis manuscript. Dr. Robert O. Felius for his companionship, suggestions and advice during great parts of the work and the preparation of the early version of the thesis manuscript. Members of the reading committee are thanked for the useful suggestions that they made for improvement of the thesis manuscript.

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SUMMARY

Results of mineralogical and geochemical studies of bauxites, kaolinitic clays and bentonites from Mozambique are presented in this thesis. The bauxite and kaolinitic clay deposits in Penhalonga area (in the central western part of Mozambique) are associated with Precambrian magmatic rocks and the bentonites resulted from weathering of volcanic rocks, belonging to the Lebombos Mountain range in the Boane district (in the south of Mozambique).

The bauxites and kaolinitic clays are the main products resulting from weathering of rock types with anorthositic, gabbroic composition and metabasalts. These parent rocks have been subjected to different degrees of weathering witnessed by the presence in the profiles of the minerals gibbsite, kaolinite, hydroxides and oxides of iron, as well as illite in variable amounts. The distribution of major and trace elements, including the Rare Earths, in the weathering profiles provides indications for the main development trends of the bauxitization-lateritization in Penhalonga area. Bauxite formation took place over the main rocks of the area mineralogically with feldspars and pyroxenes and/or amphiboles as the dominant primary components under influences of processes of weathering in tropical conditions.

Although most of the weathering sequences are truncated, due to superficial erosion, the general behaviour of the chemical elements reflects the composition of the source rock and, to some extent, the dominant conditions for the geochemical mobility and fractionation of the elements. This guides to the separation of the easily mobile elements like the alkalis and alkaline earths and the less mobile or immobile elements. The later group is represented by elements as Al, Fe, Ti, Zr, which are relatively retained in the weathered profiles, in almost all stages. Remarkable in the weathering sequences is the behaviour of the Rare Earth elements (REE), specially the elements Ce and Eu, which display anomalies, due to their chemistry. On the other hand, taking into consideration the activities of Na^+ , K^+ , Ca^{2+} and H_4SiO_4 , the composition of the waters draining the area also provides evidence of the principal mineral assemblages present in the weathering sequences.

In the Mozambican territory, associated with the volcanics of the Lebombos mountains, smectite-rich bentonites constitute deposits of economic interest. The principal mineral is montmorillonite in concentrations ranging up to an average grade of 75-79% and invariably associated with silica phases, chiefly cristobalite. According to referenced discrimination diagrams the bentonites have close affinity with parent rocks of rhyolitic and rhyodacitic compositions. However, the mechanisms of the bentonite formation are still poorly understood, although, from field relationships and the geological setting of the bentonitic masses, it seems that they have originated from miscellaneous processes of alteration of the rhyolitic parent rocks.

The bentonites are chemically of the Ca-type with high silica SiO_2 and generally low contents in Al_2O_3 and MgO , features, which are strictly related to the parent rocks of dominantly rhyolitic composition.

In some places occurrences of indurated calcium carbonate horizons are observed in a vertical profile. Geochemically the bentonites show a uniform composition, which is also reflected in the trace element content. The behaviour of the chemical elements is consistent with the general effects of an alkaline environment on the mobilization and fixation of elements propitiating formation of bentonites instead of zeolites.

CHAPTER I

1. INTRODUCTION

1.1. General considerations and concepts

In general terms, weathering is a reaction of the hydrosphere-atmosphere-biosphere with the lithosphere. It involves several processes (Pickering, 1989; Trescasses, 1992), which take place at the surface or near the surface of the earth's crust. Under conditions at the earth's surface, weathering provokes chemical decay and physical fragmentation of rocks and minerals formed at high pressures and temperatures in the interior of the earth (Press and Siever, 1986; Drever, 1988; Thorez, 1989; Trescasses, 1992). The breakdown of rocks and minerals to sediments is the result of chemical weathering combined with the forces of physical disintegration (Kronberg and Fyfe, 1989; Coleman and Dithier, 1986). In a simplified way the general schema of weathering reactions can be written (Thorez, 1989; Drever, 1988; Schuiling et al., 1994).

Parent rocks and minerals + solutions → Residual minerals + Secondary minerals + Solutions

The solutions, besides water (H₂O), contain the atmospheric gases carbon dioxide (CO₂) and oxygen (O₂) as reactants. The residual minerals are represented by the stable/resistant or still unweathered minerals.

The weathering intensity is largely dependent on the nature of the parent rock, climate, geomorphology and time (Lucas and Chauvel, 1992; Butt and Zeegers, 1992). In the geochemical processes of weathering, the original rock, usually silicate bearing, gives the lithological parameters. The mineral composition and amount, solubility of the elements and, naturally, texture and structure of the parent rock define these parameters.

The physico-chemical characteristics are given by pH-Eh conditions, state of ionic dissociation, concentrations of ions and temperature (Thorez, 1989). The action of all these parameters is rather complex and interconnected. Another important aspect to be considered is related to the duration of the reactions, which in turn is influenced by the climate, geomorphology, biological activity (vegetation and animals). Basically the processes of geochemical weathering can be visualized in terms of closed-system transformations, which influence crystallization of secondary minerals from saturated weathering solutions in sedimentary basins. In systems that are more open, the hydrosphere, climate and topography play a more dominant role in mineral transformations (Thorez, 1989; Trescasses, 1992).

These may provide the leaching conditions, chemical decomposition, hydration and hydrolysis of the minerals and rocks. Partial hydrolysis can cause the processes known as bissialitization, as a result of partial dissolution and removal of Si, Al and some alkaline earths (alkalis), which recombine to form smectites or other hydrated 2:1 layer silicates as weathering products. Under conditions of intense hydrolysis the transformations give rise to monosialitization with formation of kaolinites, where total alkaline earths and alkalis and part of Si have been removed from the system. The most advanced stage of weathering is given by allitization and ferrallitization i.e. the formation of oxy-hydroxides of aluminium and iron, respectively of bauxites and laterites, under conditions of complete leaching of Si (Thorez, 1989; Pickering, 1989; Valetton et al., 1997). Fig. 1.1 is a summarized diagrammatic representation of some weathering reactions associated with

weathering minerals. The diagram shows the relationships of the lithological parameters, the physico-chemical conditions and climatic characteristics during the weathering reactions.

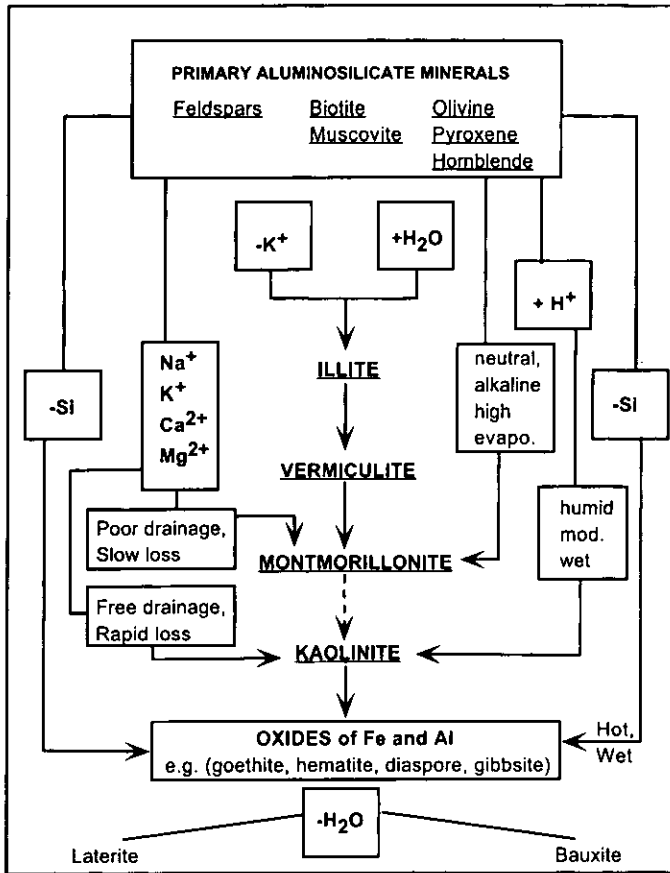


Figure 1.1: Diagrammatic representation of some weathering patterns and their associated products (after Pickering, 1989).

1.2. Products of Weathering in Mozambique

The bauxites, kaolinitic clays and bentonites represent potential and promising industrial rocks with substantial present and future demands to the benefit of industrial growth in Mozambique. These important raw materials are products of weathering and alteration, generally in situ, of different magmatic parent rocks. They developed bodies with several shapes and sizes, with both horizontal and vertical variability of the ore grades. Their probable reserves, with varying grades, have been estimated (Cilek, 1986). The deposits of bauxites, kaolinitic clays and bentonites have been subject of several studies aimed to evaluate their suitability for industrial purposes.

1.2.1. Bauxites and kaolinic clays in Penhalonga

The Penhalonga district is located in the approximately N-S oriented mountain ranges of the northern part of an E-W synclinorium, which underwent tectonic and geomorphologic events in different geological periods. This is particularly reflected by the present day morphology of the area. Plateaux, mountains and scarps dominate the landscape. The landforms are characterized by summits on small relict plateaux that resulted from cycles of erosion and landscape development of the Gondwana, post-Gondwana (Jurassic-Cretaceous) and African (Early Cainozoic) landscape cycles (King, 1967). These plateaux are separated by shallow river valleys, which formed during the following planation cycles assignable to the Late Cainozoic and Plio-Pleistocene events. In the entire area a considerable number of remnants of different sizes represent the once coherent old peneplained surface. They constitute usually the most elevated parts of the area with altitude ranging from about 1500 meters up to 1900 meters above mean sea level. Noteworthy is that most of these plateaux, which are characterized by more or less flattened tops and slightly inclined slopes, possess a lateritic mantle of weathering. The present-day climate is tropical humid, somewhat modified by altitude, with average annual rainfall of more than 2000 mm and the average annual temperature between 18° and 20°C (Atlas Geográfico, 1986). Dense tropical forests and savannah woodland at places with high grasses are the vegetation cover. Locally there are also eucalypt and pine forests.

The lateritic bauxite deposits occur in two main areas, Alumen and Marondo, along the highlands bordering Mozambican and Zimbabwean territories. The bauxite and kaolinic clays overlie basement Precambrian gabbro, anorthosite, metabasalt and granite. Geological and mineralogical characteristics of the weathering profiles indicate a complex interaction of factors involved during and after bauxite formation. The parent rock parameters and geomorphologic conditions are assumed to have influenced, to a considerable extent, the bauxitization in the area. Most profile horizons have an autochthonous character and the ages of bauxite formation are considered to be Late Cretaceous to Tertiary (Grubb, 1976).

1.2.2. Deposits of bentonites in Boane District

The Lebombo represents an extensive volcanic mountain range, which consists of a sequence of basic and acid rocks. These rocks were erupted during the Upper Karoo (Jurassic-Cretaceous) and their outcrops are widespread through Southern Africa. At present several sites are known along the Lebombos where bentonite deposits of economic interest occur. Bentonite is here defined as a clay/rock type that usually consists of several clay minerals and other silicates and non-silicates minerals as well as fragments of unaltered parent material member (Weaver, 1989). The clay minerals belong mostly to the smectite group with montmorillonite as the most dominant. Smectite-rich clay bodies of various sizes, in general closely related to the acid volcanics, are frequently observed in the Boane area. Occurrences of bentonite are widespread in the area, but the main deposits are distributed, with an approximately N-S trend, along the east slope of the Little Lebombo Mountains (Montes Pequenos Libombos), part of the larger Lebombos volcanic mountain chain. Regionally the Lebombo volcanics extend into the neighbouring countries South Africa and Swaziland. Geomorphologically the Little Lebombos stand out as a slightly elevated peneplain or platform, with a maximal altitude of about 290 meters, dipping slightly to the east (Torre de Assunção et al., 1962; Afonso, 1976; Pinna et al., 1986; Cilek 1986). The emplaced volcanics of mainly rhyolitic-rhyodacitic composition underwent bentonitization, very intense at places, evidenced by numerous sites with bentonite deposits scattered throughout the Lebombo volcanics. The bentonite masses form irregular

bodies, with thickness varying considerably from place to place. Some of the bentonitic bodies are well known and have been exploited commercially, for ceramics and animal husbandry for many years. Reserves of bentonites in the area were estimated to be between 15 and 25 million tons (Cilek, 1986).

1.3. Scope and Aim of the Thesis

Occurrences and deposits of lateritic bauxites and bentonites in Mozambique have long been identified and subjected to several evaluation studies for their commercial applications. Because of a number of considerations two different areas were selected for further studies. Firstly, the possibility to carry out reliable fieldwork and secondly, the availability to gather plausible geological data for a methodical description of mineral resources of the country. The main purpose of this study is, the description, on the basis of mineralogical and geochemical data, of two geologically different areas where bauxites and kaolinitic clays occur in one and bentonites in the other. The description aims to show the relationships between the source rock compositions and the altered or weathered mineral products. Attempts will be made to present some regularities in the major and trace elements distribution, with particular attention to the Rare Earth Elements (REE), in the weathering products and to examine and compare the interdependence of the major element chemistry of stream waters and the mineralogy of the weathering profiles. The mentioned areas have been subjects of earlier geologic studies which focused mainly on the economic evaluation of the deposits; these studies only provided some general mineralogical and petrological aspects. It is expected in this study, as starting point, to improve understanding of the mechanisms of bauxite and bentonite formation, as well as to discuss the mineralogy and chemistry of the deposits for their possible industrial use. The correct elucidation of the lateritization-bauxitization processes will, to some extent, also help with geological mapping in the area since deep weathered crusts ubiquitously cover the fresh parent rocks.

1.4. Synopsis

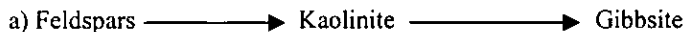
Chapter I, introduces some general considerations of weathering and a brief bibliographic review on the main factors controlling the processes and effects of weathering. The two study areas of bauxite and bentonite occurrences are in summary presented and described, emphasizing their geological and economical significance. Fieldwork, sampling and analytical methodology is reported on in **Chapter II**, without entering into details of analytical procedures for single methods used. **Chapter III** presents an overview of the geology of the Penhalonga bauxite area, with its general geologic setting, petrographical description of the principal parent rocks and mineralogical characterization of the typical bauxite-laterite profiles in the area. Based on literature data and also on field observations the possible profile development is tentatively ordered sequentially until the present day situation of the dominant geomorphology. **Chapter IV** describes the weathering sequences on anorthosite, gabbro and metabasalt parent rocks. It includes an examination of the main trends and the mineral associations of weathering profiles from mineralogical and geochemical viewpoints. Main results of the analytical work carried out on bauxite and kaolinitic clays are contained in this chapter, where different ways of studying mineral chemical weathering are referenced for the description of the weathering sequences. Special attention is given to trace element geochemistry and also to the major element chemistry of drainage waters from the considered area. **Chapter V** presents geological information on bentonites, obtained during the present study. Starting with an overview of the geology of the Boane deposits, including the principal chemistry and mineralogy, the chapter covers the identification of the principal geochemical characteristics of the alteration of rhyolitic volcanics

to bentonite. This was done taking into account aspects related to the mobilization and fixation of major and trace selected elements, including REE, during bentonite formation. Furthermore on the basis of available geological and geochemical data, ideas on the genesis of the bentonite are presented.

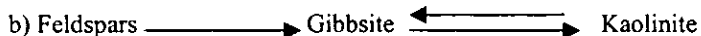
1.5. General Conclusions

A. Bauxites

1. Intensive chemical weathering, in the Penhalonga (Mozambique) mountainous area, produced deep weathering profiles on different source rocks, which is evidenced by the geochemical behaviour of the main and trace elements.
2. The variation of the main chemical elements, from the parent rocks to the uppermost part of the profiles shows clearly the main trends and the varying degree of weathering. The principal forms of mineral weathering are defined by the disintegration of plagioclase feldspars to produce kaolinitic clays and gibbsite, and pyroxene and amphibole minerals to kaolinitic clays and secondary iron minerals, such as goethite and hematite. In a simplified manner the general weathering pathways can be illustrated by the following equations, assuming that the principal parent rocks are mainly anorthosites and gabbros that contain as major minerals feldspars and pyroxenes and/or amphiboles:



or



and



3. The association of the main mineralogic components gibbsite, kaolinite and, subordinately, illite in bauxites is well supported by the characteristics of the drainage water from the area. In the mineral stability diagrams, on the basis of the activities of H^+ , K^+ , Na^+ , Ca^{2+} and H_4SiO_4 , the composition of the drainage waters occurs in a field close to the gibbsite-kaolinite boundary.
4. The behaviour of the trace elements follows largely the general tendencies of the major elements. One group, headed by alkalis and alkaline earths, is clearly removed from the most weathered part of the profiles. In contrast the other group, represented by Al, Fe, Ti, Zr and LREE (Light Rare Earth Elements), is fixed and enriched in the weathering sequences. This is also true for the transition metal elements, which appear to be residually enriched in the weathered profiles.
5. Specific behaviour during lateritization-bentonitization is exhibited by the Rare Earth Elements (REE). Due to its special chemistry, Ce produces noticeable large positive anomalies in the most weathered part of the profiles, whereas the positive Eu anomaly in anorthosite and gabbro parent rocks is substantially transferred to the weathered products. This fact can be related to a mineralogic control in the fractionation of the REE.

B. Bentonites

1. The principal mineral component of the bentonite deposits of altered rhyolitic rocks from Boane area is rich in smectite. The montmorillonite has a mixed cation exchange capacity varying from calcium to sodium-calcium, which is also reflected in the reduced swelling characteristics and cation exchange capacity values. The bentonite has always associated silica phases and remains of rhyolitic parent materials. Occurrences of hard silicified calcitic concretions are frequently observed encapsulated in bentonitic masses.
2. Geochemically the bentonitization is characterized by a relative strong migration of K, Rb, Ba and, in lesser extent, Na and fixation and enrichment of Ca, Mg and also Fe, while Si, Al, Ti are almost immobile. Other trace elements, excluding U and Co which are mobilized, have more or less consistent behaviour, and seem to be conserved, and exhibit a general tendency to accumulate in the altered rhyolites.
3. The bentonitization apparently occurred in a nearly closed-system alkaline environment, which favoured Ca, Mg and Si retention, while these principal chemical elements were encapsulated into montmorillonite clays.
4. There is little mobilization and fractionation among the REE, as no notable deviations in the composition of the bentonite samples and the rhyolites are observed.

CHAPTER II

2. SAMPLE COLLECTION AND ANALYTICAL METHODOLOGY

The samples of bauxites and kaolinitic clays have been selected at two different occasions. The first set was collected during geological field work carried out by a team of the National Directorate of Geology (DNG), Mozambique, performing economic evaluation of the deposits from the area. The samples were collected at man-made exposures (from prospecting pits, auger drill holes and trenches) and at exploration fronts of open pit mines. From the pits samples were taken from channels (about 20 cm wide) made in the pit wall. From the bottom to the top and with an interval of 1 meter, the sampling material was collected, mixed and reduced to approximately 5 Kg and stored in plastic bags. Hand specimens of possibly freshest parent rocks were also used for thin sections. This set of samples was analyzed for bulk chemistry by X-ray fluorescence spectrometry (XRFS) and for principal mineral constituents by X-ray diffraction at Institute of Mining Research, University of Zimbabwe. A second set of samples resulted from selected prospecting pits on different parent rocks. The procedure of sample collection was similar to the first and for them, the analyses were extended to trace elements. The bentonite samples were collected almost in the same way as the bauxite samples except that prospecting pits had only little depth (a maximum of 10 meters) and drillcores were used for sampling.

The field samples were afterwards reduced by quartering resulting in the laboratory specimens. For mineralogical and chemical analysis of major and trace elements, the samples were initially dried at 40°, and then pulverized using a swing disk mill. The analytical powder has been obtained after homogenization and further quartering procedures.

The petrography of the main parent rocks was studied by optical microscopy. The bulk mineralogy of the weathered materials was determined by X-ray diffraction on a Philips X-ray diffractometer Philips® PW 1400, using Ni-filtered $\text{CuK}\alpha$ radiation. Natural untreated randomly oriented aggregates of the samples were scanned at a rate $1^\circ 2\theta \cdot \text{min}^{-1}$ between 3° and $73^\circ 2\theta$ (AGL-*Internal Manual*, Procedure N.1). On the X-ray diagrams of bulk samples of bauxite and kaolinitic clays the reflection peaks used for the qualitative identification of the minerals are almost all below $50^\circ 2\theta$.

For clay mineralogy determination, the samples were prepared by sedimentation methods after dispersion in demineralized water. A mixture of sodium carbonate and sodium pyrophosphate was used as deflocculant. The $< 2 \mu\text{m}$ fractions were separated and Magnesium (Mg)- and Potassium (K)-saturated, spread on glass slides and allowed to dry. Both treated samples were X-rayed between 3° and $33^\circ 2\theta$ and again scanned, respectively, after glycol saturation and heating 2 hours at 500°C . Identification of the principal clay minerals present in the weathered samples was according to the methods of Thorez (1976), as well as, of Brindley and Brown (1984).

The chemical composition (major and trace elements) of fresh parent rocks, bauxites, kaolinitic clays and bentonitic material were determined by Induced Coupled Plasma Optical Emission

Spectrometry (ICP-OES) (ARL® 34.000). This was done following standard procedures established in the geochemical laboratory of the Faculty of Earth Sciences at the Utrecht University (AGL-Internal Manual, 1992, Procedures 1, 2, and 3). For silica analysis, samples were decomposed using lithium-metaborate fusions. For the other major (Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and for the trace elements (Cr, Ni, Co, V, Cu, Zn, Ba, Be, Sr, Li, Zr, Y) decomposition of the samples was achieved by using mixed acids HF/HClO₄/HNO₃ for dissolution of 250 milligrams of sample in Teflon beakers. The rock standards GRAN-1 and BN-02 were used to estimate precision between 2%-4% for major and 10% for trace elements. The REE (La, Ce, Nd, Sm, Eu, Tb, Yb, Lu), Ta, Hf, U, Th, Sc, Ga and Cs concentrations were obtained by Instrumental Neutron Activation Analysis (INAA). Additionally selected samples of bauxites and of bentonites have been analyzed, where especially Ga, Nb, Th and U were determined by X-ray Fluorescence Spectrometry (XRFS), with a spectrometer Philips® PW 1400 (AGL-Internal Manual, 1992, Procedures 1, 2, and 3). The sample preparation followed is similar to that described by Norrish and Chappel (1977). All major elements were analyzed on fusion beads using lithium borate as flux. Pressed powder pellets were used for the determination of selected trace elements. In all the chemical analyses, total iron is reported as Fe₂O₃. The loss on ignition values (LOI) were calculated by weight differences after heating the samples 6 hours at 1000 °C.

The sampling of the stream waters in the area of the bauxite deposits took place during two consecutive fieldwork campaigns, with a 1-year interval, during the dry season (July-August). The prevailing geomorphologic setting determined that most of the water samples have been collected a few hundred meters or even shorter distances away from the water fountainhead and mostly close to the stream bank. Samples of 500 ml were collected and stored in polyethylene plastic bottles and hermetically sealed. Since the majority of the streams are very small, the water samples can be considered representative samples of the stream waters. After pH measurements in the laboratory, samples for analysis were acidified with HNO₃ and the elements Si, Mg, Ca, Na, K, Fe and Al determined by ICP-OES. Contents of Al in the stream waters presented values below the detection limits, which was 0.03 ppm.

CHAPTER III

3. GEOLOGY OF THE BAUXITE DEPOSITS FROM PENHALONGA AREA, MANICA, MOZAMBIQUE

3.1. Introduction

Among the known mineral occurrences of Mozambique bauxites are reported from different localities of the territory. As is the case for lateritic-bauxites in south-eastern Africa, in Mozambique extensive bauxitic and kaolinitic horizons formed mainly over nepheline syenites in Milange district, Zambézia Province, and over basement Precambrian crystalline rocks in the Penhalonga area, Manica Province (Fig. 3.1). They belong to the Southeast African Province in the world geographical distribution of bauxites (Bardossy and Aleva, 1990). So far as is known the area with economically exploitable bauxite is essentially confined to the Penhalonga district. The existence of the deposits in the area has been known since the beginning of this century. Mining of chemical- and refractory- grade bauxite is reported to have started in the mid 1930's by Wankie Collieries Ltd. (Carvalho and Collin, 1943). The deposits have previously been the subject of few geological studies, the most significant of which has been carried out by Grubb (1973).

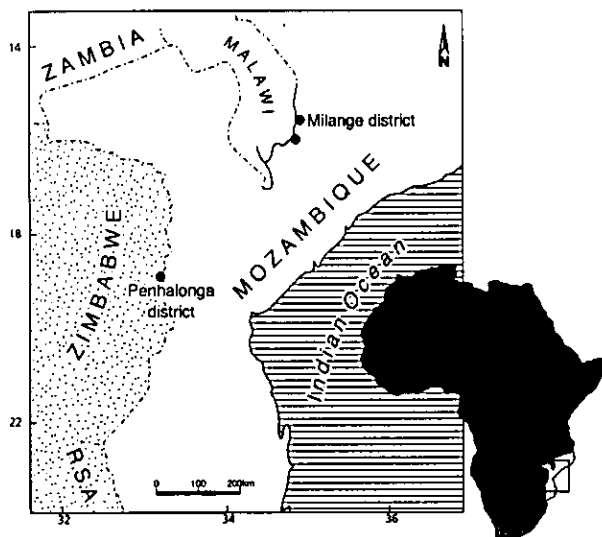


Figure 3.1: Geographical location of the main areas of bauxite occurrences in Mozambique, Penhalonga and Milange districts, within the Southern Africa region.

Several publications cover survey results from both Mozambican and Zimbabwean deposits. They are described as high-level lateritic bauxites developed on ancient plateaux under reasonably good geomorphologic and climatic conditions (Grubb, 1976).

The distribution pattern and physical and chemical nature of the bauxites are thought to be closely associated with the gabbro-anorthositic parent rocks, which apparently constitute part of a stratified mafic-ultramafic intrusive complex (Grubb, 1987). During a recent program for economic evaluation and mining the main chemical components were determined and some mineralogical analysis on the bauxite and kaolinitic clays as well as on their parent rocks have been performed. Reserves of bauxite ores with average contents of 50% total alumina, 9% total iron, 10% total silica and 1% titania were estimated at about 10 million tons and reserves of the white kaolinitic clays are assumed to be between 10 and 15 million tons (ING, 1988). This chapter gives a summary description of the main geological features of the Penhalonga bauxite deposits with a focus on the Alumen area. Field observations and mapping on available profile exposures from prospect pits, manual auger drill cores and open mine cuttings or quarry fronts provided the basis for the establishment of some observable relationships of the lithological units within the bauxitic and clayey bodies. Where parent rocks were inaccessible, similar macroscopic features in the overlying laterite-bauxite were sufficient to infer the type of parent-rocks. Main chemical components and mineralogical aspects of the laterite-bauxite profiles on various parent-rocks are presented and the bauxitization conditions are discussed.

3.2. Geographic location

The deposits of bauxite and kaolin are situated in the Penhalonga district, in the western part of Manica Province, and extend along the Mozambican-Zimbabwean border. Two main bauxite areas are known: Alumen; lat. 18° 48' 30" and 18° 52' 40" S and long. 32° 40' 30" and 32° 45' 00"E of about 8 Km², and Marondo; lat. 18° 47'50" and long. 32° 48' 20" E of about 4 Km² in size. The altitude of both areas is around 1600 meters above mean sea level. The areas are situated about 20 Km north of the Harare-Beira railway and highway and are connected by roads with Zimbabwe. However, direct roads links within and to Mozambique are poor (Fig. 3.2).

3.3. Geomorphologic aspects

The Penhalonga district is located on the approximately N-S oriented mountain ranges of the northern part of an E-W synclinorium, which underwent tectonic and geomorphologic events in different geological periods. This is particularly reflected by the present day morphology of the area. Plateaux, mountains and scarps dominate the landscape. The landforms are characterized by summits on small relict plateaux that resulted from cycles of erosion and landscape development of the Gondwana, post-Gondwana (Jurassic-Cretaceous) and African (Early Cainozoic) landscape cycles (King, 1967). These plateaux are separated by shallow river valleys, which formed during the following planation cycles assignable to the Late Cainozoic and Plio-Pleistocene events. Throughout the entire area a considerable number of remnants of different sizes represent the once coherent old peneplained surface. They constitute usually the most elevated parts of the area with altitudes ranging from about 1500 meters up to 1900 meters above mean sea level. Noteworthy is that most of these plateaux, that are characterized by more or less flattened tops and slightly inclined slopes, possess a lateritic weathering mantle. The present day climate is tropical humid, modified by

altitude, with average annual rainfall of more than 2000 mm and the average annual temperature between 18° and 20°C (Atlas Geográfico, 1986). Locally, dense tropical forests and savanna woodland with high grasses are the main type of vegetation cover. At places, there are also planted eucalyptus and pine forests.

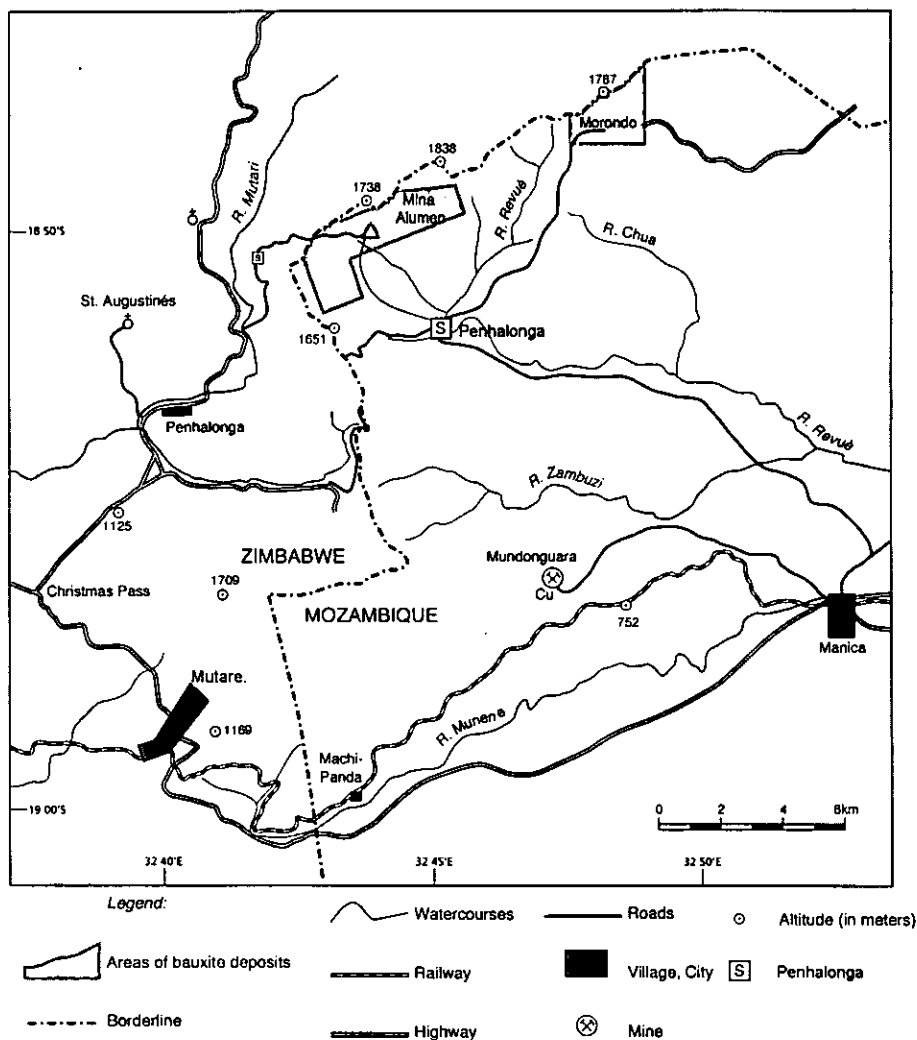


Figure 3.2: Location map of the main areas of bauxite and kaolinitic clays deposits in Penhalonga district, NW of Manica Province, Mozambique.

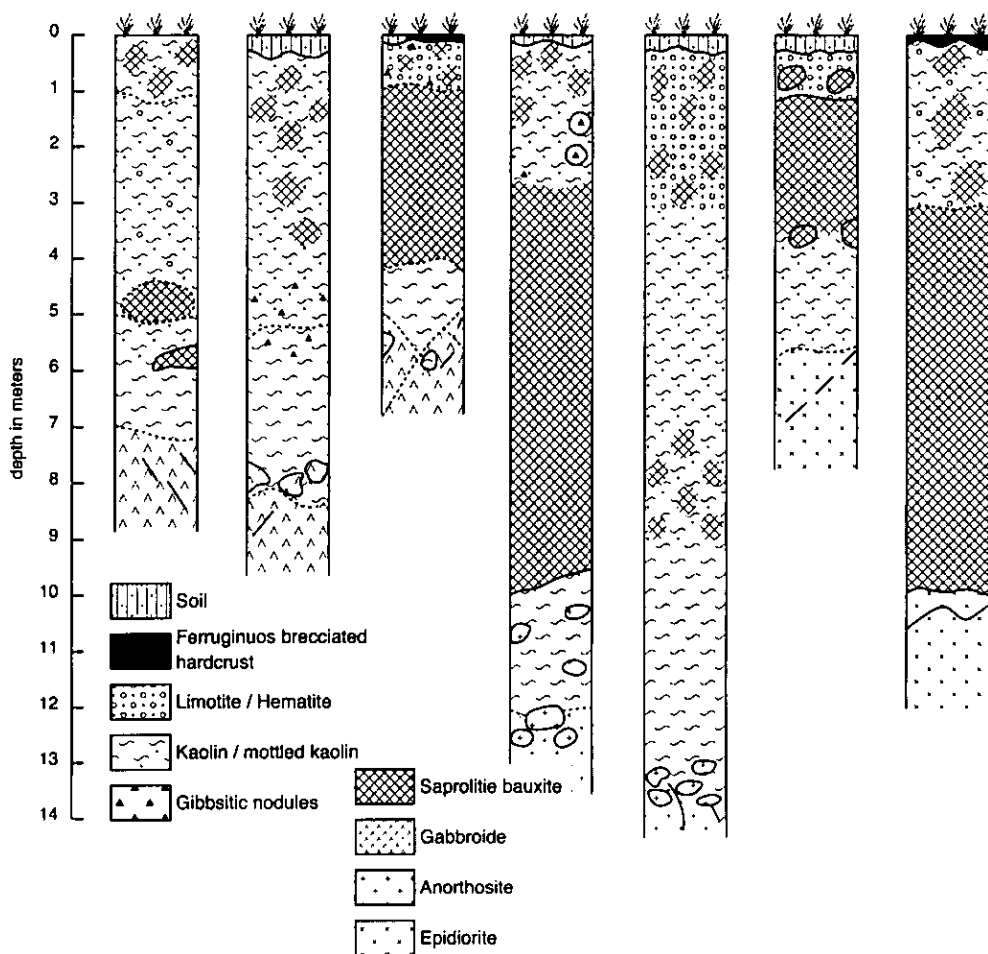


Figure 3.3: Sketches of some typical weathering profiles on different parent rocks in the area of the Penhalonga bauxite deposits

3.4. Geology

3.4.1. General setting

The bauxite and kaolinitic clay occurrences are within the Precambrian unit of the Manica Group, which is built up of Archean and Proterozoic, as well as Phanerozoic magmatic and metamorphic rocks (Araújo and Gouveia, 1965; Afonso, 1976). The Macequece and MBeza-Vengo Formations constitute the Manica Group. These geological formations occur in the easternmost part of the Odzi-Umtali Greenstone Belt and they are regionally correlated with the Bulawayan and Shamvayan Groups respectively, in Zimbabwe (Carvalho and Collin, 1943; Afonso, 1976; Pinna *et al.*, 1986).

The Macequece Formation is composed mainly of "greenstones" including metabasalts, greenschists, serpentinites, talcschists, and komatiitic basalts (Phaup, 1937; Araújo and Gouveia, 1965; Stagman, 1978) and the Mbeza-Vengo Formation represents a metasedimentary sequence of schists, metagreywackes and metaconglomerates. Granitic rocks of different ages, mostly Late Archean (around 2500 Ma, Phaup, 1973) surround all the rock units. Subsequent Proterozoic and Phanerozoic intrusions generated several bodies of granites, dolerites, felsites and porphyries (Appendix A). Tectonically the area was subjected to several events. Folding generated the E-W synclinorium which subsequently underwent NW-SE, NE-SW and subordinately N-S faulting and medium grade

3.4.2. Geological features of the deposits

3.4.2.1. *The weathering profiles*

In the study area the laterite-bauxite blankets overlie mainly basement Precambrian gabbros, anorthosites, diorites, granites and metamorphosed basic volcanic rocks (greenstones), as well as dolerites. The weathering crusts occur extensively and the profiles considered herein are on flattened tops and upper parts of the gently dipping slopes of plateaux. On all the rocktypes the observed weathering profiles are truncated or reduced and in many places the division of them into typical horizons is strongly obscured. Their thickness varies from place to place from a few meters up to more than 30 meters. General features of the considered horizons can be described as follows (Fig. 3.3).

i) *The soil horizon*; with a maximum thickness of about 1 meter is normally present and is composed of a dark brown, red or yellow-brown clayey soil with blocks of variable sizes of gibbsite and goethite mixed with plant remains. In some places, mostly on slopes, the soil is not residual and contains also mechanical transported sandy grains and small blocks of gibbsite.

ii) *The duricrust horizon*; occurs rarely, but when it occurs, it is always a few meters thick. It is an iron-rich, dark-brown or reddish-brown hard cap overlying profiles of greenstones and gabbroic rocks. It generally possesses a breccia-like texture with fragments of different sizes of granitic rocks, gibbsite, quartz, goethite and magnetite cemented by a matrix composed of kaolinitic clays and iron oxides and iron hydroxides as well.

iii) *Laterite-bauxite horizon*; represents the most complex horizon in the area of the deposits. In most cases it is heterogeneous with strong vertical as well as lateral variations in its textures, colors and compositions. As gabbroic and anorthositic parent rocks are genetically interconnected, the bauxite horizon over these rocks displays comparable structures that are preserved. Frequently gibbsitic nodules or concretions occur within a mantle of mottled kaolinitic clays and also as large sheets filling planes of pre-existent fractures. In places, "core boulders" of partly unweathered parent rock are enclosed in bauxitic clays. The color varies from white to orange, reddish brown and brown, through pinkish, yellowish and also variable mottled colors. This horizon is often strongly intermixed with the underlying saprolite.

iv) *Saprolite horizon*; appears to be the best represented horizon in all observed profiles and is almost completely composed of white or mottled kaolinitic clays. Commonly the clays are

intercalated with narrow bauxitic masses or contain blocks of which the cores are fresh parent rock. Locally saprolite overlying gabbroic and anorthositic rocks reaches more than 20 meters thickness.

v) *Parent rocks*; the principal petrographical characteristics are summarized in Table 3.1.

The gabbroic and anorthositic rocks are end-members of a series of various types, recognizable through the relative proportions between plagioclase feldspars and amphibole minerals generated by the pyroxene uralitization. This indicates that they have undergone metamorphism and should be considered, therefore, as meta-anorthosites and metagabbros. Metabasalts represent the result of metamorphosed basic volcanic rocks where the primary textures and structures are no longer recognizable.

Table 3.1: Principal petrographic features of the main parent rocks of the bauxites in the Penhalonga area.

Parent rock	Mineralogy	Characteristics
Anorthosite	Plagioclase feldspars and accessories	Coarse-grained, white or pale grey, with small darker patches of pyroxenes/amphiboles.
Gabbro	Pyroxenes/amphiboles, plagioclase feldspars and opaque minerals	Medium to coarse grained, black, black-greenish with whitish spots.
Metabasalt	Epidote/zoisite, amphibole plagioclase, chlorite and traces of calcite.	Dark green, greenish black, fine grained. Typical columnar jointing and also schistosity.

3.4.3. The bauxite deposits and mining

3.4.3.1. *Bauxites and kaolinitic clays*

As stated earlier, the production of bauxites and kaolinitic clays from the deposits of Alumen and Marondo in the Penhalonga area started in 1935 and was carried out continuously until 1974. During that period roughly 4000 tons of ore per annum were mined for the manufacture of aluminium sulphate and some refractory bricks. After an interruption of 10 years, production was resumed in 1985 and until the beginning of the nineties about 6000 tons per annum were extracted from seven different quarries. The different ore grades are used mainly for the manufacture of aluminium sulphate for use in water purification.

3.4.3.2. The grades and distribution of the ore bodies

The bauxitic clays occur in the northern margin of the Precambrian greenstone belt in Manica Province, and extend along the Mozambican/Zimbabwean border. The ore bodies, of residual character, overlie gabbro-anorthositic rocks, metabasalts, talcschists and also granites. Intensive bauxitization-lateritization through weathering and leaching has developed on slightly inclined, plateau-shaped, old erosion surfaces. These surfaces have been dissected in stream valleys so that in the present day situation only remnants of different sizes are preserved which contain the main ore bodies.

Table 3.2: Chemical composition of representative ore grade type samples from Penhalonga deposits (ING, Internal Report, 1988)

Oxid (wt %)	Ore type A	Ore type B	Ore type C	Ore type D	Kaolinitic clay *
Al ₂ O ₃	58.43	49.65	44.02	57.16	39.60
Fe ₂ O ₃	1.55	13.81	17.78	0.64	0.91
TiO ₂	0.27	0.84	3.07	0.00	0.01
SiO ₂	9.00	9.19	9.92	16.92	43.90
L.O.I.	28.62	23.96	24.12	24.05	15.00
Na ₂ O	0.04	0.04	0.07	0.11	0.09
K ₂ O	1.65	1.20	0.10	0.58	0.19
CaO	0.02	0.08	0.00	0.03	0.00
MgO	0.27	0.09	0.00	0.00	0.00
P ₂ O ₅	0.01	0.04	0.21	0.02	0.00
MnO	0.06	0.03	0.07	0.06	0.02
Total	99.92	98.93	99.36	99.57	99.72

(* kaolinitic clay, after separation from gibbsite nodules by wet screening)

According to their principal petrographic and chemical characteristics, four main ore types/grades can be distinguished and results of chemical analysis are presented in Table 3.2.

- A.** white saprolitic bauxite, friable, texturally porous and light. Primary parent rock structures, notably joints and fractures, are often preserved.
- B.** yellowish brown saprolitic bauxite presenting similar characteristics as grade A.
- C.** reddish brown to dark brown, ferruginous, saprolitic bauxite. Fine grained, friable, but also indurated in some places, with lateritic appearance showing ferruginous cement
- D.** white kaolinitic clays, with concretionary, colomorphic gibbsite. The contents of gibbsite nodules are very variable and so are their sizes and shapes. The clay is sticky when wet and extremely fine and friable when dry.

There is a conspicuous relationship between the bauxites/kaolinitic clays and the parent rocks. The white bauxites of the type A and the kaolin of type D are related to anorthosites. The type B bauxite is from intermediate members of the gabbro-anorthosite series, while bauxite formation from gabbros and metabasalts results in ferruginous bauxites of type C. The variety of the source rocks, and their interrelationship have greatly contributed to the variation of the ore grade even over short

distances. They are also responsible, together with erosion, for the lens-shaped occurrence and restricted size of the ore bodies/masses, which show lengths varying from 100 to around 500 meters, and widths from 25 to 200 meters. The thicknesses are variable, from few meters to over 30 meters in places. Since the weathering and leaching intensity differ locally, the depths of the unaltered bedrock are generally irregular and often unpredictable.

3.4.3.3. Grades and potential uses

Approximately 85% of the global consumption of bauxites and Al-laterites is used in the production of metallic aluminium (Kuzvart, 1984). Table 3.3 lists some categories of bauxites required for the main industrial users. Industrial rock bauxite is also used in the refractory industry, in different branches of chemical industries and in the production of special cement. As can be seen, the bauxites from the Penhalonga deposits are characterized by relatively high contents of total iron, silica and alkalis. These components are critical in determining the quality of the raw material for the different users.

Table 3.3: Categories of bauxite according to its uses (modified after Harben and Dicksen, 1986 in Edwards and Atkinson, 1986)

<i>Use ></i>	<i>Metallurgy</i>	<i>Chemistry</i>	<i>Cement</i>	<i>Refractory</i>	<i>Abrasive</i>
Requisites	High alumina Low iron low silica low titania	High gibbsite Very low iron Low silica	Moderate high alumina low silica high iron	high alumina low iron low silica very low alkalis	high alumina low iron low silica low titania
Al ₂ O ₃	> 50 %	> 55 %	45 - 50 %	> 58 % (85%)	80 - 88 %
SiO ₂	< 5 %	5 - 9 %	< 6 %	< 5 % (8%)	4 - 8 %
Fe ₂ O ₃	5 - 30 %	1.5 - 3 %	> 10 %	< 2 % (2.5%)	2 - 5 %
TiO ₂	0 - 6 %	2 - 4 %	< 3 %	< 3 % (4%)	2 - 5 %
Na ₂ O+K ₂ O	none	none	none	< 0.2 %	none

A general classification, based on the iron and silica contents, of the bauxites and kaolinitic clays from Penhalonga deposits is presented in Figure 3.4. For practical purposes the white ore type A and D are considered together as first quality, high-grade (I) bauxite and kaolin. The type B is regarded as second quality bauxite grade (II) whereas type C is third quality, with Al₂O₃ contents less than 45%, and is deemed to be waste. High-grade bauxite and kaolinitic clay, type A and D, were tested for ceramic properties, refractories and abrasives. Due to their high content in total alkalis (Na₂O + K₂O), they do not meet the requirements of the common industrial users. Furthermore, the iron content induces a red colour on kaolinitic clay specimens, which considerably limits the suitability of that material for ceramics. Despite these chemical properties, bauxites from Penhalonga deposits are commercially exploited for the chemical industry, for aluminium sulphate production.

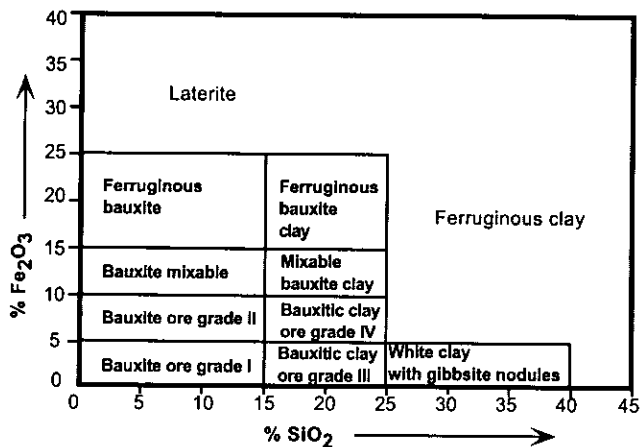


Figure 3.4: Schematic classification of the bauxites and kaolinitic clays ore types from Penhalonga deposits, according to iron and silica contents, on the diagram of percentual concentrations of Fe_2O_3 and SiO_2 .

3.5. Chemistry and mineralogy of the bauxites

The bauxites and the kaolinitic clays overlying the parent rock possess similarities in their chemical and mineralogical properties. The major minerals in all the samples are gibbsite and kaolinitic minerals (kaolinite/halloysite). Other minerals that may also be present are goethite, illite and traces of a 14Å clay mineral. Typical whole-sample X-ray diffraction patterns of bauxites from different rocktypes are shown on Fig. 3.5. Gibbsite is one of the most common components of lateritic bauxites as a result of intensive weathering of crystalline rocks (Aleva, 1983; Bardossy and Aleva, 1990). Table 3.4 gives the chemical composition of a selection of the most represented parent rocks and their weathered materials. Generally, the main chemical components show distribution patterns described elsewhere for plateau type laterite-bauxite profiles developed on most basic magmatic rocks (e.g. Valetton, 1972; Chesworth *et al.*, 1981; Bardossy and Aleva, 1990, Nesbitt and Wilson, 1992). However, there exist chemical variations, which reflect the variation in composition of the gabbroic-anorthositic parent rocks. Dykes of dolerites often dissect these parent rocks, and these may also have contributed to the variability in chemical composition of the bauxites. The chemical composition of the weathered products is clearly related to the main mineralogical components. Average contents in Al_2O_3 , SiO_2 , MgO , CaO , Na_2O , K_2O and LOI of all bauxite types indicate the transformation of the primary rock-forming plagioclase feldspars and mafic minerals to gibbsite and kaolinitic clay minerals. Although not clearly evidenced by X-ray diffraction, the content in Fe_2O_3 and TiO_2 of the bauxites from metabasalt and gabbro suggests presence of minerals bearing them. In the X-ray diagrams goethite is found in traces in the bauxites from metabasalts (Fig. 3.5B).

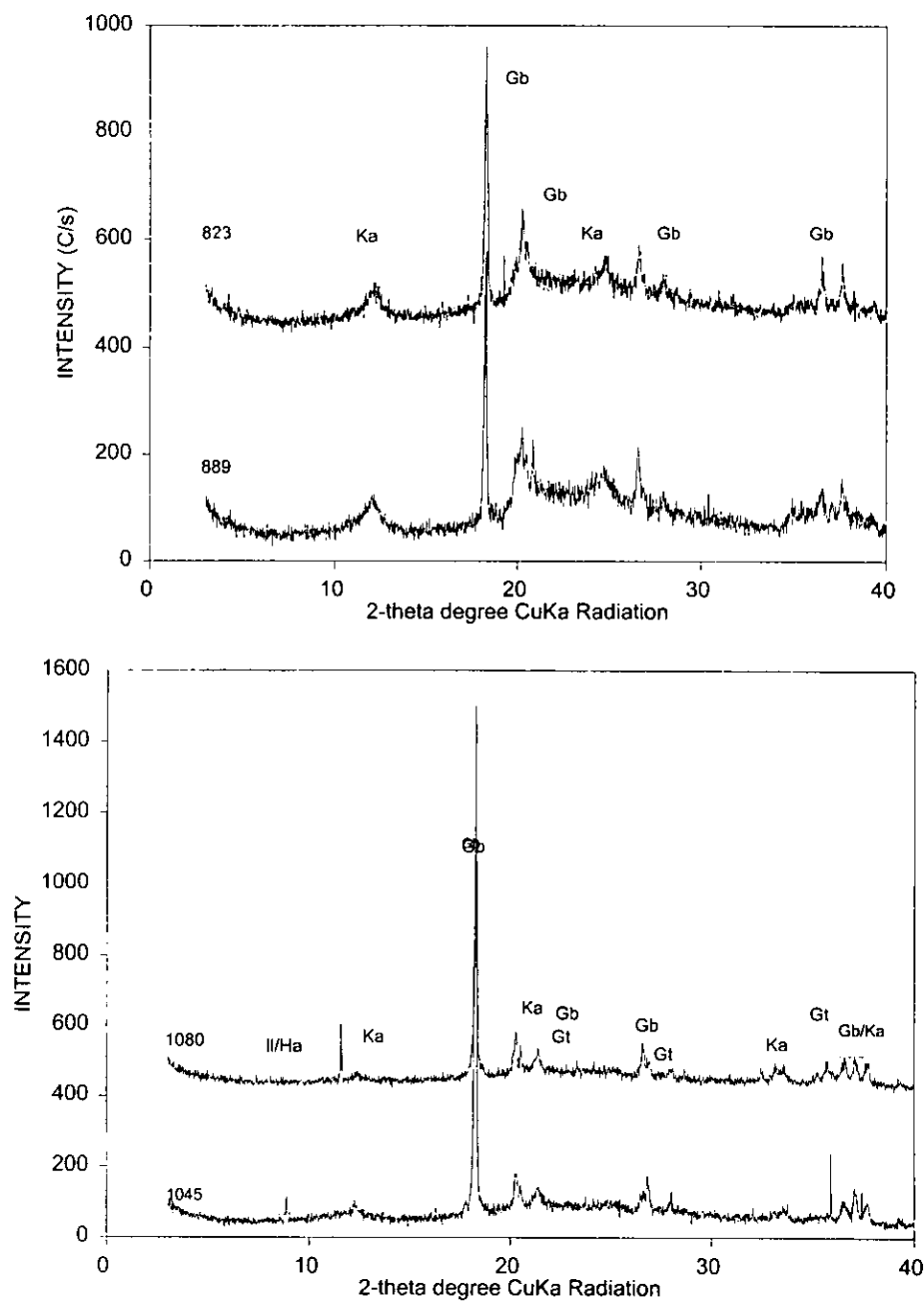


Figure 3.5: A, B: X-ray diffractograms of bulk samples of weathered materials derived from the main parent rock types (A: anorthosite and B: gabbro) of bauxite deposits of the Penhalonga district. Ka=Kaolinite, Gb=Gibbsite, Gt=Goethite, H=Halloysite, Il=Illite.

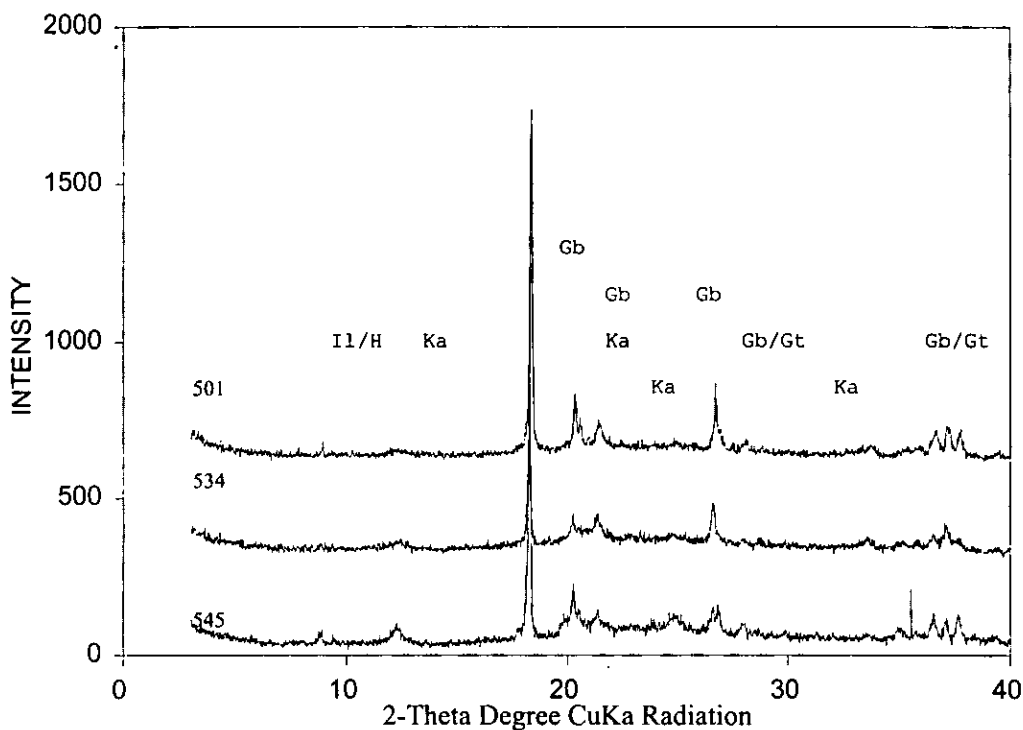


Figure 3.5: C: X-ray diffractogram of bulk samples of weathered materials derived from parent rock gabbro in the Penhalonga bauxite deposits (Legend on Figure 3.5 A, B).

Table 3.3: Major chemical components (Wt%) of the main parent rocks and their corresponding laterite-bauxites from the Penhalonga District, Mozambique

Oxid Wt%	An. (n=9)		Baux. (n=12)		Gab. (n=4)		Baux. (n=8)		Mb. (n=3)		Baux. (n=12)	
	mean	st.d.	mean	st.d.	Mean	st.d.	mean	st.d.	Mean	st.d.	Mean	St.d
SiO ₂	53.69	2.32	25.30	13.11	48.29	2.11	15.36	3.78	47.74	3.23	8.48	1.34
TiO ₂	0.27	0.81	0.18	0.27	1.35	0.84	2.05	1.81	1.41	0.35	3.24	1.19
Al ₂ O ₃	30.07	2.23	48.84	9.23	22.23	2.97	42.34	4.54	15.81	1.94	40.19	5.48
Fe ₂ O ₃	1.07	1.33	1.30	0.67	9.12	2.17	15.94	5.71	13.11	1.75	22.52	7.32
MnO	0.25	0.53	0.06	0.16	0.15	0.21	-0.12	0.14	0.20	0.21	0.42	0.66
MgO	0.65	0.77	0.10	0.07	4.07	1.62	0.13	0.12	5.02	0.81	0.11	0.09
CaO	6.46	0.98	0.29	0.43	12.04	2.35	0.04	0.04	14.25	2.23	0.02	0.02
Na ₂ O	2.08	2.01	0.16	0.30	0.50	0.12	0.03	0.03	0.86	0.76	0.03	0.02
K ₂ O	0.14	0.09	0.48	0.52	0.34	.021	0.85	0.83	0.09	0.08	0.60	0.52
P ₂ O ₅	0.03	0.08	0.02	0.02	0.00	0.00	0.03	0.04	0.70	0.59	0.09	0.15
LOI	5.29	1.53	22.89	4.04	1.91	1.76	22.55	2.34	1.09	0.61	23.56	3.06
Total	99.98	0.20	99.70	0.53	99.99	0.03	99.43	0.59	100.28	0.49	99.33	0.46

An=anorthosite; Gab=gabbro; Mb=metabasalt; Baux=laterite-bauxite; n=number of samples; st.d.=standard deviation; LOI=loss on ignition.

In the ternary diagram of the components SiO_2 - Al_2O_3 - Fe_2O_3 (Fig. 3.6) the overall changes in the main chemical composition of the original rocks during the laterite-bauxite and kaolinitic clay development are shown. This diagram is commonly used to illustrate the general trends during rock weathering. Si, Al and Fe (Ti) represent the main components of residua resulting from monosiallialitic alteration of primary rock-forming minerals (Valeton, 1972; Chesworth *et al.*, 1981, Thorez, 1989; Nesbitt and Young, 1984, 1989).

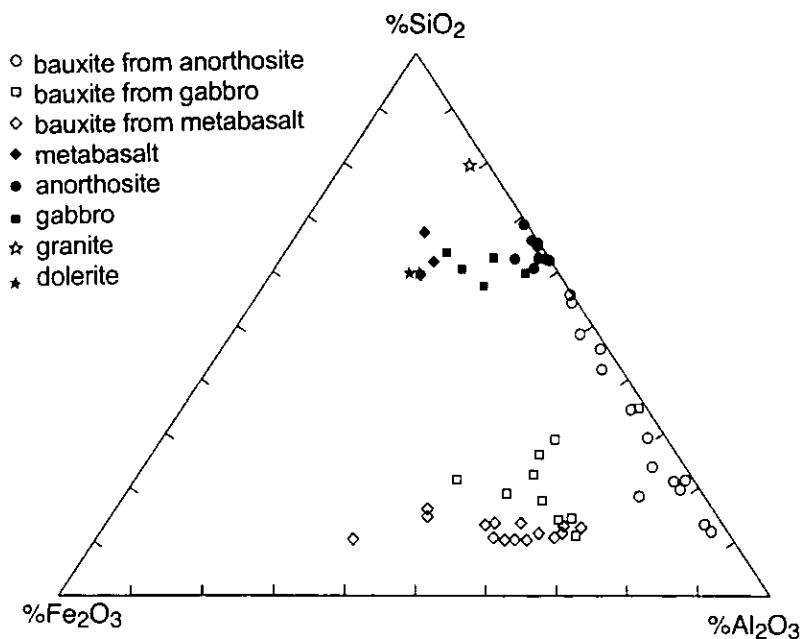


Figure 3.6: Ternary composition diagram SiO_2 - Al_2O_3 - Fe_2O_3 illustrating the variation of bauxites derived from different source rocks. Bauxites from anorthosite have a continuous development from fresh rocks to bauxite (Al_2O_3 -rich apex), passing through kaolinitic minerals with corresponding Si:Al ratios (around 1:1).

The residua develop towards either iron- or aluminium-rich end products, after intense leaching which releases all silica in a mechanism known as allitization, and which leads to the accumulation of an Al-rich end product. A similar mechanism produces an Fe-rich end product through ferralitization (Tardy, 1971; Thorez, 1989; Valeton *et al.*, 1997). Relative ratios between SiO_2 and Al_2O_3 in the diagram (Fig. 3.6) are useful to estimate relative proportions of kaolinitic minerals and gibbsite in bauxites.

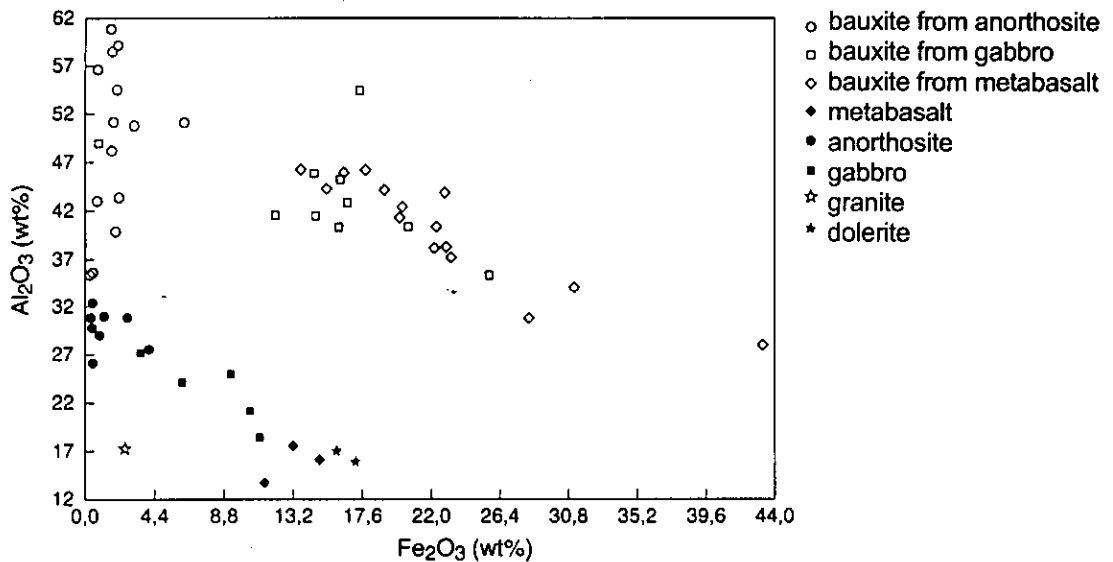


Figure 3.7: Bauxite (Al_2O_3) versus laterite (Fe_2O_3). Bauxite samples from anorthosite are clearly plotted at low iron margins whereas laterites/bauxites from gabbro and metabasalt are positioned in a different field with much higher iron contents. For legend see Figure 3.6.

The plots show the general development trend from the unaltered rocks to bauxite, which appears to proceed mainly towards the Al-rich side for all bauxite types. It is interesting to note (Fig. 3.6) that there is a continuous trend in development from anorthosite parent rock to the bauxites. This may indicate that in the deposits there are bauxites with different stages of development, which correlate to different horizons in the weathering profiles. Differences, in their major chemistry, between bauxites of gabbro and metabasalt are not very significant, contrary to those of anorthosite, which have lower iron contents. In another illustration (Fig. 3.7) the differences among the bauxite types in terms of Al_2O_3 and Fe_2O_3 are shown. The weathered materials from anorthosites plot clearly in a separate field from the other bauxite types. The diagram also shows the extent of Fe and Al accumulation in the bauxites from the different source rocks. In all cases the enrichment of both elements in bauxites is about 2 times more than in the fresh rocks. The gabbros have 10-12% Fe_2O_3 and about 15-20% Al_2O_3 and their bauxites and kaolinitic clays show Fe_2O_3 and Al_2O_3 up to 25% and 45% respectively. This is also valid for bauxites from anorthosites.

3.6. The development of the laterite-bauxite profiles

In the Penhalonga area the development of weathering crusts and bauxite formation took place on old erosion surfaces. The period of most intense weathering is assumed to have been during Late Cretaceous probably extending to Tertiary times. It is associated with both Gondwana and post-Gondwana planation surfaces and also with the African and post-African peneplains (Grubb, 1976). Butt and Zeegers (1992) pointed out for the presence of several planation levels as a direct result of repeatedly denudation of old surfaces and their renewal at lower levels. As mentioned earlier most of the profiles observed are truncated or reduced and occur on slightly inclined plateaux between a relatively close-spaced drainage pattern. The weathering profiles are mostly truncated and overlain by allochthonous material. As can be observed in the petrographical and mineralogical features of the weathering profiles, it seems that different controlling factors have prevailed during and after lateritization-bauxitization. The fabric of the products of weathering and the association/relation of the minerals gibbsite, kaolinite and Fe-hydroxides suggest interaction of several factors. One of the most essential factors in favour of the *in-situ* development of the weathering profiles is considered to be the predominantly coarse grained, fractured or fissured character of the parent rocks of the gabbro-anorthosite suite. This clearly provided optimum drainage conditions for percolating solutions and thus ensured the removal of dissolved alkalis, earth-alkalis and also silica. After bauxite formation preferential erosion have affected the spatial distribution of the bauxites. At places, especially on profiles on metabasalts, gabbros and serpentinites a hard iron-rich crust is observed. The hardening of the accumulation of Al and Fe oxy-hydroxides to form cuirasses in the near surface is widespread in the development of tropical relief (Butt and Zeegers, 1992). Weathering under tropical and sub-tropical climates is indicated in Penhalonga area as evidenced by the iron duricrust formation and severe leaching, that also caused SiO₂ removal from the weathering profiles (Schwarz, 1997; Hill *et al.*, 2000). Mechanical surface erosion is responsible for the reduced thickness and also disappearance of most bauxite horizons resulting in a more than 15 meter thick kaolinitic saprolite observed in many places (Fig. 3.4). There are, however, profiles where the lack of the bauxite horizon coincides with a reduced or absent saprolite horizon so that fresh parent rock is outcropping in the middle of some bauxite patches. Similar situations are also described in places where the weathering conditions have been influenced by tectonically or climatologically induced mechanical erosion (Bardossy and Aleva, 1990). There exist a strong relation between the physiographic-geomorphological development of the landscapes and the bauxitization-lateritization processes. These relationships can be explained in terms geomorphologic conditions, tectonic activity and climate (Butt and Zeegers, 1992; Schwarz, 1997; Milnes *et al.*, 1987). The variation of one of the mentioned parameters can cause drastic changes in the landscape development, i.e., change in the water table, erosion and leaching rates by tectonic uplift or climate changes. For many lateritic bauxite deposits these relationships have been demonstrated (e.g. in Brazil, Valetton *et al.*, 1991; and in Surinam, India, Australia and Brazil, Aleva, 1981, 1983; Bardossy and Aleva, 1990; Grubb, 1970). In the case of the Penhalonga deposits tectonic and geomorphologic conditions do not seem to have exerted influence in the same extent everywhere. In some places, mostly on flattened hill tops, the dense vegetation limited surface erosion, while in others the formation of hard ferruginous crusts clearly protected profiles from surface erosion. This can be observed also in the present day situation in the area where several hills, in different levels, are separated by the main stream valleys.

3.7. Conclusions

On the basis of the above described geological parameters the bauxites from the Penhalonga area have many features in common with frequently described lateritic bauxite deposits on magmatic rocks in humid tropical environments. Genetically the deposits are residual in origin and are derived from different Archaen and Proterozoic magmatic parent rocks. Most of the weathering mantles are mainly composed of bauxites with relict structures of the parent rock. For most profiles mineralogical determinations indicate gibbsite and kaolinitic clay minerals as the principal components. According to Bardossy and Aleva (1990) the relative proportions of gibbsite and kaolinitic clay minerals can be used as an indicating parameter for the development stage of the laterite-bauxite. Characteristic advanced stage bauxite-laterite has gibbsite as the dominant mineral component. The present day setting of the bauxites from Penhalonga indicate a rather incompletely developed weathering mantle, which is characterized by saprolitic materials rich in kaolinitic clays. This can be accepted when it is assumed that in most places surface erosion removed the upper parts of the weathering profiles. In the area the representative profiles show an irregular distribution. Pockets of kaolinitic clay are often surrounded by gibbsite masses or nodules of gibbsite are encapsulated in kaolinitic clays. Very probably this configuration implies different superimposed weathering phases acting during the bauxite formation. The heterogeneous structure in the laterite-bauxite horizon is explained as a result of repeated leaching and redeposition of the major chemical constituents, Al, Fe and Si, leading to a complicated polyphase bauxite development under specific geomorphologic conditions (Bardossy and Aleva, 1990). The brecciated duricrust seems to have protected the laterite-bauxite horizons and in the present situation these are mostly found on top of small plateaux or on flanks of gently sloping hills and especially on bauxites from metabasalt or gabbro. This irregular distribution of the hard crusts can be attributed to intensive erosion after the formation of the bauxite and duricrust.

CHAPTER IV

4. THE GEOCHEMISTRY OF THE WEATHERING SEQUENCES IN PENHALONGA DISTRICT, MANICA PROVINCE, MOZAMBIQUE

4.1. Introduction

The characterization of chemical weathering of rocks, under variable geological and climatic environments, has been studied since many years. Different approaches include: mineralogical parageneses in weathered rocks (Hughes, 1980; Velde and Meunier, 1987; Fritz, 1988), the relationship between rock weathering and river water chemistry (e.g. Tardy, 1971; Drever, 1971, 1988; Miller and Drever, 1977); the distribution patterns of major elements in weathering profiles (Chesworth *et al.*, 1981; Nesbitt and Young, 1989; Nesbitt *et al.*, 1980; Kronberg *et al.*, 1987; Topp *et al.*, 1984) and of trace-elements particularly the rare-earth elements (e.g. Zeissink, 1971; Nesbitt, 1979; Duddy, 1980; Cullers *et al.*, 1987; Middelburg *et al.*, 1988; Brimhall *et al.*, 1991; Condie *et al.*, 1995; Valetn, *et al.*, 1991; Valetn *et al.*, 1997). Detailed geochemical studies on weathering profiles developed in tropical terrains have received special attention. Highly weathered, old surfaces developed under conditions of intensive leaching, oxidation and low pH (McLennan, 1995). The layers of lateritic mantles covering the underlying fresh parent rock can have thicknesses of up to hundred meters. Several studies have been undertaken in different tropical environments on geochemical mineral prospecting and the physico-chemical parameters controlling the distribution and mobilization of the chemical elements on lateritic profiles (e.g. Davies, 1985; Boski and Herbosch, 1990; Roquin *et al.*, 1990; Braun *et al.*, 1990 and 1993; Trescasses, 1992; Nahon and Tardy, 1992; Butt and Zeegers, 1989 and 1992). Most of the above mentioned studies aimed for qualitative and quantitative assessment of the major weathering factors governing/determining the mineral stabilities of the minerals present in the different parent rocks and in the newly formed phases, and the mineralogical control of the distribution of the elements within a weathering profile. Extensive weathered mantles covering different rocks occur in the Penhalonga area of the central west Manica Province, Mozambique. The lateritic profiles are considered to have developed *in situ* and their geochemical characteristics must reflect the composition of the underlying parent rock and give some indications of the dominant conditions during weathering. The purpose of this study is to explain the principal trends of weathering describing the distribution patterns of major and trace elements in the lateritic-bauxitic sequences developed in the area on the Precambrian gabbro, metabasalt and anorthositic rocks.

4.2. General setting and description of the sequences

The area bearing the weathering sequences considered in this study lies on Precambrian terrains in the Penhalonga area, west of the Manica Province in Mozambique. The petrographic characteristics of the anorthosite, metabasalt and gabbro parent-rocks on which the weathering sequences are developed, are briefly described in the following sections. Approximate division and description of the weathering profiles are made according to Bardossy and Aleva (1990). The sampled sequences are located in the central part of the Alumen mine area (Fig. 4.1).

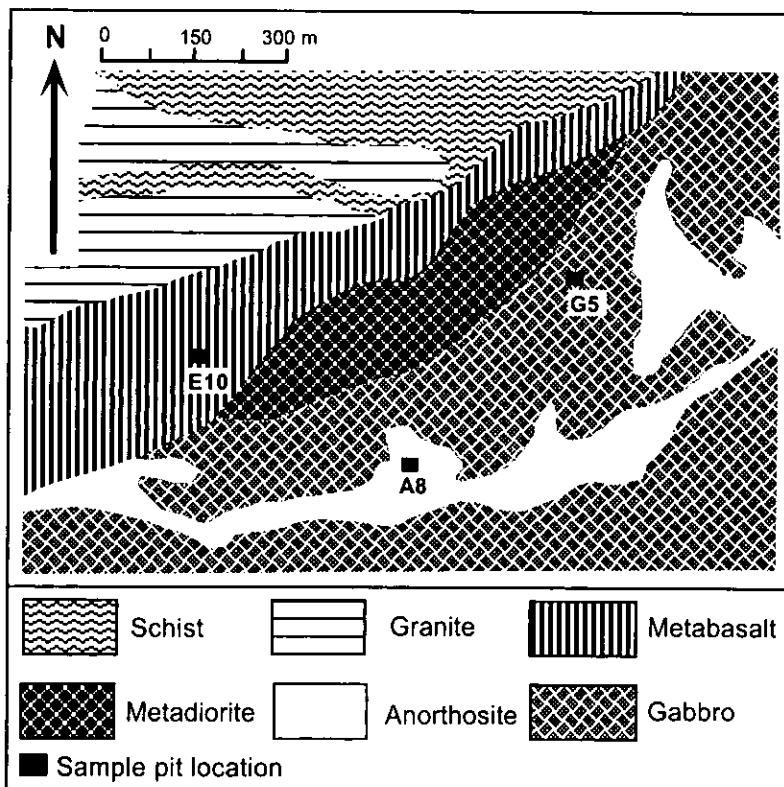


Figure 4.1: Generalized geological sketch map of the central part of the bauxite deposits from Alumen in the Penhalonga area, west of Manica, Mozambique.

4.2.1. Description of the weathering sequences

4.2.1.1. Sequence on anorthosite (Figure 4.2A)

The sampled sequence in a pit of 9 meters deep was divided, roughly, in four horizons defined on basis of principal mineralogical features. From the bottom to the top the main horizons are:

1. *Fresh or partially weathered anorthosite*: in the lower parts of the sequence, as a massive, coarse grained white rock with plagioclase feldspar as the major mineral, pyroxenes/amphiboles and accessories.
2. *White kaolinitic saprolite*: approximately 3 meters thick, friable, showing preserved textures of parent rock. The dominant mineral is kaolinite with traces of illite and gibbsite. Occurrence of core boulders of the parent rock is common in this section of the sequence.
3. *The mottled zone*: overlying the saprolite, appears to represent the remaining upper part of the sequence. The mottles define generally small red-yellowish domains in a whitish clay matrix or

in a porous friable mass of kaolinite and gibbsite, where the parent-rock texture is still recognizable. Another feature of this zone is the presence of hard gibbsite nodules.

4. *The topsoil cover*, with a maximum 50 cm thickness, is a gritty soil layer with organic matter.

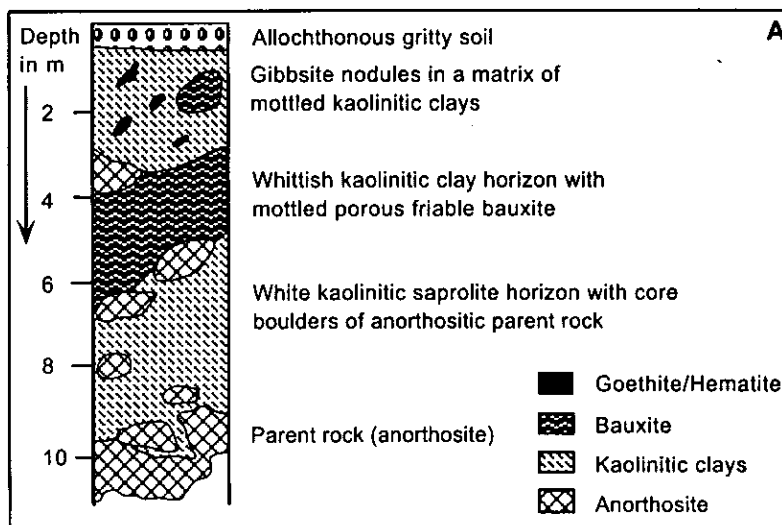


Figure 4.2A: Weathering sequence over anorthositic parent rock. The section location is indicated in Figure 4.1.

4.2.1.2. Sequence on metabasalt (Figure 4.2.B).

This sequence is usually located on a flattened hilltops and is generally some 10 meters thick

1. *The fresh partially altered parent rock:* at the bottom. A freshest section of metabasalt has a dark green, fine-grained matrix of amphibole minerals, epidote and minor plagioclase feldspars, calcite and accessories.
2. *A saprolitic zone:* where plagioclase feldspars and amphiboles are disaggregated and transformed dominantly into gibbsite, kaolinite and Fe-minerals. The brown-yellow bottom parts with extensive friable masses of completely weathered parent rock pass gradually to a red-brown upper section richer in Fe-minerals.
3. *The top of the profile:* consists of a 20-50 cm thick reddish brecciated/indurated Fe-rich layer (duricrust), which in turn has a thin soil cover.

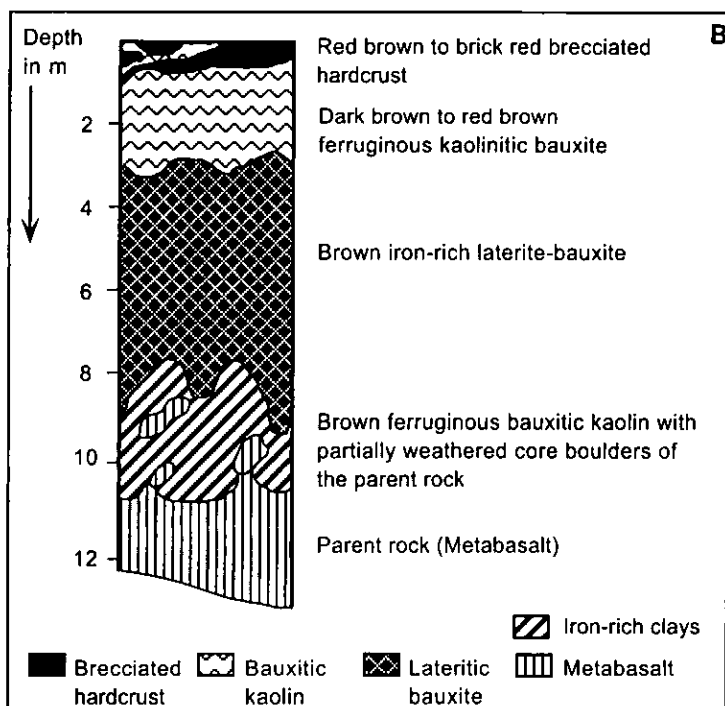


Figure 4.2B: The sampled weathering sequence developed on metabasalt. The location is shown in Figure 4.1 (Central part of Alumen deposits, in Penhalonga).

4.2.1.3. Sequence on gabbro (Figure 4.2C)

The main horizons in the sequence of 4 meters thick are the following (from bottom to top):

1. *The parent rock:* is a coarse-grained gabbro showing dark parts of pyroxene-amphibole minerals adjacent to grey-whitish plagioclase feldspars.
2. *A saprolitic horizon:* overlying the parent rock is a clayey layer of about 2 meters thick. This friable yellowish-brownish zone preserves the original structure of the gabbro and is mainly composed of kaolinite minerals associated with aluminium and iron oxyhydroxides.
3. *An indurated ferruginous horizon:* consisting of yellow-brown-reddish material with white yellowish spots of mainly kaolinite overlies the clayey rich zone. In this layer the parent texture is still well recognizable.
4. *the topsoil horizon:* the upper part of the sequence which consists of isolated ferruginous nodules (gibbsite, goethite), in a dark brown clayey material. Near the surface it is mixed with organic matter.

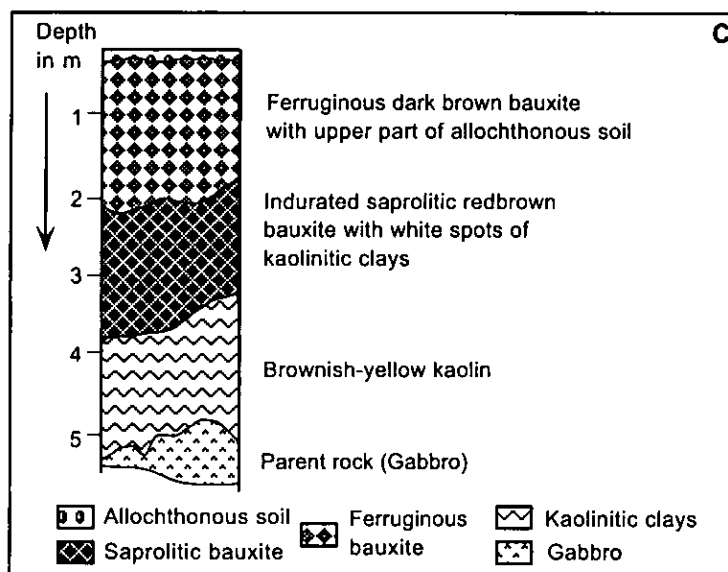


Figure 4.2C: Profile of weathering developed over gabbroic parent rock in the central part of the bauxite deposits from Alumen in Penhalonga area.

4.3. Petrographic features and mineralogy of the weathering products

As indicated before, the principal mineralogy of the samples from each horizon in the three weathering sequences was determined by X-ray diffraction analysis (XRD), and by optical microscopy for the parent material. Particular attention was given to the fraction less than 2 microns (Table 4.1) in order to search for the principal clay minerals present.

Table 4.1: Particle size distribution on selected samples of bauxites from Penhalonga deposits. Sequences of weathering (A) = anorthosite; (G) = gabbro; and (E) = metabasalt.

Sample Code	>1000 μ m (wt %)	1000- 210 μ (wt %)	210- 50 μ (wt %)	< 50 μ (wt %)	< 16 μ (wt %)	< 2 μ (wt %)
A823 t	4.03	7.45	10.17	35.77	27.75	14.53
A889 b	0.69	5.84	9.41	39.80	30.40	13.85
G501 t	16.33	5.23	12.58	27.56	24.15	14.17
G545 b	10.83	8.68	7.31	34.76	27.15	11.26
E108085 t	22.57	8.42	8.58	23.60	22.94	13.88
E1045 m	13.00	8.99	5.87	32.69	27.24	12.79
E1001 b	12.62	6.23	4.48	36.87	28.56	11.24

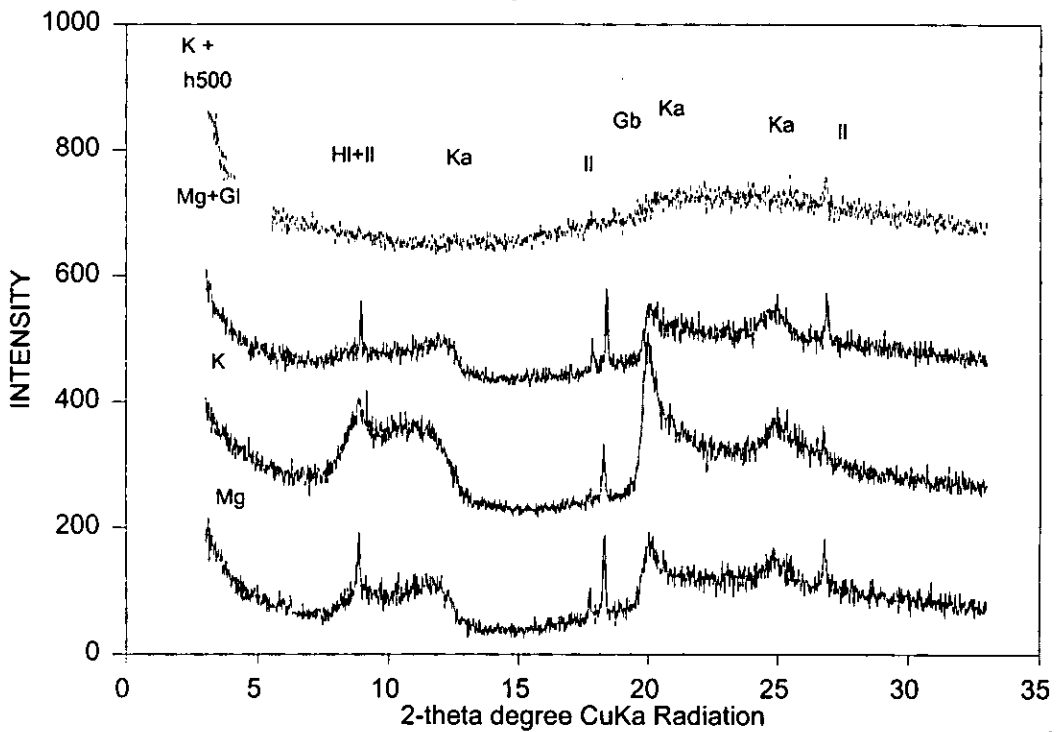
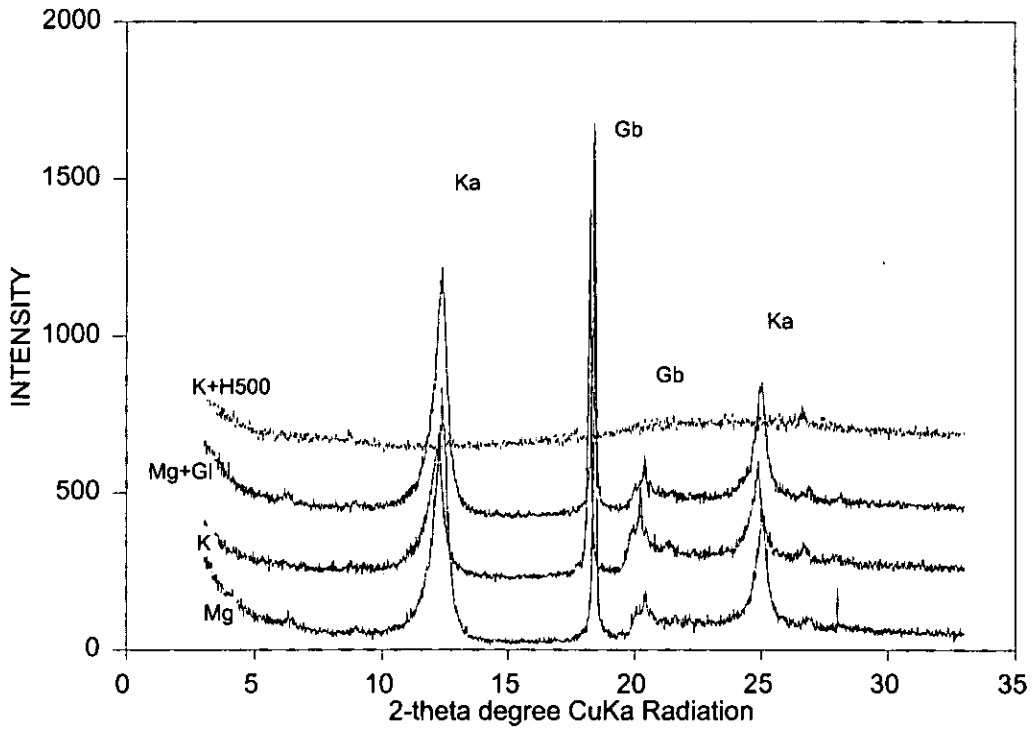
Position of the samples in the weathering profiles: t = top; m = middle; and b = bottom.

In the clay zone, above the fresh or slightly weathered parent rock, kaolinite represents the main component, together with gibbsite. This is remarkable on *the sequence on anorthosite* (Fig. 4.3), with kaolinite showing (XRD) diagrams with different degrees of crystallinity from the bottom sample (b) up to the most upper one (t). The middle samples are similar to those from the top and they show different colours, with yellowish-red spots in a kaolinitic white matrix, induced by the presence of oxy-hydroxides, mostly of iron. In the same sequence gibbsite is present either as tiny patches within kaolinitic masses or as pebbles/boulders with different *habitus* and sizes.

The sequence on metabasalt is much more uniform and contains relatively less kaolinite and more gibbsite and oxy-hydroxides of iron. In the sampling site the upper part of this sequence contains a brecciated hardcap composed of grains of gibbsite, goethite/hematite, quartz and also magnetite as well as pieces of granitic rock, cemented in a yellowish, reddish matrix. This indurated duricrust seems to have collected mineral and rock grains from the nearby outcropping rock types, such as granites, serpentinites and schists. There exist no distinguished mineralogical features among the samples in the remaining part of the sequence (Fig. 4.4), since gibbsite and kaolinite are throughout the major minerals.

The sampled *gabbro weathering profile* has interesting petrographic features. On top of the parent rock, a yellow-brownish kaolinite-rich basal saprolitic zone occurs, followed by the upper saprolitic horizon. The latter is hard, porous and lightweight with a well preserved fabric of gabbro, and also with regular blocky-shaped weathered material following fractures/joints of the parent rock. The joint surfaces are sometimes covered with a thin black coating of Mn oxy-hydroxides displaying typical dendritic structures, although no Mn-mineral has been detected with the X-ray diffraction determinations. Various MnO₂ polymorphs may form under surface to near-surface conditions (Brookins, 1988). The porous patches are sites of former plagioclase feldspars, which contain fine grains of white gibbsite and kaolinite and they are set a yellow to brown hard matrix. Gibbsite and kaolinite are the major constituents, both in the lower and upper parts of the profile (Fig. 4.5).

Figure 4.3: (next page) X-ray diffraction patterns of a fraction less than 2 microns of (A) top sample and (B) bottom sample from the profile on anorthosite after different treatments. K+H500=Potassium-treated and heated under 500°C; Mg+Gl=Magnesium-saturated and glycolated; K=Potassium-saturated sample; and Mg=Magnesium-saturated sample. Ka=Kaolinite; Gb=Gibbsite; Il=Illite; Gt=Goethit; Hl=Halloysite.



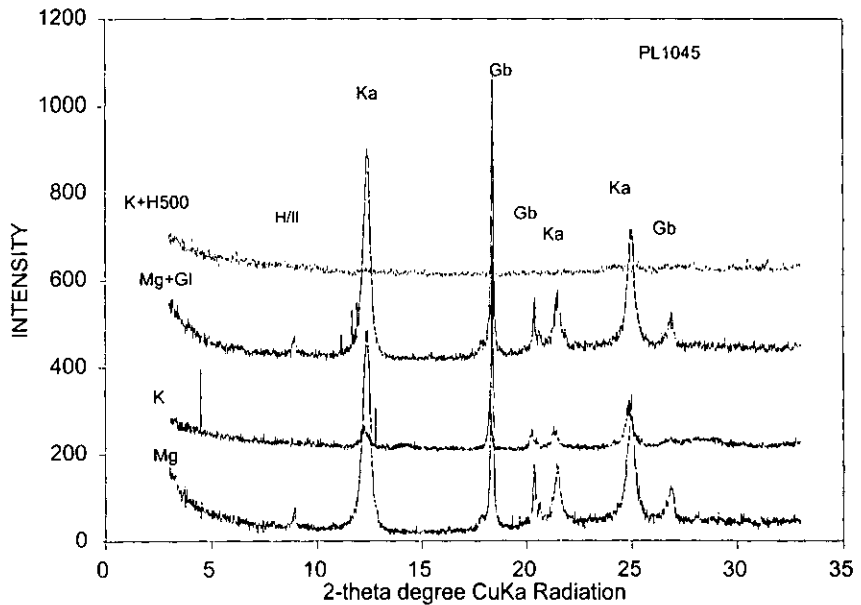
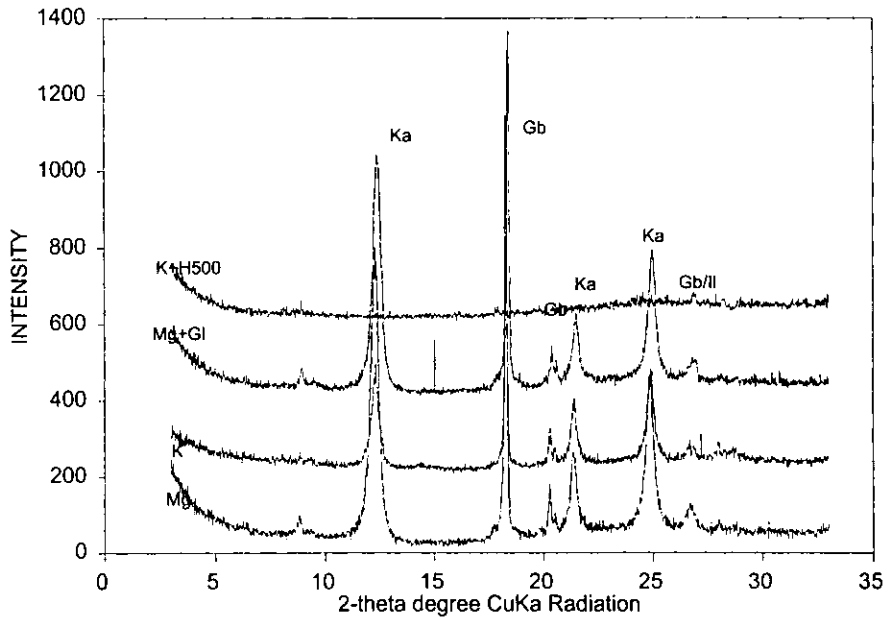


Figure 4.4: X-ray diffraction patterns of a fraction less than 2 microns of (A) top, (B) middle sample from the profile on metabasalt after different treatments. K+H500=Potassium-treated and heated under 500°C; Mg+Gl=Magnesium-saturated and glycolated; K=Potassium-saturated sample; and Mg=Magnesium-saturated sample. Ka=Kaolinite; Gb=Gibbsite; II=Illite; Gt=Goethite; HI=Halloysite.

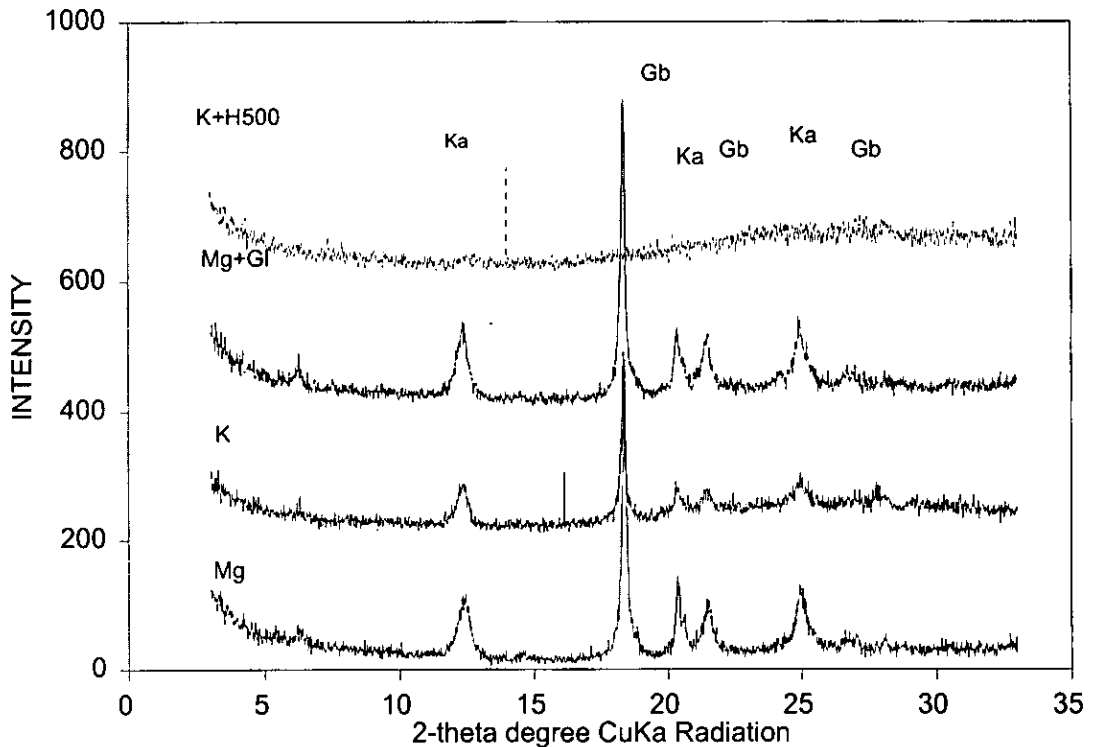


Figure 4.4: X-ray diffraction patterns of a fraction less than 2 microns of (C) bottom sample from the profile on metabasalt after different treatments. K+H500=Potassium-treated and heated under 500°C; Mg+Gl=Magnesium-saturated and glycolated; K=Potassium-saturated sample; Mg=Magnesium-saturated sample. Ka=Kaolinite; Gb=Gibbsite; Il=Illite; Gt=Goethit; Hl=Halloysite.

4.4. Weathering trends

4.4.1. Chemical weathering reactions

According to many researchers (e.g. Nesbitt *et al.*, 1980; Kühnel, 1987; Trescasses, 1992) the most important processes in chemical weathering are: the decomposition of rock-forming minerals and leaching of elements by hydrolysis from primary minerals during their degradation to clays; secondly the processes of fixation of elements by ion exchange and adsorption of the same elements onto secondary clay minerals and other minerals. In fact, chemical weathering is a complex geochemical process involving several reactions that take place between primary minerals and permeating fluids, the products of which are secondary minerals that form the weathering profile and the dissolved material that is removed from the profile through migrating waters (Trescasses, 1992). The main reactions acting in the chemical weathering include dissolution, oxidation, mineral-solution interfacial exchange and precipitation of secondary minerals. Typical secondary mineral phases are the clay minerals (Kronberg *et al.*, 1987), but also poorly crystallized Ti-Fe-Mn-Al-oxy-hydroxides and silica (Kühnel, 1987).

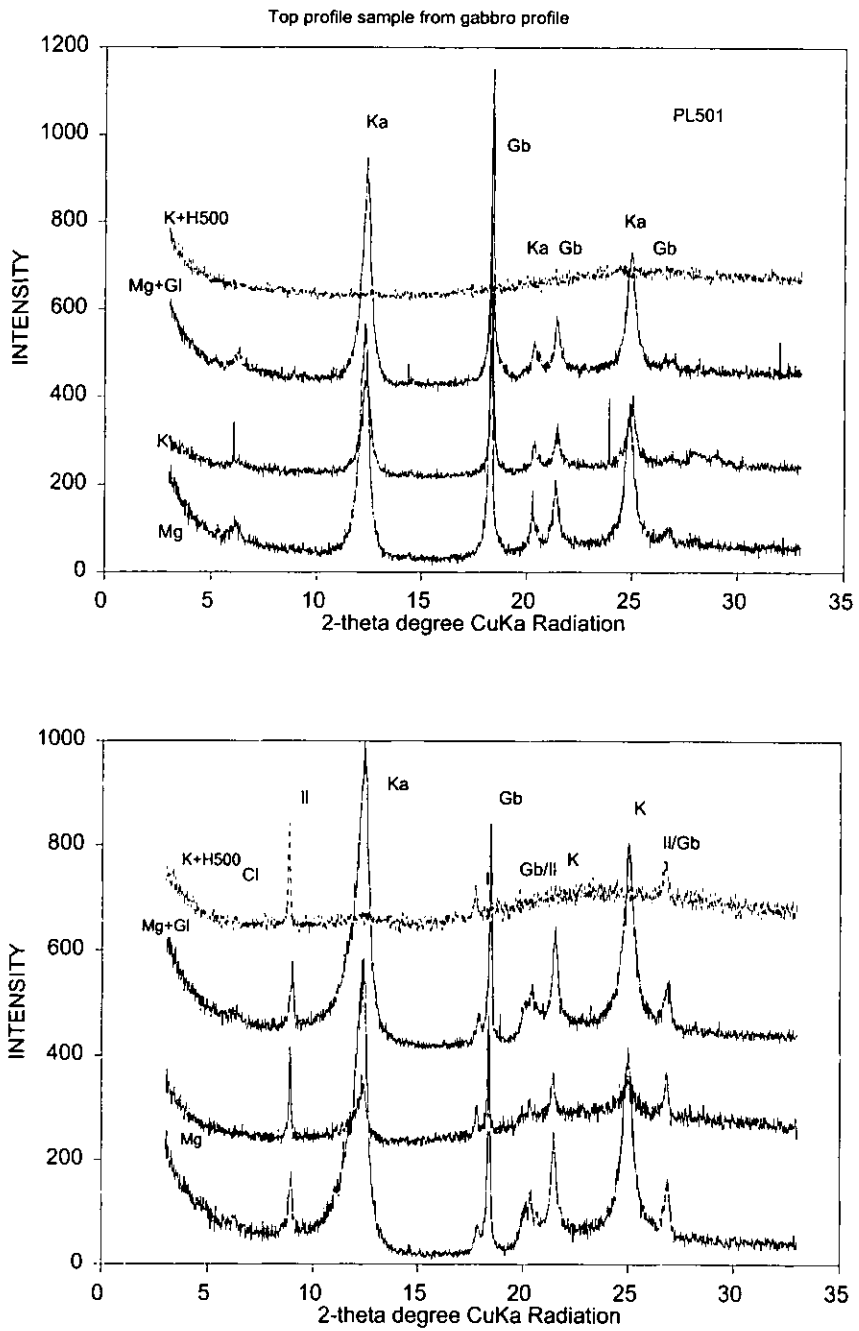


Figure 4.5: X-ray diffraction patterns of the fraction less than 2 microns of the (A) top and (B) bottom samples of the profile on gabbroic parent rock after different treatments. (For legend see figure 4.3).

4.4.2. Surface water characteristics

It has long been recognized that the chemistry of surface waters is controlled by interactions with the rocks of the drainage area and is related to specific rock alteration reactions (Garrels, 1967; Miller and Drever, 1977; Drever, 1982). The stream water compositions results primarily from the reactions taking place within the weathering profile (Nesbitt *et al.*, 1980). With a view to gain a qualitative impression of possible dynamics of the weathering process, samples of stream waters were collected in the area of Penhalonga. The sampling took place during the dry season (July-August) in the main streams draining the area of bauxite occurrences. This is based on the assumption that the sampled stream waters contain a major contribution from the ground waters percolating the weathering sequences. Therefore it should be expected that the stream waters obtained their characteristics mainly from the weathering reactions written in the previous section. The waters draining the study area show relatively high amounts of Ca, Mg, and SiO₂ with associated pH values around 7, indicating that they are closely related to chemical weathering of the predominantly basic silicate rocks (Table 4.2). Together with Na₂O and K₂O, the components CaO, MgO and silica constitute the most easily detectable additions to stream waters, which are also the major rock-forming elements with aqueous affinities (Kronberg, *et al.*, 1987). The neutral to alkaline pH values of the sampled waters from the area indicate that they were in interaction with clay minerals and partially weathered materials, in absence of organic materials. This means in contact with solutions from the lower zones of the weathering profile. In this zone the pH is increased as a result of ion-exchange processes of the previously leached alkalis and alkaline earths onto the clays adjacent and within the fractures (Nesbitt *et al.*, 1980). This is different from the waters percolating the soil zone, which have dissolved CO₂ produced by oxidation of organic materials and also acquire humic acids, making them aggressive solutions, with low pH (Nesbitt *et al.*, 1980).

Table 4.2: Principal chemical composition of water samples collected in the bauxite area of the Penhalonga District.

Sample	pH	SiO ₂	MgO	CaO	Na ₂ O	K ₂ O
PL-03	7.30	3.13	0.85	1.22	1.07	2.56
PL-05	7.13	4.33	0.62	0.80	1.12	0.45
PL-07	7.76	3.56	1.51	1.06	1.12	0.64
PL-08	7.13	4.70	1.04	1.41	1.23	1.09
PL-1A	7.70	2.58	1.94	0.90	0.35	0.37
PL-1B	7.70	2.60	1.94	0.91	0.37	0.36
PL-2A	7.92	1.87	0.76	0.72	0.04	0.24
PL-3A	8.04	2.09	0.19	0.36	0.06	0.30
PL-4A	7.85	4.11	3.68	1.28	0.63	0.35
PL-5A	7.70	3.26	4.25	0.97	0.29	0.24
PL-6A	7.84	2.49	0.73	0.94	0.34	0.30
PL-7A	7.47	3.70	4.32	6.22	1.41	0.24
PL-8A	7.26	5.51	3.02	3.49	2.08	0.36
PL-9A	6.95	3.31	1.59	2.69	1.26	0.24

The values are given in ppm

The low pH values of the soil waters cause exchange of H^+ for alkalis and alkaline earth elements leached from primary minerals and sorbed onto clays. During weathering the leached elements are transported to the lower profile zones and to the fractures of the parent rock.

Lithologically, the Penhalonga area is dominated by mafic and also ultramafic rocks, such as anorthosites, gabbros, metabasalts, schists and serpentinites. Thus, principal minerals represented by plagioclase feldspars, pyroxenes/amphiboles are the main source for Ca (Na), Mg, Al, Fe and SiO_2 . These elements are described to be present in the solutions percolating the saprolites of the weathering profiles. Furthermore, also the solutions migrating from fractures in the parent rocks towards the weathering front are able to dissolve primary minerals and get the more soluble elements into solution (Nesbitt *et al.*, 1980). It is, therefore, understandable that the waters percolating through the weathering zone to the ground waters and/or stream waters contain the major rock/mineral-forming elements. In general, chemical equilibrium between surface waters and minerals would not be expected since the reactions occur in an open system, subjected to water flushing. Nevertheless, it is important to assess a general relationship between the weathering products and surface waters. An approach for this can be made by examining the predominance diagrams of stability relationships between primary and secondary minerals (Miller and Drever, 1977; Stumm and Morgan, 1970; Nesbitt and Young, 1984). In terms of the concentrations of Ca^{2+} , Na^+ , K^+ , H^+ and H_4SiO_4 the waters from the Penhalonga area plot in the diagrams after Stumm and Morgan (1970) close to the boundary between kaolinite and gibbsite fields (Fig. 4.7).

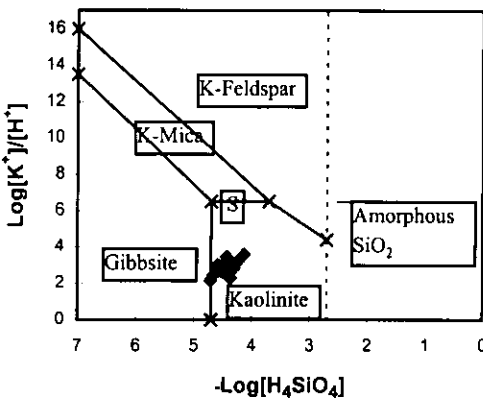


Figure 4.7: A: Plot of the composition of waters draining the bauxite deposits in the Penhalonga area in the predominance diagram A. It illustrates the stability relations between K-Feldspar and its weathering minerals. Logarithmic values of molar ratio K^+/H^+ are plotted against the relative logarithm of H_4SiO_4 concentration. The collected water samples fall close to the gibbsite-kaolinite boundary. (S) represents average of sea water (diagrams after Stumm and Morgan, 1970).

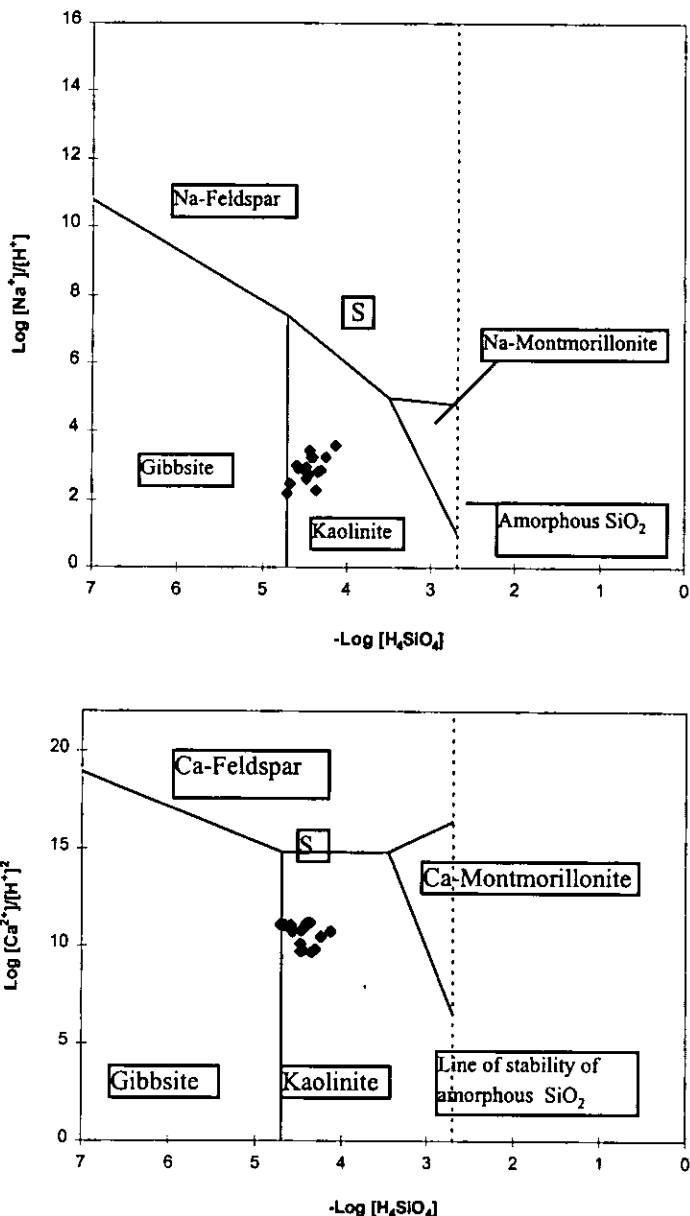


Figure 4.7: B and C: Plot of the composition of waters draining the bauxite deposits in the Penhalonga area in the predominance diagrams. These illustrate the stability relations between Na- and Ca-Feldspars and their weathering minerals. Logarithmic values of molar ratio of Na^+/H^+ and $Ca^{2+}/(H^+)^2$ are plotted against the relative logarithm of H_4SiO_4 concentration. The collected water samples fall close to the gibbsite-kaolinite boundary. (S) represents average of sea water (diagrams after Stumm and Morgan, 1970).

There seems to exist a close correspondence between the character of the waters and the gibbsite-kaolinite mineralogy of the weathering sequences. The water chemistry suggests furthermore the immobility of Al, which in waters shows concentrations below detection limit (0.03 ppm). As stated earlier Al is fixed, or removed from the solutions, in all stages of weathering first in kaolinitic clays and afterwards in gibbsite.

4.4.3. Bulk composition variation and degree of chemical weathering

An approach to assess the rock bulk chemical changes resulting from weathering has been developed by Nesbitt and Young (1984, 1989). Using mineralogical and chemical data combined with thermodynamic, kinetic and mass balance constraints an attempt was made to evaluate major element data from weathering profiles in terms of mineralogical changes and degree of weathering. To that purpose ternary diagrams A-C-K and A-CN-K-FM have been used for specification of composition variations during weathering of a variety of igneous rocks (Nesbitt and Young, 1984). Major element chemical data plots of the weathering profiles on anorthositic, gabbro and metabasaltic rocks are shown in Figure 4.8A and B (following page).

Figure 4.8.A illustrates the changes of plagioclase feldspars and pyroxenes/amphiboles of the parent rocks to kaolinite and gibbsite. As can be seen, the weathering products evolved along the edge CN-A indicating that essentially Ca and Na have been released. These trends were calculated and observed on weathering profiles developed on basic plutonic and volcanic rocks (Nesbitt and Young, 1994, 1989). In the A-CN-K-FM-diagram (Figure 4.8B) they appear to evolve initially parallel to the CNK-A edge, because of removal of Ca and Na, and then along the FM-A edge. All rocks appear to be developed towards the advanced stages of continental weathering, with minerals such as kaolinite and gibbsite represented in the figures by the A apices. The advanced stages of these weathering sequences are also consistent with both the Chemical Index of Alteration (CIA)* of Nesbitt and Young (1982) and the Chemical Index of Weathering (CIW)** of Harnois (1988). Both indices give essentially a measure of the degree of depletion in major mobile components relative to immobile components during mineral or rock weathering. In the studied rocks the values of CIA and CIW increase from 32 (metabasalt), 45 (gabbro) and 55 (anorthosite) to approximately 100 in the most weathered material. This is a direct reflection of the transformation of the primary minerals to clay minerals and gibbsite, the major mineral components in the sequences.

*CIA = $[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$ (Chemical Index of Alteration, in molar proportions)

**CIW = $[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O})] \times 100$ (Chemical Index of Weathering, in molar proportions)

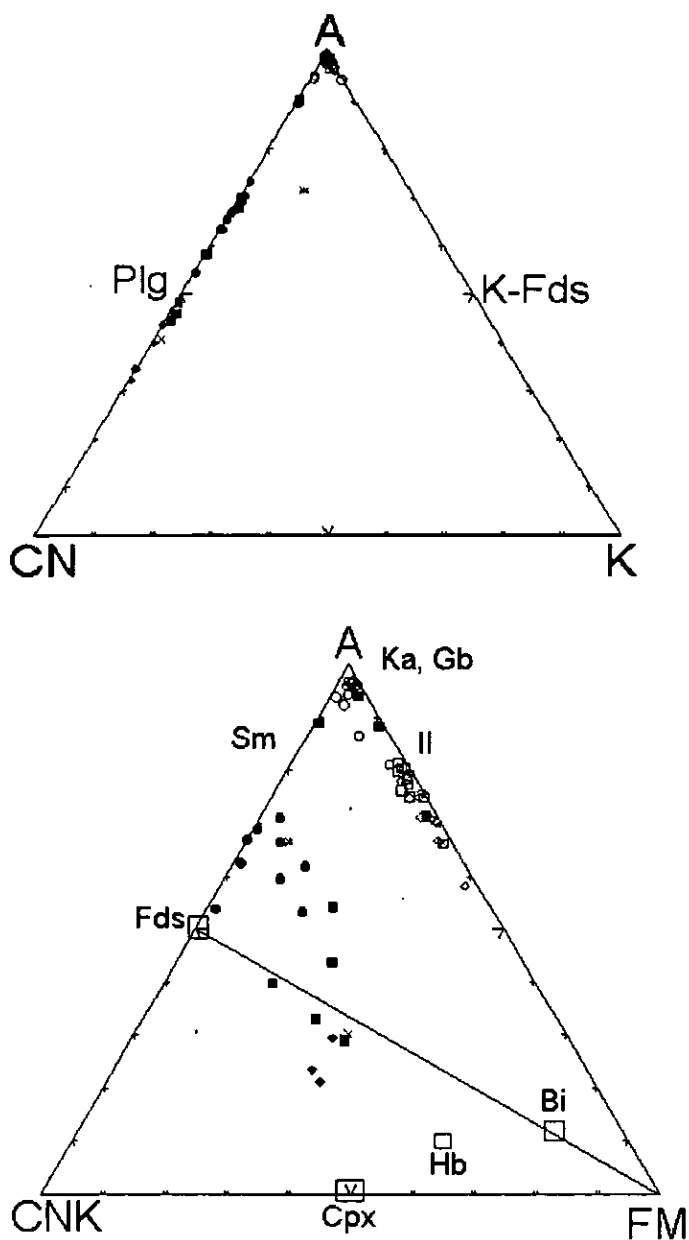


Figure 4. 8: The main trends of the weathering sequences in Penhalonga area on the ternary Plots A-CN-K and A-CN-K-FM (after Nesbitt and Young, 1984, 1989). The positions of the principal rock-forming minerals are also shown. Values in mole fraction; A=Al₂O₃, C=CaO, Na=Na₂O, K=K₂O, F=total iron as FeO and M=MgO. The A apex represents the minerals kaolinite (Ka) and Gibbsite (Gb). *Key to the symbols:* filled boxes=gabbro; filled circles=anorthosite; filled diamond=metabasalt, open box= Bauxite of gabbro; bauxite of anorthosite and bauxite of metabasalt. Plg=plagioclase, Fds=feldspar, Cpx=clinopyroxene, Hbl=hornblende, Bi=biotite, Sm=smectite and Il=illite.

4.5. Distribution of the elements in the weathering sequences

To evaluate the relative mobility of chemical elements during weathering processes several approaches have been considered. In most cases estimates are made by assuming one element to be immobile (Nesbitt, 1979; Middelbur *et al.*, 1988; Marsh, 1991; Brimhall *et al.*, 1991; Krauskopf and Bird, 1995). In this study the concentration variation of the elements was estimated by normalizing to Al or Fe the concentrations of the elements in each weathered sample and the resulting ratio divided by the Al- or Fe-normalized concentrations in the freshest parent rock. Marsh (1991) adopted a similar approach:

$$\text{Concentration ratio} = [(C_{e,w}/C_{i,w}) / (C_{e,p}/C_{i,p})], \quad (1)$$

where $C_{e,w}$ and $C_{e,p}$ are the element concentrations in the weathered sample and the parent rock, respectively, and $C_{i,w}$ and $C_{i,p}$ are the concentrations of Al or Fe, selected as immobile, in the same weathering sequence. The relative immobility of the selected elements was estimated using the approach proposed by Chesworth *et al.* (1981) i.e. comparing ratios between the Al, Ti and Fe concentrations in the sequences. Fe appears to be relative immobile on the metabasalt sequence and Al in the other considered sequences. The results of the calculations indicate different groups of elements depending on their behaviour.

4.5.1. Anorthosite weathering sequence

One of the most important mineralogical characteristics indicated by X-ray analysis is that the bottom of the weathering sequences on anorthosite contains predominantly kaolinite/halloysite and gibbsite. In the upper sections halloysite almost disappears in favour of gibbsite. This situation is commonly observed in weathering sequences of kaolinitic minerals. Hughes in his descriptions constructed a generalized weathering/ crystallinity sequence for 1:1 layer silicates as a qualitative assessment of weathering stages. Thus, halloysite and/or disordered kaolinite appear to represent the early stages of later parageneses dominated by ordered kaolinite with high crystallinity and gibbsite. These changes in mineralogy in weathering profiles greatly influence the distribution patterns of the chemical elements as documented in a number of studies (e.g. Fleische and Altschuler, 1969; Nesbitt, 1977; Braun *et al.*, 1990; Nesbitt and Wilson, 1992; Beauvais and Colin, 1993), especially of the trace elements.

Table 4.3: Chemical composition of the weathered samples on anorthositic rock. Samples APR1 and APR2 represent the less weathered anorthosite.

Sample	A801	A812	A823	A834	A845	A856	A867	A878	A889	APR1	APR2
wt%											
SiO ₂	16.70	14.97	25.90	22.44	32.35	38.85	36.21	42.60	43.99	53.93	56.17
TiO ₂	0.20	0.12	0.10	0.10	0.05	0.04	0.04	0.03	0.02	0.02	0.02
Al ₂ O ₃	51.69	54.56	48.20	51.10	43.39	39.88	43.02	35.62	35.42	29.86	26.01
Fe ₂ O ₃	2.96	1.86	1.58	1.64	1.98	1.80	0.62	0.34	0.28	0.32	0.33
MnO	0.02	0.02	0.03	0.04	0.04	0.02	0.03	0.02	0.01	0.01	0.01
MgO	0.11	0.09	0.07	0.06	0.07	0.08	0.08	0.07	0.05	0.14	0.20
CaO	0.08	0.09	0.04	0.06	0.06	0.07	1.00	0.61	1.27	5.10	6.18
Na ₂ O	0.06	0.07	0.07	0.08	0.05	0.07	0.12	0.42	1.05	4.79	6.26
K ₂ O	0.22	0.25	0.27	0.24	0.12	0.16	0.16	0.16	0.14	0.12	0.11
P ₂ O ₅	0.06	0.05	0.04	0.04	0.03	0.03	0.04	0.03	0.02	0.02	0.01
LOI	27.67	27.73	22.96	24.18	21.28	18.13	18.56	19.85	16.66	6.20	4.52
Total	99.77	99.81	99.26	99.98	99.42	99.13	100.41	99.75	98.81	100.51	99.82
Ppm											
Cr	88	62	42	23	144	20	15	9	6	13	9
Ni	36	32	82	71	52	16	25	13	9	6	4
Co	14	18	24	48	65	87	70	13	10	9	32
V	49	31	26	24	14	10	10	6	3	5	4
Cu	27	32	52	31	15	11	11	16	13	21	16
Zn	10	11	13	16	52	81	39	17	12	16	15
Ba	64	72	157	160	778	413	138	82	63	44	39
Sr	3	4	4	3	3	7	6	18	27	146	175
Zr	10	5	3	9	1	1	1	1	3	1	2
Be	0.48	0.40	0.52	0.38	0.37	0.45	0.51	0.74	1.37	0.78	0.76
Li	21.96	24.19	26.03	25.81	21.88	26.06	32.68	34.57	31.56	14.90	14.85

Major element distribution. The chemical analyses of the set of samples (A801 to APR) from the anorthosite weathering sequence are given in Table 4.3. The data are arranged in decreasing order of weathering degree, as can be noted in the changing values of SiO₂ (from 16.70 to 56.17%), Al₂O₃ (from 51.69 to 26.01%) and LOI (from 27.67 to 4.52%). Most of the major elements behave predictably as a result of the parent rock bulk chemistry, degree of weathering and weathering products mineralogy. With respect to Al, the major elements except Ti, Fe and K are impoverished with increasing weathering degree (Fig. 4.9A). It is interesting to observe the enrichment of the major elements Al, Ti and Fe, which, according to the data are 2 times for Al and 10 times for Ti and Fe. The relative immobility of Fe and Ti during chemical weathering has been reported in other weathering sequences as well (Chesworth *et al.*, 1981 and Marsh, 1991). Conditions of weathering have great influences on the mobility of these elements, as they can be Eh and pH dependants. Strongly depleted are Ca and Na, particularly in the earlier weathering stages. This clearly indicates that they are readily released during the breakdown of the plagioclase feldspars and removed from the residuum. This section of the profile contains essentially white kaolinite as the main mineral with minor illite and gibbsite. Mg and Si appear to be systematically depleted as the weathering intensity increases. Manganese and P show a more erratic behaviour. The middle part of the sequence appears to have developed anomalously, as is also reflected in the trace element patterns.

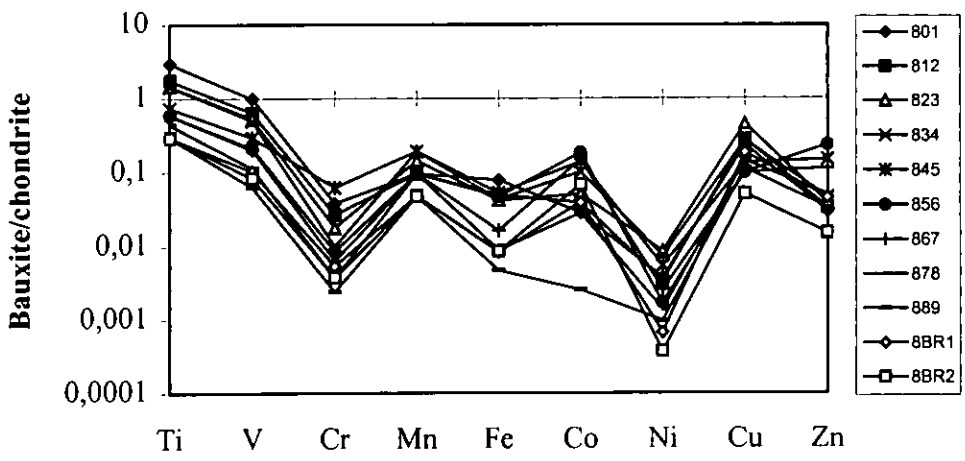
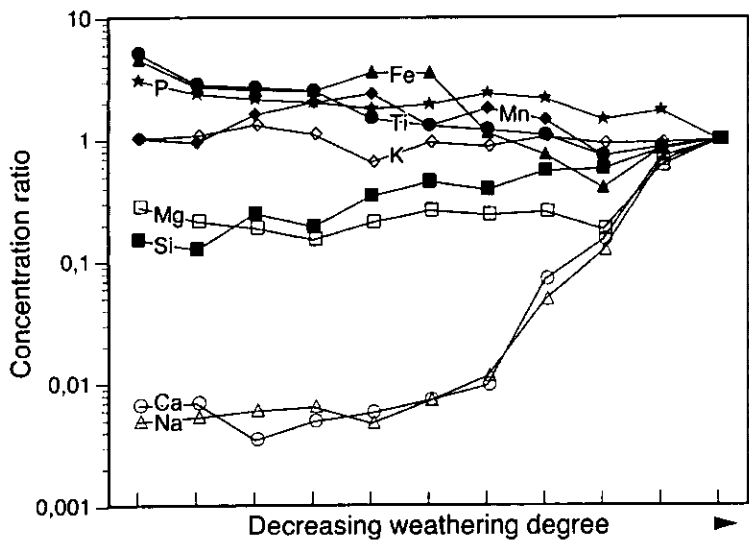


Figure 4.9: Variation diagrams of the major elements (A), in the weathering sequence on anorthosite. Reference element is Al considered to be immobile in the profile. B: normalized chondritic values for first series transition metals in bauxites from anorthosite (chondrite values of Langmuir et al. (1977) in Rollinson (1993).

Trace elements distribution. The distribution pattern of the trace elements mimic to some extent the pattern of one of the major elements. The pattern displays a complicated disposition in the middle part of the sequence where most of the elements have a generally erratic behaviour. This may probably be related to compositional heterogeneity of the parent rock. The behaviour of Cr, V and Ni can to some extent be compared to that of Ti and Fe, showing an increase in concentration ratios upwards in the sequence (Fig. 4.9B). Despite the mentioned anomalous behaviour of the elements in the middle section, the general tendency is of depletion of Co, Be and Zn like Mg and Si. The distribution of Li, Ba and Cu appears to be much as Mn and P. The distribution of Be is similar to MgO and Sr behaviour mimics that of Na and Ca, showing strong depletion. Elements of the first series transition metals (Fe, Mn, Cr, Ti, Ni, Co, Ni) are described as redox-controlled constituents (Butt and Zeegers, 1989; Middelburg *et al.*, 1988) and, during weathering they are mobilized and reprecipitated (Butt and Zeegers, 1989; Nesbitt and Markovics, 1997; Nesbitt and Wilson, 1992).

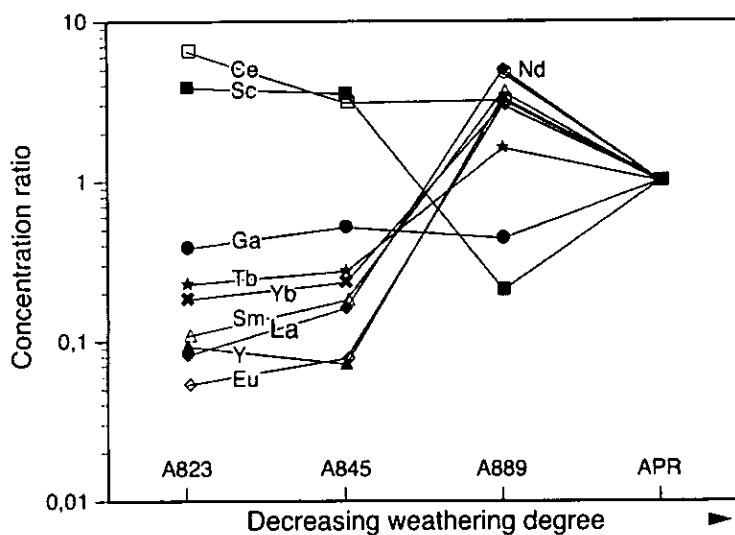


Figure 4.9: C: Variation diagram of REE, Sc, Ga and Y in the weathering sequence on anorthosite.

Rare Earth Elements, Y, Ga and Sc. The behaviour of these elements, particularly the REE, has a unique character. Sc is impoverished in the first weathering stages and accumulates in the upper parts of the profile, while Ga is to some extent depleted in the weathered mantle but shows a nearly constant ratio to Al (Fig. 4.9C).

Table 4.4: REE, Y, Sc and Ga concentrations (in ppm) in selected samples from the weathering sequence on anorthositic. Samples A832 and A889 represent the upper and lower zones, respectively, overlying the parent rock (APR).

	La	Ce	Sm	Eu	Tb	Yb	Lu	Y	Sc	Ga	La _n /Yb _n	Gd _n /Yb _n	Eu/Eu*
A823	0.76	53.20	0.15	0.24	0.10	0.18	<dl	0.6	19	26	2.82	1.83	2.96
A845	1.37	23.10	0.23	0.32	0.11	0.21	<dl	1.0	16	32	4.36	1.93	2.88
A889	34.10	19.30	3.69	9.82	0.52	2.16	0.32	26.0	1	22	10.57	1.33	8.28
APR	6.15	5.42	0.92	2.96	0.29	0.65	0.09	7.0	3	44	6.33	7.04	7.65

$Eu/Eu^* = Eu_n / (Sm_n \times Gd_n)^{1/2}$ where Gd was estimated by $Gd_n = (Sm_n \times Tb_n^2)^{1/3}$ of Condie et al. (1995), n=normalized chondritic values in Rollinson (1993) from Nakamura; <dl=below detection limit.

The distribution of REE and Y is particularly remarkable (Table 4.4 and Fig. 4.9C). They are enriched in the kaolinitic zone (sample A889), but show depletion in the advanced stages of weathering, except for Ce, which is clearly fractionated from the other REE. There is mobilization and some fractionation of the REE. The LREE are relatively more mobilized than the HREE. In the initial weathering stage all REE are enriched with slight preferential accumulation of the LREE. This tendency is reversed in the most weathered part of the sequence, as indicated by the La/Yb ratios (Table 4.4). Similar results are reported by Ronov *et al.* (1967) on weathering sequences from different crystalline rocks. It is related to changes in the weathering conditions during the transition from the acid stage in the top of sequence to the alkaline stage at the bottom parts. Surprisingly, Y which is commonly associated with HREE (Ronov *et al.*, 1967, Duddy, 1980) behaves almost like the LREE showing general depletion in the last stages of weathering. In the Chondrite normalized patterns, the enrichment of all REE in the kaolinite rich zone is displayed and also shown is the large positive Eu anomaly and only a slight Ce positive anomaly (Figure 4.10). It appears the Eu anomaly prevails in all weathered samples, although it is slightly enhanced in the kaolinite zone, and again diminishes in the upper horizons. A preferential accumulation of Ce in the most weathered samples is shown by their very large positive anomalies in the abundance patterns. Positive Eu-anomalies prevail in the more weathered samples.

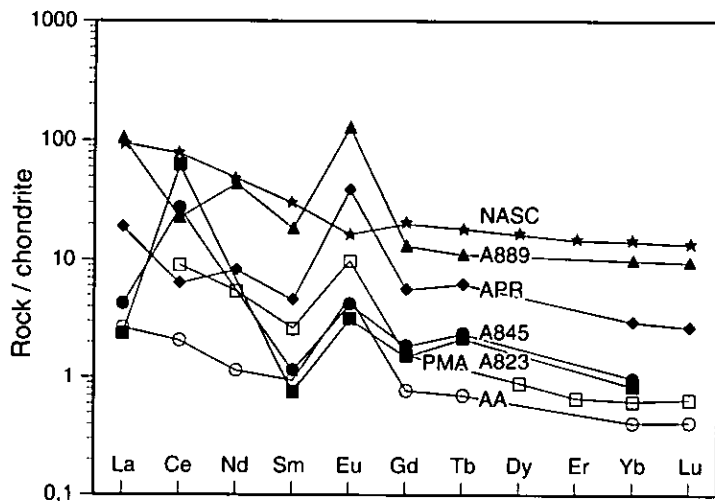


Figure 4.10: Chondrite-normalized patterns for samples of the weathering sequence on anorthosite. The REE composition of the rocks [NASC (North American Shale Composite), PMA (Post-Archaean Anorthosite) and AA (Archaean Anorthosite) in Taylor and McLennan (1985)] are also plotted for comparison. Chondrite values of Nakamura (1974) except Tb of Haskin *et al.* (1968) in Rollinson (1993); Gd estimated by $Gd_n = (Sm_n \times Tb_n^2)^{0.33}$.

4.5.2. Metabasalt weathering sequence

Analytical bulk chemistry data of the samples from the sequence on metabasalt are reported in Table 4.5. The analyses show the drastic composition change from the unweathered parent rock sample to the more weathered ones and how uniform the composition is of the deeply weathered samples. This probably indicates that the sample EPR does not represent exactly the base of the sequence, but rather cores of preserved unweathered parts of the parent rock adjacent to intensively weathered parts. However, the chemical composition of the sample EPR can still provide an indication of the likely source-rock composition. Comparison of the weathered and unweathered samples suggests that the sequence has undergone a significant degree of weathering. Higher contents in Al_2O_3 , Fe_2O_3 , TiO_2 and LOI, as well as much lower values in CaO and Na_2O are distinct features of the sequence samples. As mentioned earlier, the relative mobility of the elements in the metabasalt weathering sequence was estimated by normalizing to Fe_2O_3 the concentrations of the other elements (Table 4.5).

Table 4.5: Chemical analysis of weathered products derived from metabasalt. Sample EPR is representative of fresh parent metabasalt.

Sample	E1010	E109	E108	E107	E106	E105	E104	E103	E102	E101	E100	EPR
wt%												
SiO ₂	9.25	7.15	8.96	7.25	7.20	8.12	7.73	8.69	8.15	9.32	9.96	50.27
TiO ₂	3.27	3.80	3.23	3.38	4.77	4.40	2.20	4.52	2.05	4.85	1.60	1.42
Al ₂ O ₃	41.37	42.38	37.29	38.37	40.31	44.12	46.26	44.30	45.91	38.34	30.82	13.72
Fe ₂ O ₃	19.940	20.06	23.19	22.87	22.26	18.94	17.74	15.24	16.35	22.22	28.26	11.33
MnO	0.18	0.28	0.26	0.26	0.18	0.28	0.24	0.22	0.36	2.24	1.74	0.20
MgO	0.04	0.14	0.08	0.11	0.13	0.28	0.18	0.14	0.20	0.18	0.18	5.91
CaO	0.01	0.04	0.01	0.01	0.03	0.04	0.06	0.04	0.04	0.03	0.04	14.16
Na ₂ O	0.01	0.02	0.02	0.02	0.05	0.06	0.06	0.04	0.04	0.04	0.04	1.73
K ₂ O	0.08	0.46	0.27	0.52	1.29	1.36	0.90	0.84	1.32	0.97	0.94	0.18
P ₂ O ₅	0.15	0.07	0.11	0.07	0.06	0.08	0.06	0.06	0.05	0.62	0.06	0.60
LOI	25.47	24.67	25.54	26.26	22.73	22.40	24.02	25.27	25.43	20.81	25.47	1.33
Total	99.77	99.07	98.96	99.12	99.01	100.08	99.45	99.36	99.90	99.62	99.11	100.85
Ppm												
Cr	347	265	286	270	153	143	246	228	122	139	248	36
Ni	29	36	53	56	54	88	61	40	83	389	441	59
Co	84	143	167	127	129	144	155	123	280	227	887	87
V	594	425	472	435	500	322	319	293	212	537	687	766
Cu	48	43	55	98	67	69	67	53	80	58	30	180
Zn	10	22	32	41	35	28	39	23	36	26	121	240
Ba	25	17	18	20	25	26	27	27	25	30	33	20
Sr	1	2	1	1	1	1	1	1	2	5	10	109
Zr	22	18	34	20	17	19	25	34	26	35	27	17
Be	1.11	1.52	1.82	1.90	2.27	1.97	1.47	1.18	1.04	2.59	<dl	1.74

<dl>=less than detection limit

Figure 4.11A depicts the distribution of the *major elements* from the unweathered sample (EPR) to the top of the sequence. The overall uniformity in the variation of the major elements throughout the sequence is notable. SiO₂, P₂O₅, MgO, Na₂O and CaO contents in the weathered samples are clearly less than in the unweathered rock, and appear to maintain constant ratios to iron in the sequence. CaO, Na₂O and MgO have been strongly depleted and particularly CaO is almost completely stripped. Relatively less depleted are SiO₂ and P₂O₅. Element association is observed between MgO and Na₂O and between SiO₂ and P₂O₅. They are not fractionated from each other in the sequence (see Fig. 4.11A). The constituents TiO₂, Al₂O₃, MnO and K₂O are fractionated from iron. Fe-Al-hydroxides, kaolinitic and illitic clay minerals are the most frequent minerals in the sequence.

The development of the *trace elements* is similar to those of the major elements showing again the general uniformity in chemical composition throughout the sequence. Preliminary examination of the distribution of the elements in the sequence suggests that after the initial stages of chemical changes of the parent rock most of the elements tend to be retained in the profile, keeping almost the same ratio to Fe₂O₃ (Fig. 4.11B). Among the alkalis and alkaline earths, K, Ba, Li and Be are retained in the sequence, in contrast to Sr and Mg. These elements are relatively less mobile than the other alkalis and alkaline earths and are fixed in secondary minerals at the weathering site and are removed during mass wasting of continental weathering profiles (Nesbitt *et al.*, 1980).

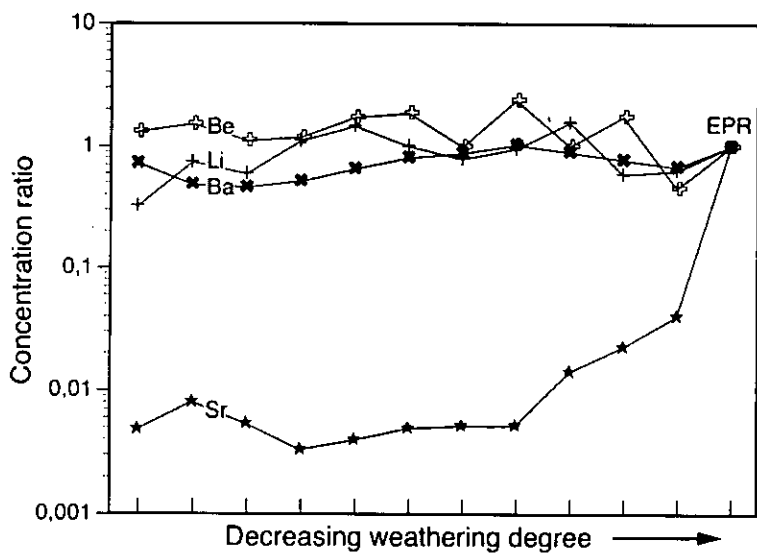
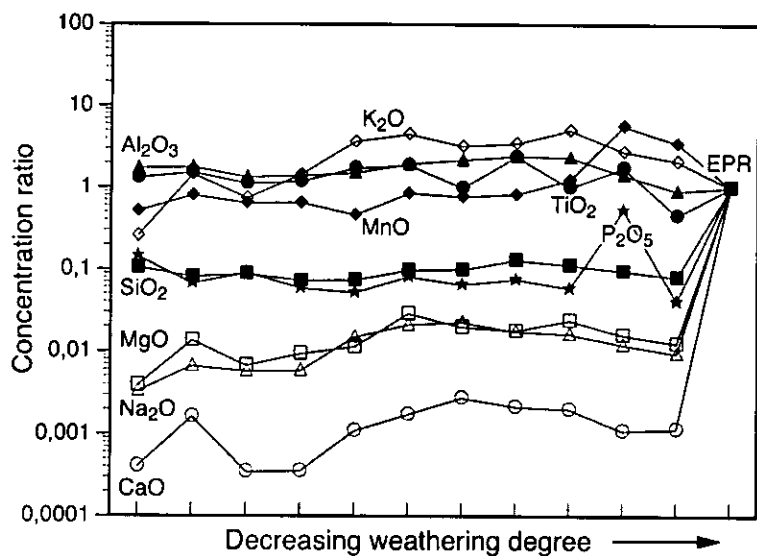


Figure 4.11: Variation diagrams of the content of major elements (A) and trace elements (B) in the weathering sequence on metabasalt. Reference element is Fe as it is considered immobile in the profile.

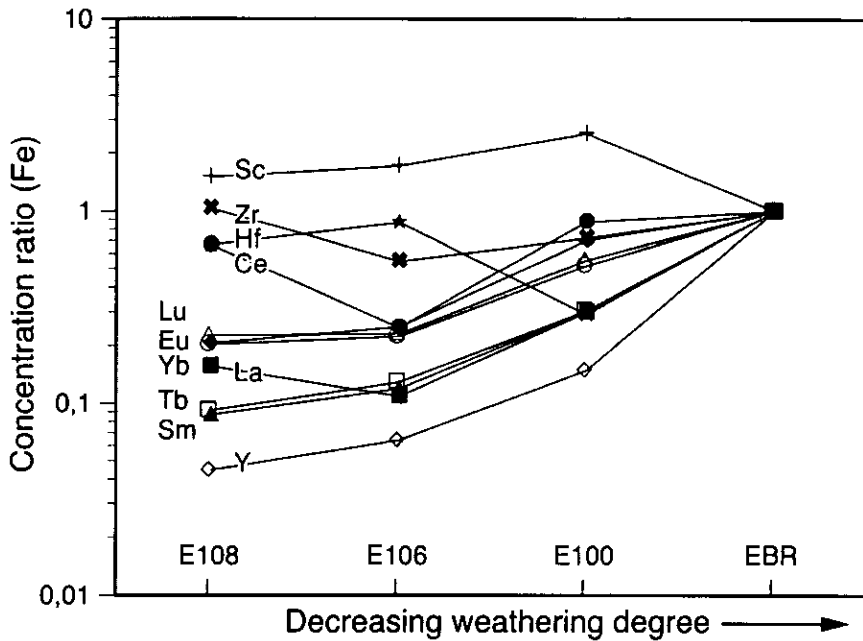


Figure 4.11C: Variation diagrams of REE, Sc, Zr, Hf and Y in the weathering sequence on metabasalt. Reference element is Fe as it is considered immobile in the profile.

Calcium and Sr display a similar distribution pattern and have been dramatically leached and so, but to a lesser extent, were Na and Mg. Wronkiewicz and Condie (1987) and Nesbitt and Wilson (1992) discussed the selective leaching of alkalis and alkaline earths, especially Na, Ca and Sr from weathering profiles on different source rocks. The ready mobilization of the soluble cations (Ca, Na) and immobilization of K was also observed in the weathering of metamorphic rocks (Gardner and Walsh, 1996). These elements, as well as Mg are described to be mobile cations in supergene environments, while K, Ba, Li, Cs and Be as weakly mobile cations (Perel'man, 1977, Nesbitt *et al.*, 1980), that are often fixed in weathering profiles by preferential exchange and adsorption on secondary minerals (Nesbitt *et al.*, 1980; Wronkiewicz and Condie, 1987; Nesbitt and Wilson, 1992).

The distribution of the first series transition elements in the weathering sequence of metabasalt has some features that differ from some described from weathering profiles on basic rocks (Fig. 4.11). Chromium is clearly accumulated in a similar manner as Fe, Ti and Sc. Depletion in the weathering sequence is observed for V, Cu and Zn (Fig. 4.12). Nesbitt and Wilson (1992) reported a decreasing tendency of Cu and fluctuating ratios to Ti of Zn in basaltic weathering profiles. Cobalt and Ni concentration ratio values increase in the lower parts of the sequence and decrease to the top. Zirconium shows very little fractionation from Fe and this situation, in the upper sections of the sequence, is also valid for Hf.

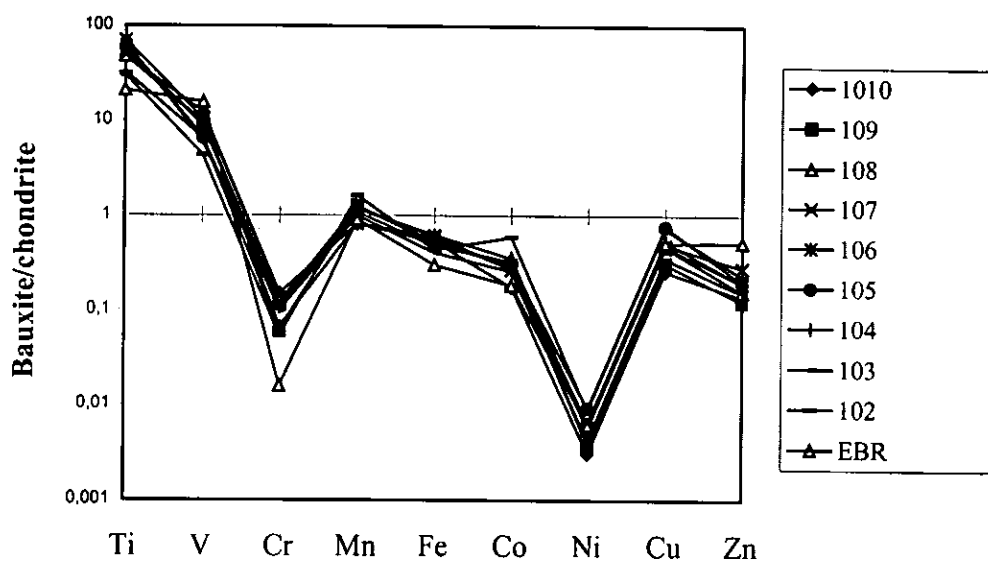


Figure 4.12: Transition element concentrations in bauxites and in the metabasalt parent source normalized to chondritic values. The normalized values indicated that in the weathered material almost all elements display higher chondritic values than the fresh metabasalt. Chondrite values of Langmuir *et al.*(1977) in Rollinson (1993).

Studies of *Rare Earth Elements and Y* report a different behaviour in weathering profiles developed on various types of crystalline rocks (e.g. Ronov *et al.*, 1967; Nesbitt, 1979; Duddy, 1980; Marsh, 1991; Braun *et al.* 1993). The REE's decrease systematically towards the top (Table 4.6 and Fig. 4.13) relative to iron, with exception of Ce. Very little fractionation is observed between LREE and HREE, with some tendency of HREE to be relatively enriched in parts of the weathering sequence. It is interesting to note how the negative Eu anomaly becomes positive in the weathered metabasalt. A large positive Eu anomaly is expected to develop on weathering profiles when the

REE's are dominantly controlled by feldspars in the parent rock (Condie *et al.* 1995). Furthermore general low contents in all REE are expected to result.

Table 4.6: REE, Y, Sc and Hf concentrations (in ppm) in selected samples from the weathering products on metabasalt (EPR).

	La	Ce	Sm	Eu	Tb	Yb	Lu	Y	Sc	Hf	La _n / Yb _n	Gd _n / Yb _n	Eu/ Eu*
E108	1.53	20.1	1.09	0.62	0.26	2.26	0.38	7	132	3.65	0.45	0.63	1.48
E106	1.02	7.19	1.43	0.72	0.35	2.38	0.37	10	144	4.56	0.29	0.68	1.30
E100	3.29	33.0	4.24	2.38	0.97	6.53	1.05	26	250	1.79	0.34	0.70	1.49
EPR	5.02	15.5	6.41	1.54	1.45	5.71	0.86	81	45	2.80	0.59	1.20	0.64

$Eu/Eu^* = Eu_n / (Sm_n \times Gd_n)^{1/2}$, where Gd was estimated by $Gd_n = (Sm_n \times Tb_n^2)^{1/3}$ following Condie *et al.* (1995); n=chondritic normalized [values of Nakamura (1974) in Rollinson (1993)].

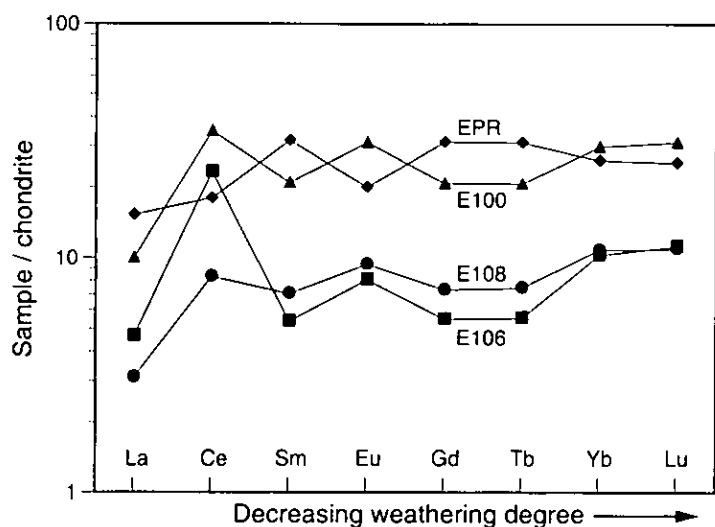


Figure 4.13: Chondrite-normalized REE patterns for samples of the weathering sequence on metabasalt. Chondrite values of Nakamura (1974) except Tb of Haskin *et al.* (1968) in Rollinson (1993); Gd estimated by $Gd_n = (Sm_n \times Tb_n^2)^{0.33}$.

The chondrite-normalized REE distributions of the sequence display higher values for the most REE in the parent rock, except for Ce (Fig. 4.13). Another distinct aspect is related to the relatively more significant depletion of Yttrium in the most weathered parts of the profile. In comparison with the other chemical elements, Y appears to have been mobilized in a similar way as Ca and Sr. Nesbitt and Wilson (1992) observed decreasing Y with increasing weathering of basaltic rocks. This suggests that Sr and Y are mostly controlled by primary Ca-bearing minerals and are easily removed from the weathering profile, once released from the source rock.

4.5.3. Gabbro weathering sequence

Data on the chemical composition of samples of weathering sequences of gabbroic rock are presented in Table 4.7. For this sequence, Al_2O_3 was selected as immobile following similar criteria as in the other described sequences.

Table 4.7: Chemical analysis of weathered products derived from gabbro parent rock. Sample GPR represents the less weathered parent rock.

Sample	G501	G523	G534	G545	GPR
Oxide (Wt%)					
SiO ₂	12.55	15.90	16.44	21.40	44.64
TiO ₂	1.38	6.32	1.82	1.04	0.15
Al ₂ O ₃	42.92	40.40	35.46	41.67	27.17
Fe ₂ O ₃	16.55	15.97	25.70	11.87	3.40
MnO	0.17	0.35	0.28	0.12	0.04
MgO	0.12	0.12	0.14	0.19	3.13
CaO	0.04	0.11	0.04	0.05	4.78
Na ₂ O	0.05	0.04	0.04	0.07	2.26
K ₂ O	0.55	0.53	0.68	1.16	0.37
P ₂ O ₅	0.08	0.05	0.08	0.05	0.02
LOI	25.04	20.11	19.65	21.46	14.75
Total	99.45	99.90	100.33	99.08	100.71
Traces (ppm)					
Cr	586	170	346	242	18
Ni	77	87	61	16	33
Co	108	162	130	73	22
V	301	191	272	179	50
Cu	25	27	29	26	4
Zn	33	29	22	28	29
Ba	60	47	75	112	58
Sr	2	2	2	2	83
Zr	30	28	29	20	21

The chemical changes in major, trace and Rare Earth Elements accompanying weathering are depicted in Figure 4.14. Amongst the *major elements* there is a decrease in the concentration ratios of CaO, Na₂O, MgO and SiO₂. This decrease is rapid in the lowermost section of the sequence corresponding to the disintegration of the plagioclase feldspars. Of the other major elements TiO₂ and MnO are slightly enriched in the profile, whereas very little variation is observed in the concentration ratios of the remaining elements (Fig. 4.14).

Figure 4.14B indicates that, except for Sr, which is strongly depleted, the *trace elements* were not removed from the weathering sequence. The first series transition elements are preferentially accumulated (Fig. 4.15). Zirconium, Li, Be and Ba are basically not fractionated from Al₂O₃. Recent studies on weathering of basalts describes similar behaviour for most of the considered trace elements. The main reason is related to the primary mineralogy of the parent rock, which hosts the trace elements (Nesbitt and Wilson, 1992).

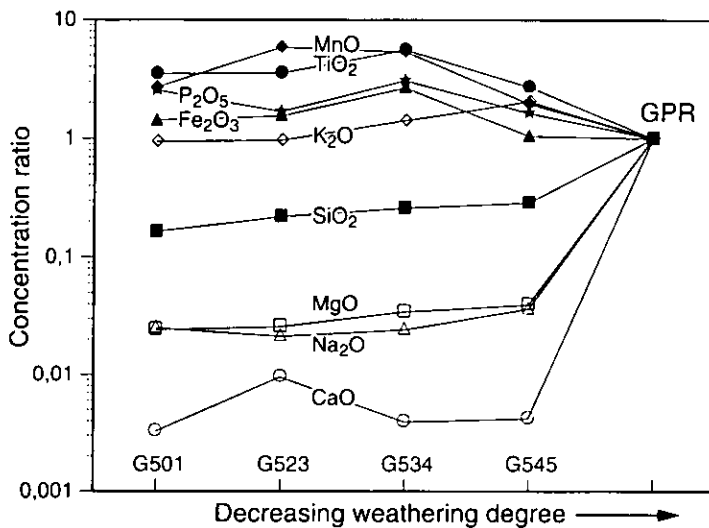


Figure 4.14: A: Variation diagrams of the major element content in the weathering sequence on gabbro. Reference element is Al as it is considered immobile in the profile.

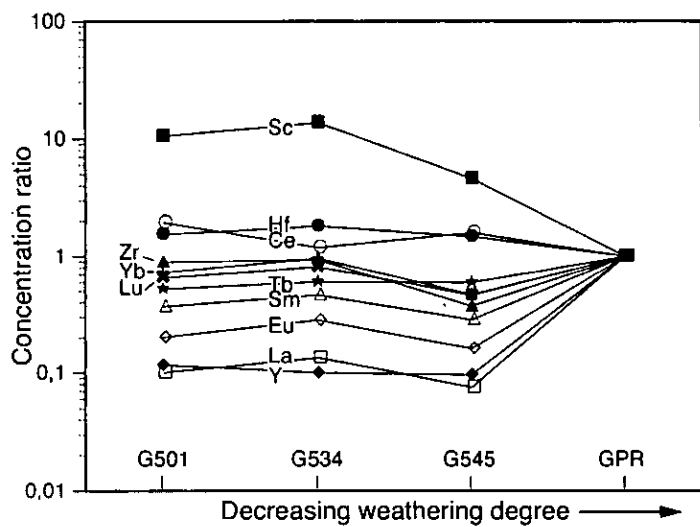
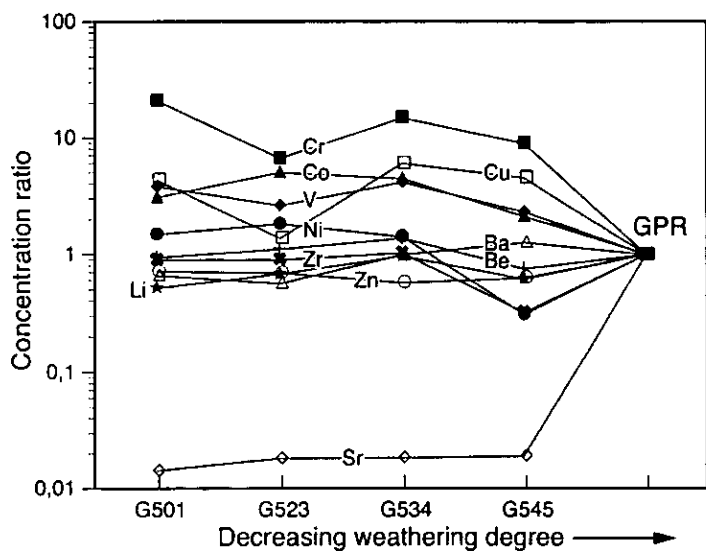


Figure 4.14: (B and C): Variation diagrams of trace elements (B), and REE, Sc, Zr, Hf and Y (C) in the weathering sequence on gabbro.

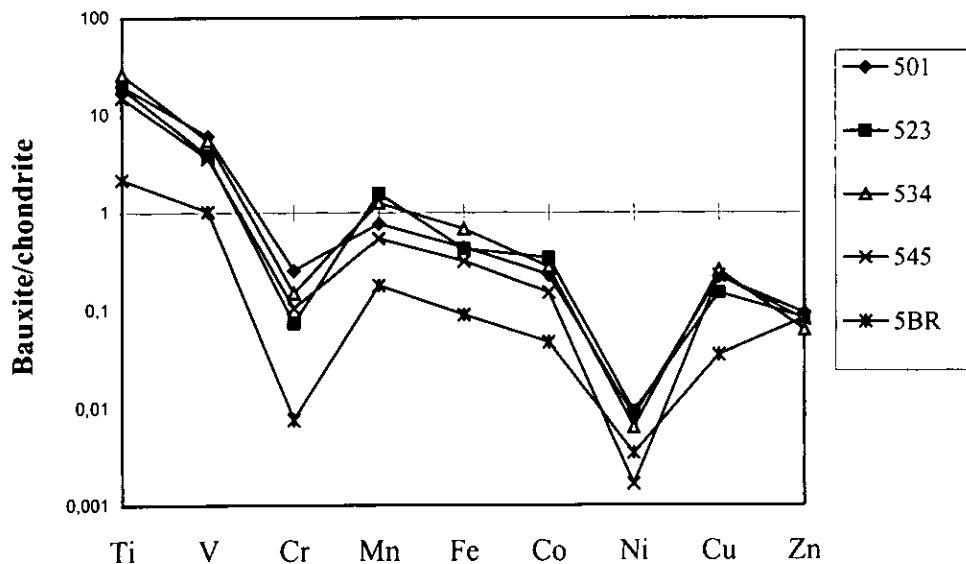


Figure 4.15: Chondrite-normalized values of the first series transition elements in the weathering profile of gabbroic rock. [chondrite values of Langmuir *et al.* (1977) in Rollinson (1993)]

Selected samples from the weathering sequence on gabbro parent rock were analyzed for *Rare Earth Elements, Y, Sc and Hf*. The analytical results are presented in Table 4.8. The distribution pattern of these elements has similarities to sequences discussed previously. The scandium concentration ratio increases with increased weathering degree, whereas Hf does not change significantly (Fig. 4.14C).

Table 4.8: REE, Y, Sc and Hf concentrations (in ppm) in selected samples from the weathering sequence on gabbro parent rock (GPR).

	La	Ce	Sm	Eu	Tb	Yb	Lu	Y	Sc	Hf	La _n / Yb _n	Gd _n / Yb _n	Eu/ Eu*
G501	1.11	17.4	0.62	0.57	0.19	0.90	0.15	3	90	1.75	0.82	0.90	2.05
G534	1.37	9.69	0.71	0.73	0.20	1.02	0.18	2	108	1.88	0.90	0.86	1.92
G545	0.70	11.8	0.40	0.38	0.18	0.53	0.08	2	33	1.39	0.89	1.27	2.01
GPR	7.00	5.66	1.06	1.78	0.23	0.87	0.13	17	5	0.72	5.38	1.26	4.52

Eu/Eu* = Eu_n / (Sm_n × Gd_n)^{1/2}, where Gd was estimated by Gd_n = (Sm_n × Tb_n)^{1/3} following Condie *et al.* (1995); n = chondritic normalized values in Rollinson (1993) from Nakamura.

With exception of Ce, which is preserved in the weathering sequence, the LREE and Y appear to have been more mobilized than the HREE. The concentration ratios for HREE do not display significant changes compared to the LREE and Y, as the latter tend to be depleted relative to the parent rock. As evidenced by [La/Yb]_n ratios (Table 4.8) HREE tend to be enriched in the more weathered samples

REE chondrite-normalized abundance patterns (Fig. 4.16) of gabbro and its related weathering products illustrate the general trends of the REE. Important changes are observed in the Ce and Eu anomalies. The very large positive Eu anomaly of the parent rock diminishes in the weathered samples, whereas the Ce anomaly is markedly enlarged with increasing weathering.

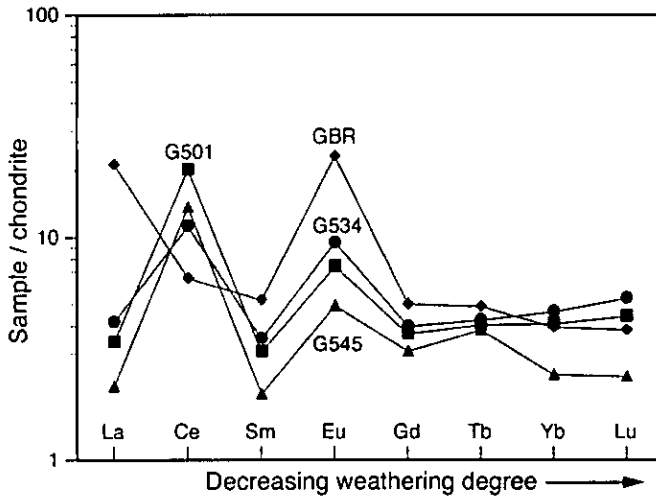


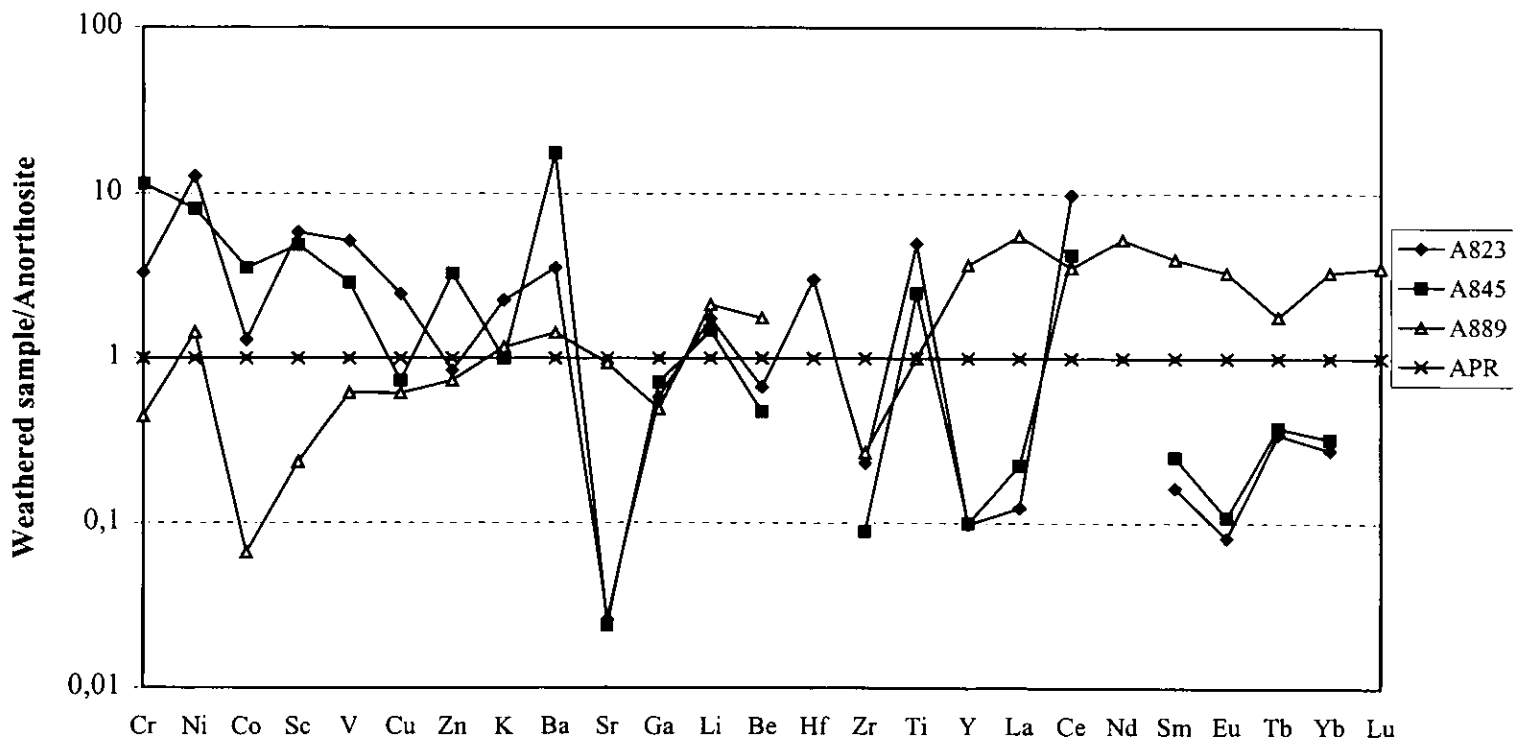
Figure 4.16: Chondrite-normalized patterns for samples of the weathering sequence on gabbro. Chondrite values of Nakamura (1974) except Tb of Haskin *et al.* (1968) in Rollinson (1993); Gd estimated by $Gd_n = (Sm_n \times Tb_n^2)^{0.33}$.

4.6. Discussion

The geochemical characteristics of the above described weathering sequences on anorthosite, metabasalt and gabbro in the Penhalonga area reflect the main chemical trends in an environment of dominantly plagioclase feldspars and pyroxenes/amphiboles transformation to kaolinitic clay minerals, (illite) and secondary Fe-Al-Ti-minerals. Percolating waters caused desintegration of the primary minerals of the parent rocks and precipitation of the secondary phases. The distribution of most chemical elements in the sequence is consistent with the general behaviour observed during supergene alteration of crystalline rocks (Ronov *et al.*, 1967; Nesbitt, 1979; Chesworth *et al.*, 1981; Marsh, 1991; Roquin *et al.*, 1990).

On the figures 4.17, 4.18 and 4.19 diagrams are presented, which illustrate the overall overview of the patterns of elements distribution on the three weathering sequences. These patterns suggest that they developed in response to destruction of plagioclase feldspars when these elements are being released and leached from the weathering rock. These smaller cations among the alkaline and alkaline earth elements are generally considered to be more readily leached during chemical weathering (Nesbitt and Young, 1984; Rollinson, 1993; Nesbitt *et al.*, 1980; Kronberg *et al.*, 1987).

Figure 4.17: Diagram showing the relative variation of trace elements in weathering products in relation to the anorthositic parent rock.



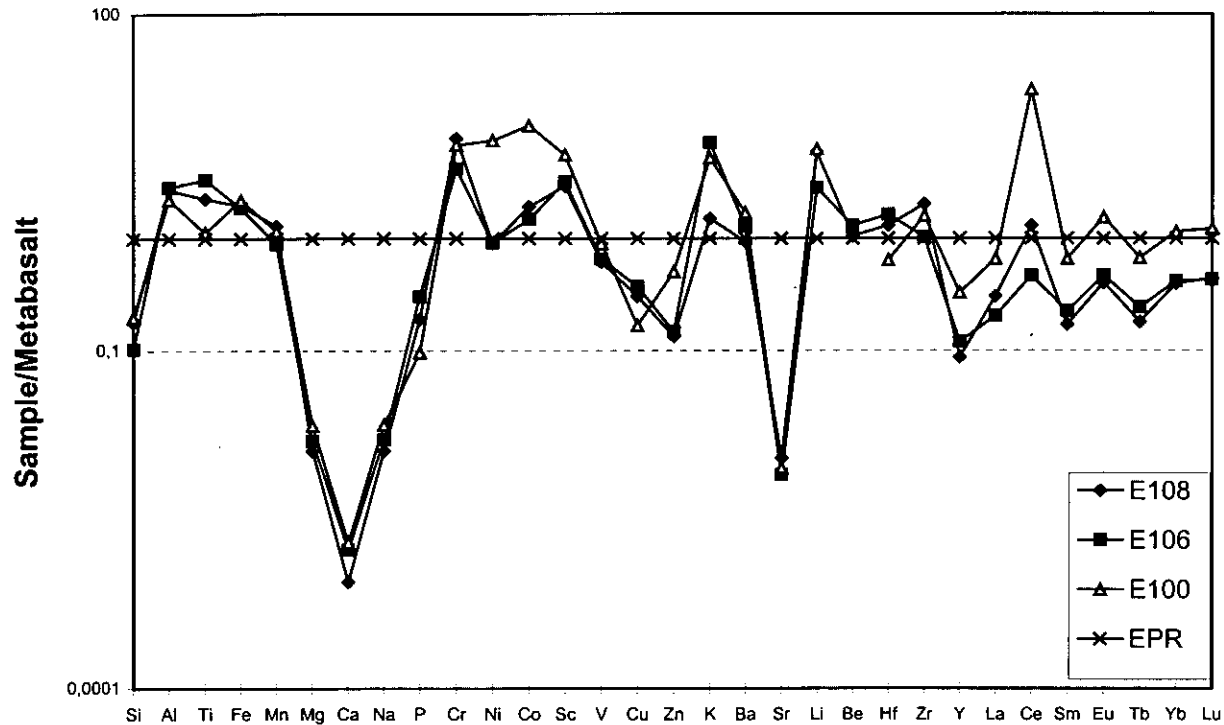


Figure 4.18: Diagram showing the relative variation of major and trace elements in weathering products in relation to the metabasalt parent rock.

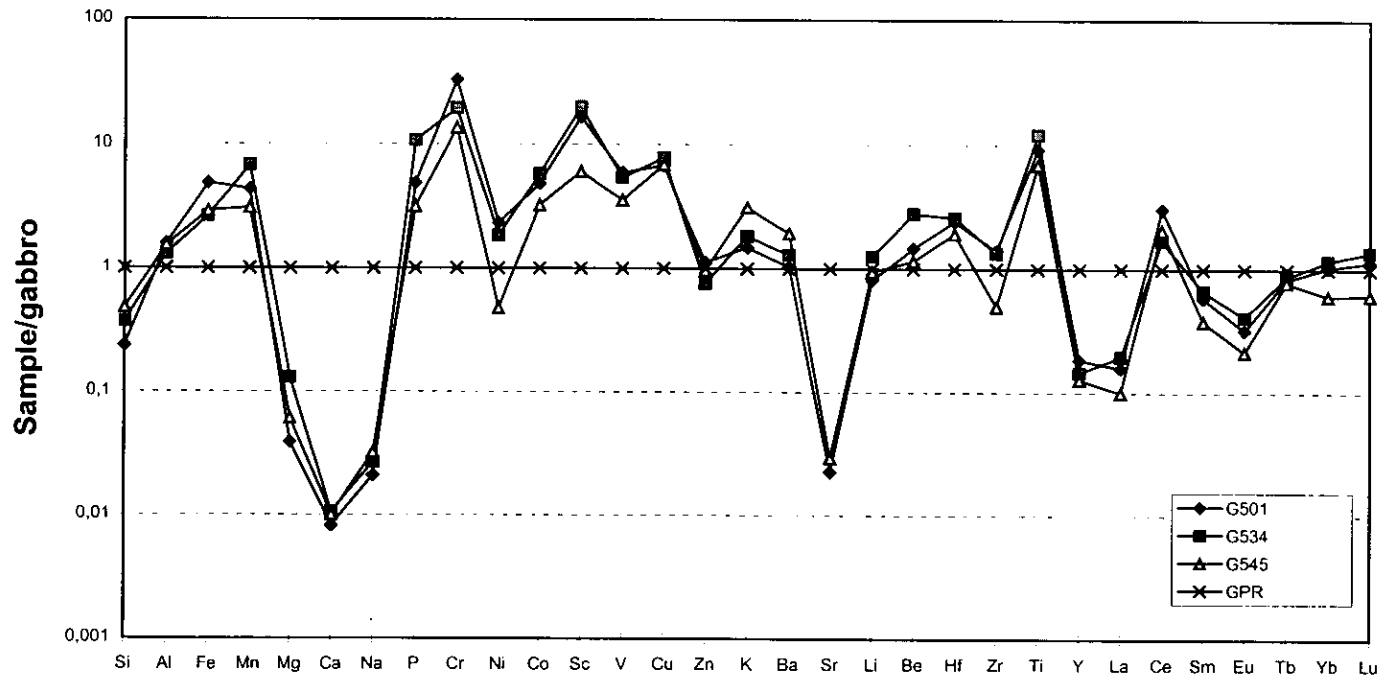


Figure 4.19: Diagram showing the relative variation of trace elements in weathering products in relation to the gabbroic parent rock.

Potassium appears to be retained in the weathering sequence as it can be used in the formation of illite. From the distribution of the other trace elements it is observed that the transition elements Cr, V, and Ni are enriched in the sequence, following the trend of Al, Fe and Ti. The insolubility of Al in nature is well known over much of the natural pH range and, it possess only one important valence (Brookins, 1988). In contrast the elements of the first series transition metals are strongly influenced by oxidation-reduction transformations (Middelburg, *et al.*, 1988, Milnes *et al.*, 1987; Ball and Gilkes, 1987; Narayanaswamy and Gosh, 1987; Butt and Zeegers, 1989). Although little information exists concerning the redox reactions during weathering the fixation/precipitation or mobilization/solubilization of some of these elements may be used for indication of natural environments of weathering/alteration (Middelburg *et al.*, 1988, Marsh, 1991). From the relative concentrations of the major elements can be deduced that, in the weathering sequences Fe- and Ti-minerals control the abundances, including also Cu, of the above mentioned redox-controlled elements. Zinc and Co have an erratic behaviour, but show general depletion. Association of goethite and anatase with Mn, Ni, Co, Zn, Cu and V is a feature of other laterites (Boski and Herbosch, 1990; Topp *et al.*, 1984; Milnes *et al.*, 1987). Relative immobility of Cr and Zn in weathering of dolerite has been interpreted as resulting from alkaline conditions (Marsh, 1991). The REE and Y accumulated in the horizon above the anorthosite, which is enriched with respect to both the parent and most weathered horizons. In the more altered sections of the profile a small fractionation appears between LREE and HREE. This behaviour of the REE during chemical weathering is a pH dependent process. It is described in studies of weathering profiles developed on different crystalline rocks, under different climates (Ronov *et al.*, 1967; Nesbitt, 1979; Duddy, 1980; Braun *et al.*, 1991; Braun *et al.*, 1993; Marsh, 1991; Mongelli, 1993). The usual scheme proposed explains how low pH waters percolate through the upper zones of a weathering sequence removing the chemical elements, including the REE's. In the bottom sections these acidic solutions subsequently interact with reactive phases of the parent rock, thus increasing their pH values. Under these conditions the relatively insoluble species, such as the REE's are precipitated, exchanged or adsorbed onto mineral surfaces (Ronov *et al.*, 1967, Nesbitt, 1979, Duddy, 1980). Such accumulation of REE is reported by Condie *et al.* (1995) as being controlled mineralogically. The change from acidic conditions in the weathered mantle to alkaline at the interface with the fresh parent rock is accompanied by the occurrence of transfer of REE from REE-bearing minerals from the fresh rock to the clays. Clay minerals are the dominant phases in the sections above the anorthosite parent rock and, as depicted in the chondrite-normalized patterns, the total REE of the clay-rich zone is very similar to the parent rock. As mentioned earlier, Ce is fractionated from the other REE in most weathered samples. The developed positive Ce anomalies in the upper parts of the sequence resulted from oxidation of Ce^{3+} to Ce^{4+} (Ronov *et al.*, 1967; Middelburg *et al.*, 1988; Braun *et al.*, 1990; Marsh, 1991; Prudêncio *et al.* 1995). It is important to note that the positive Eu anomaly of the anorthosite parent rock is transferred to the weathered samples. If the REE are inherited only from feldspars then low total REE contents and large positive Eu anomalies are characteristic for residual clays, which are products chiefly of the weathering of feldspars (Condie *et al.*, 1995; Nesbitt and Markovics, 1997). Except for Ce, most weathered anorthosite samples in the sequence show relatively low REE concentrations.

4.7. Conclusions

The weathering sequences discussed above are characterized by two successive and related trends, namely formation of kaolinitic minerals and formation of Al-Fe secondary minerals. Specific element associations developed in the weathering process. The similarities in the variation patterns of the elements observed among the three rocks are remarkable. The parent rock normalized patterns of selected samples show clearly that in all sequences, weathering was accompanied by drastic impoverishment of the elements Ca, Na and Sr. This is attributed to plagioclase feldspar disintegration. Comparatively less depletion is shown by Mg, Si, Co, Be and Zn. Iron, Ti, Al, Sc, Cr, Ni, V and, to some extent also Zr and Cu are quantitatively retained in the weathered samples. Metabasalt and gabbro sequences are similar, in contrast to the sequence of anorthosite, which shows a more erratic element distribution. The REE and Y display mobilization along the weathering sequence. Among REE and Y, Ce is fractionated most from the others in all profiles. Total REE content is less in the weathering sequences. This includes also Eu, although its positive anomaly is often preserved in the weathering sequence. They show enrichment in the clay-rich zone above the parent anorthosite and depletion in the upper zones. Strong fractionation is observed between Ce and all other REE in the most weathered part of the sequences. Ce appears to behave similarly to Sc, Cr and Ti.

CHAPTER V

5. ALTERATION OF RHYOLITIC ROCKS TO BENTONITE IN LEBOMBOS VOLCANICS, BOANE, SOUTH MOZAMBIQUE

5.1. Abstract

Ca-type bentonite deposits of economic interest are associated with rhyolitic rock sequences of the Upper Karoo age in the Lebombo mountain chain in the Boane District, South Mozambique. The rocks of rhyolitic-rhyodacitic composition underwent alteration to bentonite producing beds with thickness of more than 20 meters in places. The shape and sizes of the bentonitic bodies are strongly variable, reflecting the dominant tectonic structures of the Lebombo volcanics. Bentonite is mainly composed of dioctahedral smectite and contains also considerable amounts of silica phases. Chemically the bentonites are characterized by relatively high concentrations of SiO_2 , inherited from the silicic parent rocks, and highly immobile element ratios Zr/TiO_2 and Nb/Y indicating rhyolite, rhyolite-dacite composition. Generally low Al_2O_3 and MgO contents are a typical feature of the bentonites. The bentonite deposits appear to be autochthonous in origin and resulted from the weathering/alteration of the rhyolitic volcanics in an alkaline environment with interaction of MgO -rich water solutions.

5.2. Introduction

In the volcanics of the mountainous chain of Lebombo several associated bentonite occurrences are reported (Grim and Güven, 1978; Tavares, 1973; Wachendorf, 1971; Zúberc *et al.*, 1981). The volcanic rocks, of Upper Karoo age, are mainly rhyolites and basalts and were alternately and successively erupted from fissures. The emplacement of the Lebombo volcanics took place in association with magmatic processes during the break-up and dispersal of Gondwana in the Jurassic-Cretaceous periods (180-60 Ma) (Hawkesworth *et al.*, 1999). The mountain range has an N - S trend with E - W extension and stretches for more than 500 Km (Torre de Assunção *et al.*, 1962; Pinna *et al.*, 1986). The actual distribution of the bentonites and the variety of the alteration assemblages throughout is still not clear. This chapter proposes to illustrate some geological aspects of the volcanics of the Little Lebombo rhyolite series, in Boane District, where extensive bentonitic beds overlie, mainly, altered tuffs and volcanic glasses. Based on chemical, mineralogical and petrographical data, some aspects of the petrology and mineralogy of bentonite and parent rocks will be discussed. Furthermore, an attempt will be made to find out the mineralogical and geochemical formation of bentonites by alteration of rhyolitic rocks of the area. Complementary to the geological setting, the descriptions and discussion of the element mobilization and fixation are stressed, based on data from mineralogical determinations and chemical analysis of the major and trace elements, both in bentonites and unaltered rock samples.

5.3. Geographic setting

Boane is a district in Maputo Province in the South of Mozambique. The area considered in this study is located between latitudes $25^\circ 18'$ and $26^\circ 07'$ South and between longitudes $32^\circ 12'$ and $32^\circ 18'$ East, about 40 Km SW of the capital city Maputo (Fig. 5.1). Occurrences of bentonite are widespread, but the best known deposits are along the east slope of the Little Lebombo (Pequenos Libombos) Mountains.

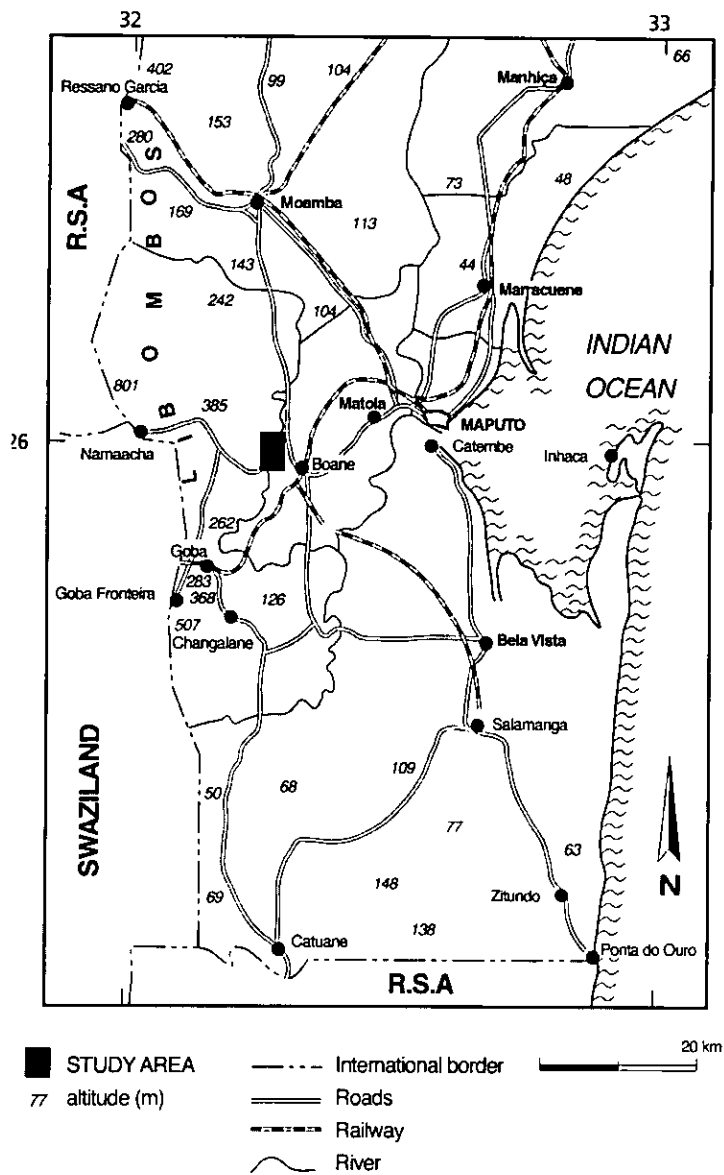
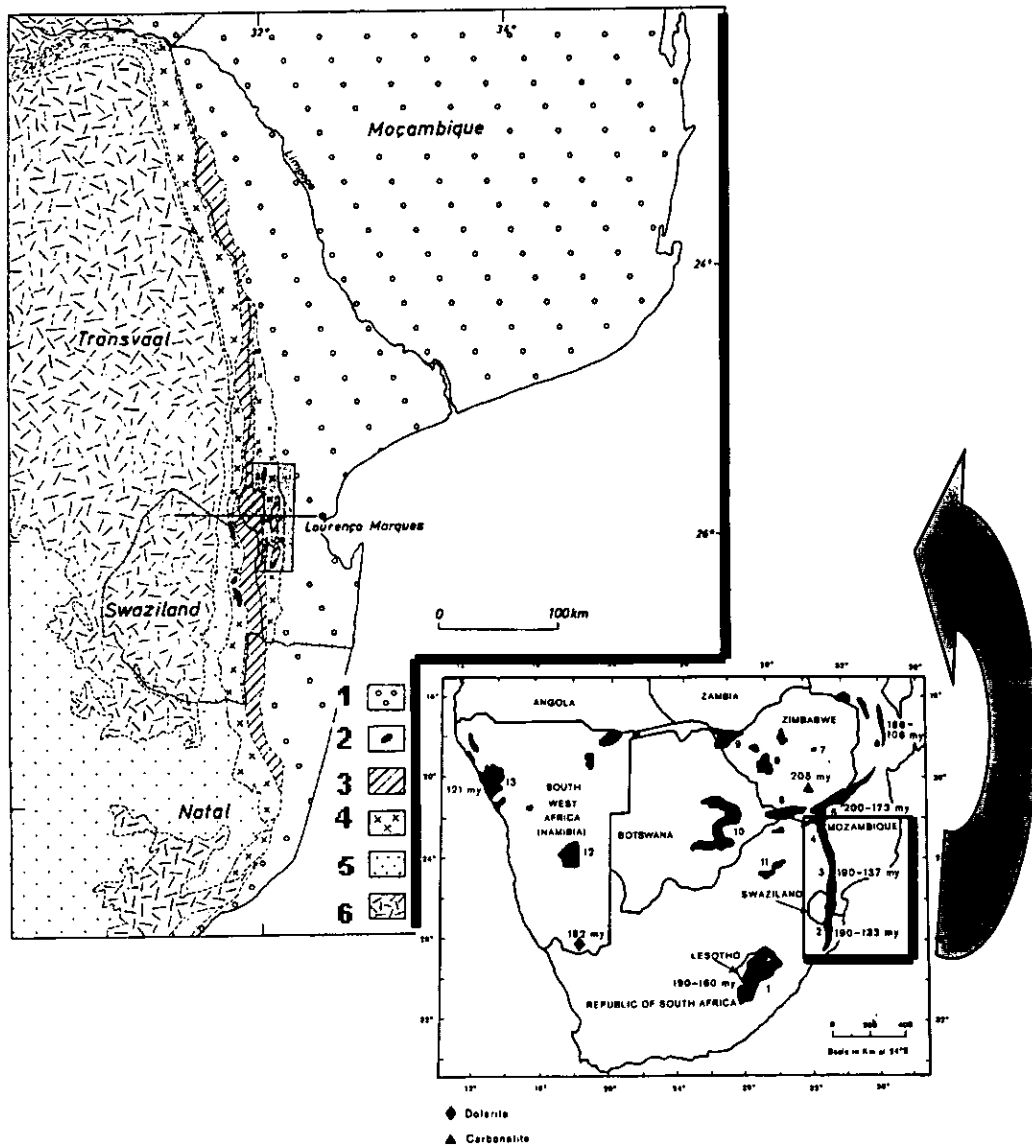


Figure 5.1: Geographic location of the Boane district in southern Mozambique and the position of the study area in the Lebombos mountain range (Atlas Geográfico, 1986).

The studied occurrences are situated in the Little Lebombo Rhyolites, west of the junction of the Movene and Umbelúzi rivers. The Little Lebombos trend N-S over a distance of about 60 kilometers with average width of 5 km, is bordered on its West side by older basaltic rocks from the Lebombo Group and on its East Side by the Movene Basalts, also designated as Lebombo Superior Basalts (Pinna *et al.*, 1986). The Movene Basalts are considered to represent the youngest formation of the Lebombo Group. They are well represented in the study area (Torre de Assunção *et al.*, 1962;

Wachendorf, 1971) (Figure 5.2). The area displays a general characteristic of tilted platform showing a sharply inclined W slope and smooth E slope.



LEGEND:

- 1 = Tertiary and Quaternary sediments
- 2 = Alkaline Intrusives
- 3 = Rhyolites
- 4 = Basalts
- 5 = Karoo sediments
- 6 = Precambrian

Figure 5.2: Geographical distribution of Lebombos volcanics in Southern Africa. (Compiled from Wachendorf, 1971 and Bristow and Saggerson, 1983).

5.4. Geology of the area

The geologic units presented herein constitute part of the volcanic Formation of Upper Karoo of Liassic age (Torres de Assunção, *et al.*, 1962; Wachendorf, 1971; Afonso, 1976; Pinna *et al.*, 1986). It is elongated approximately N-S and is characterized by mainly the volcanic rocks rhyolites and basalts, which overlie older Karoo sediments (Fig. 5.3).

The rocks resulted from a fissural type volcanism and represent a formation, which concordantly overlies Permo-Triassic sediments. The rocks are fine grained to glassy rhyolite, basalts and their tuffs, all exposed throughout the area. These rocks form a 10° - 20° dipping monocline warped downwards to the east along the margin of the Karoo volcanic Province (Cleverly and Bristow, 1979; Bristow and Saggerson, 1983). The rocks of the monocline consist of a sequence of approximately 10.000 meters of rhyolites and basalts. Further east the volcanics are covered by Cretaceous, Tertiary and Quaternary sediments (Wachendorf, 1971; Bristow and Saggerson, 1983; Pinna *et al.*, 1986). During the Cretaceous subordinate volcanic activity, related mainly to the African rift system (Çilek 1986), produced younger and smaller bodies of basalts and intrusive rhyolitic and alkaline bodies (Pina Mendes, 1965; Wachendorf, 1971, Bristow and Saggerson, 1983). Structurally the area is controlled by faults and joint systems with mostly N-S, NE-SW and E-W orientation, usually dipping 70° - 80° NW. These almost vertical faults and joints in the rhyolite are generally filled with basaltic dikes and sills.

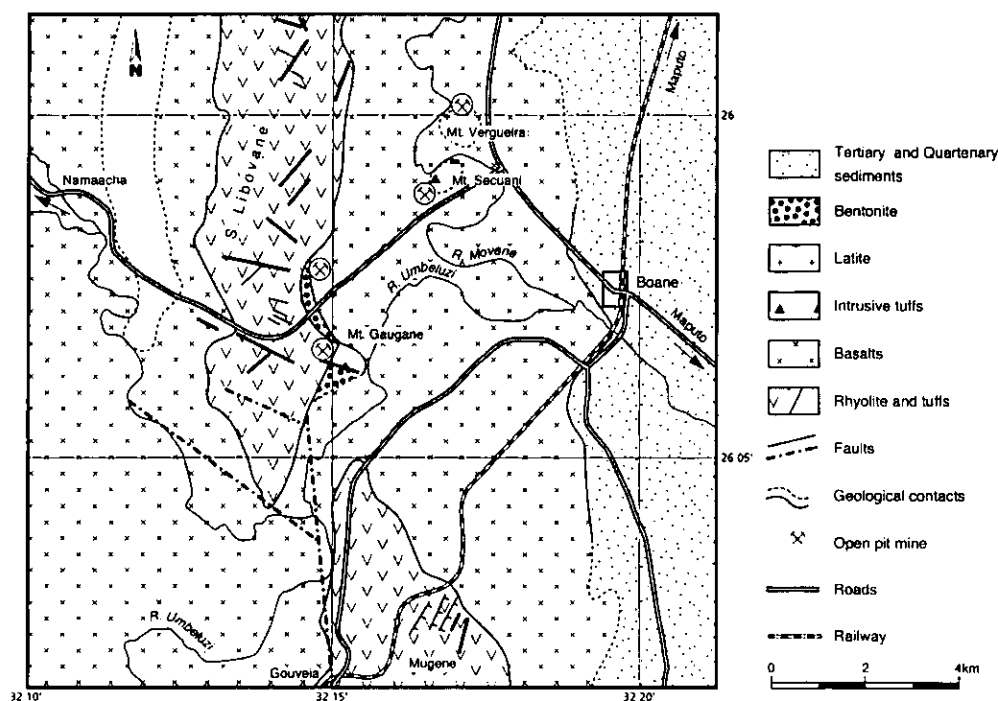


Figure 5.3 Geology of the area of bentonite occurrences in Boane district (adapted from Wachendorf, 1971).

5.5. Geology of the bentonite deposits

The bentonites are associated with volcanic rocks, particularly rhyolites, tuffs and glasses of Upper Karoo age. These rocks underlie Upper Cretaceous-Tertiary and Quaternary sediments, mostly argillaceous sands and unconsolidated conglomerates, which can reach some 5-8 meters in thickness. In the area as a whole the bentonitic layers vary in thickness from some centimeters to more than 20 meters. In places interbeds few cm thick occur with slightly altered parent material. The bentonitic bodies are generally lens shaped, showing thicknesses decreasing outwards from the central part of the body. Lower contacts with the underlying rocks are not always sharply defined, commonly there is a transition zone of some centimeters, where boulders of relatively fresh material occur. Frequently in this transition zone the relict structures, such as flow banding, banded rhyolitic, volcanic breccia and glass of the parent rock may remain macroscopically recognizable. In places, hard silicified concretions containing calcite, as well as single calcitic concretions occur interbedded with bentonitic masses at the middle and lower levels of a vertical profile (Fig. 5.4). This is probably related to the downward movement of percolating solutions causing alteration. Opaline silica, unlike the calcitic concretions, is disseminated in bentonite and occurs also as veinlets along former fractures evidenced by the appearance of the veinlets adjacent to basaltic dikes with almost subvertical position, clearly filling fractures in rhyolites.

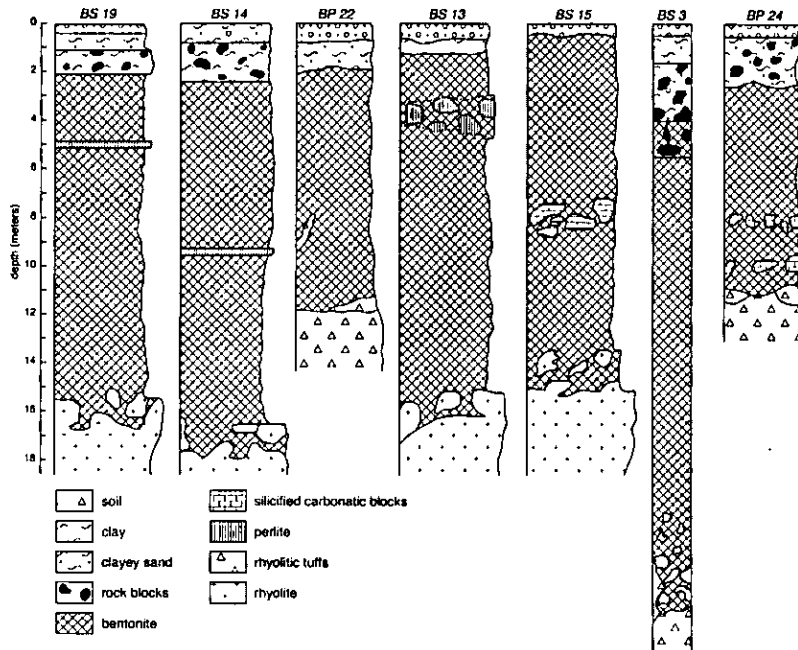


Figure 5.4: Vertical sections of pits and bore holes from the area of bentonite deposits in Boane district.

The top of the bentonite beds is variable and mostly composed of different alluvial and colluvial deposits. Locally, a hard silicified, red-brownish tuff with glassy appearance overlies, with flattened boundaries, the top of the bentonitic layers. In outcrop the coloration is generally yellowish-green, whitish, greyish or red-pinkish. Reddish, brownish types may also occur, normally close to basaltic dykes, due to enrichment in Fe-oxides and -hydroxides and the greyish horizons are restricted to the

top levels of the vertical section as a result of intermixture with overlying clayey sediments and or soils.

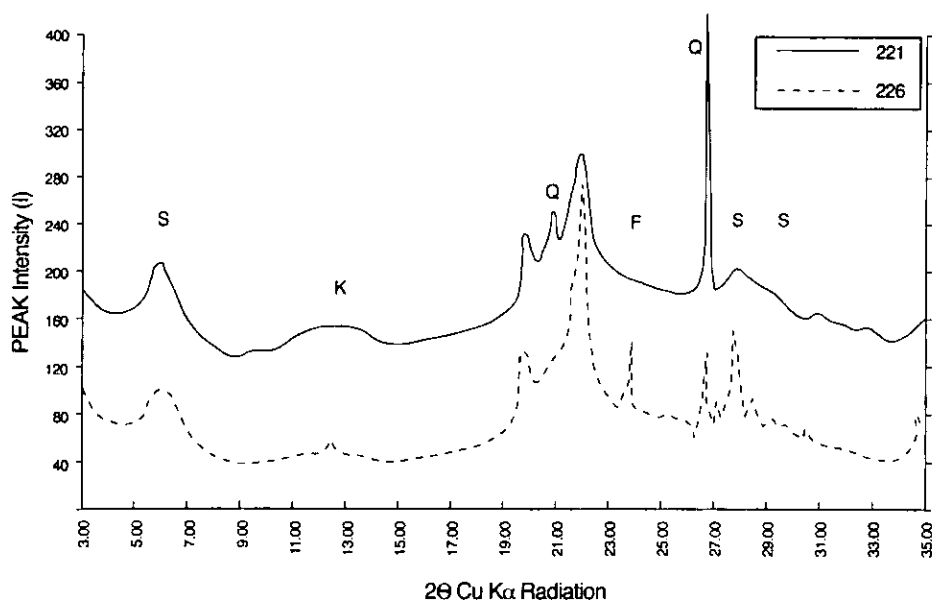


Figure 5.5: X-ray diagrams of bulk samples from bentonitic material depicting the major mineralogical constituents. S=smectite; K=kaolinite; Q=quartz; C=cristobalite; F=feldspar.

5.5.1. Mineralogical features of the bentonites

The XRD-patterns obtained from the samples reveal that the bentonite consists largely of smectite and cristobalite (Figure 5.5). Other components that also can be present are quartz, feldspars, kaolinite, calcite and illite. The X-ray diffraction data from the d(001) basal reflection indicate montmorillonite (14-15 Å) as major clay mineral and traces of kaolinite (7Å).

The patterns of the < 2µm fractions of the K-saturated samples display values of 11-12 Å. The glycolated samples exhibit the basal (001) reflection expanded up to 16.77 Å. K-treated samples show a collapse after heating and the values of the basal reflection shift to 9.9-11.5 Å (Fig. 5.6A). In all analyzed samples the (060)-reflection is present between 1.49 Å and 1.51 Å, which is a characteristic of dioctahedral smectites (Fig. 5.6B). Data on exchangeable cations shows that the montmorillonite is of Ca-type (Cilek,1986; ING, *Internal Report*, 1992), although some samples have also Na, K and Mg as interlayer cations. Cristobalite and quartz are the silica phases detected in the bentonites. Cristobalite is also present in the less than 2 µm fractions in some samples. Kaolinite and illite have been also detected by X-ray diffraction, however, their patterns present diffuse reflections.

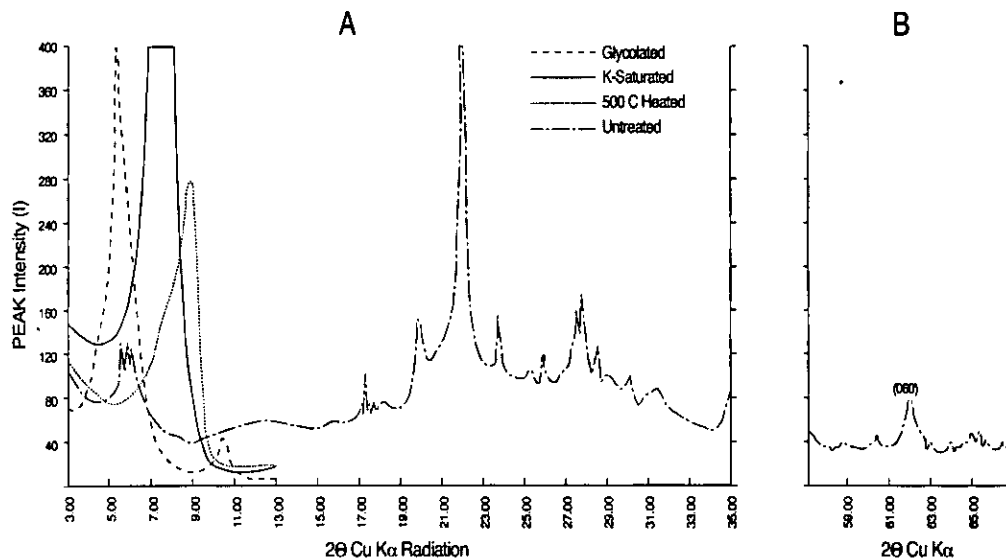


Figure 5.6: X-ray diagrams of the fraction $< 2 \mu\text{m}$ of bentonite samples after different treatments. (A) Mg-saturated (Mg); K-saturated (K); Mg-saturated and glycolated (Mg+Gl) and; K-saturated and heated at 500°C (K+H500) and (B) the position of the (060) reflection in the diagram between 61 and 63 2° Cu $K\alpha$.

5.5.2. The parent rocks and bentonite affinities

As mentioned the dominant lithology in the study area is rhyolite, which encompasses beside the true rhyolite also vitric tuff, volcanic breccias and volcanic glasses/perlite. These rocks are fine grained, cryptocrystalline and massive, displaying laminar, flow-banded and typical fluidal structures. Common varieties are pink, greyish and brown-red coloured, with locally some green rhyolite. Feldspars (sanidine and plagioclase), quartz and minor pyroxene are the main components; accessory minerals apatite, zircon and iron oxides are often present. Calcite, chlorite and chalcedony are common secondary minerals. Characteristic phenocrysts are quartz and feldspars. Typical are the subeuhedral shapes of the feldspars in a fine grained matrix that also contains glass.

Table 5.1: Chemical composition of selected rhyolitic rocks from the area of bentonite deposits in Boane district.

Oxid (wt%)	58-A	49-BR	BBR	L-17*	L-18*	L-45*	L-48*
SiO ₂	76.15	78.35	73.49	75.00	75.50	76.00	75.75
TiO ₂	0.17	0.16	0.77	0.50	0.20	0.80	0.43
Al ₂ O ₃	9.56	10.83	12.51	12.10	12.00	11.20	11.37
Fe ₂ O ₃	2.51	2.21	5.36	3.20	2.40	3.60	3.21
MnO	0.03	0.01	0.01	0.05	0.02	0.06	0.03
MgO	0.75	0.16	0.47	0.20	0.00	0.30	0.31
CaO	0.34	0.27	0.16	0.40	0.60	0.40	0.36
Na ₂ O	1.28	2.25	0.17	1.60	2.60	0.50	1.4
K ₂ O	2.85	4.42	2.04	5.10	5.20	2.60	3.7
P ₂ O ₅	0.02	0.04	0.00	0.04	0.05	0.05	0.03
LOI	7.17	1.11	3.85	1.70	1.30	4.20	3.22
Total	100.83	99.81	98.83	99.89	99.87	99.71	99.82
Traces in (ppm)							
Ba	1113	466	1430				
Sr	54	25	25				
Co	15	16	21				
V	18	16	15				
Cu	7	13	14				
Zn	56	80	68				
Y	213	264	209				
Ce	324	254	115				
Zr	304	254	115				

* element data from Wachendorf, (1971).

The chemical composition of selected rhyolitic rocks (Table 5.1) shows their silicic character, with contents of more than 75 per cent SiO₂ and Na₂O + K₂O ranging from 3.17 up to 7.80 weight per cent. Chemically these rocks can be grouped within the subalkalic series (Middelmost, 1985; Le Maitre, 1989) with SiO₂- and (Na₂O+K₂O)-contents of the normal rhyolites and rhyolite dacites (Figs. 5.7A and B).

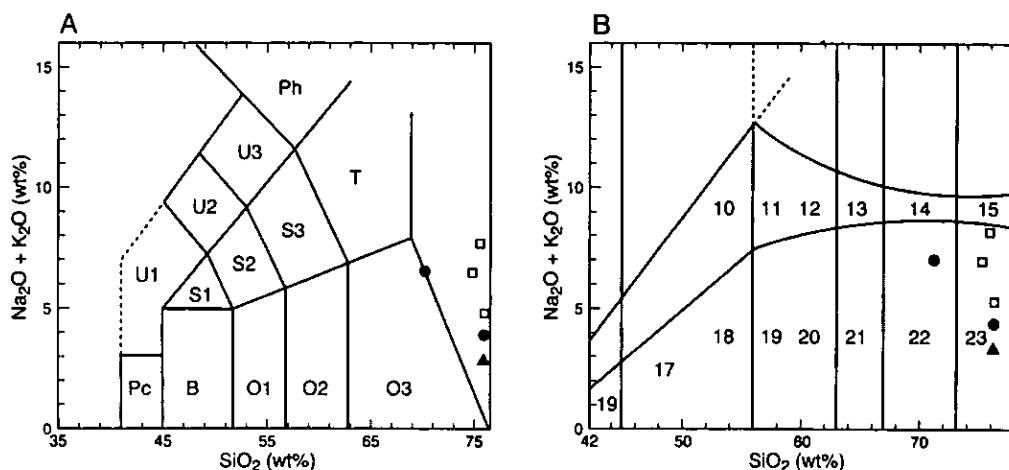


Figure 5.7: Plots of the chemical composition of selected rhyolitic rocks of Boane district in the diagrams SiO_2 - $\text{Na}_2\text{O}+\text{K}_2\text{O}$. A (after Le Maitre, 1989): Pc=microbasalt, B=basalt, O1=basaltic andesite, O1=andesite, O3=dacite, S1=trachybasalt, S2=basaltic trachyandesite, S3=trachyandesite, T=trachyte (Q<20%)/trachydacite (Q>20%), R=rhyolite, U1=tephrite (Ol<10%)/basanite(Ol>10%), U2=phonotephrite, U3=tephriphonolite and Ph=phonolite. B (after Middelmost, 1985): 10=trachyandesite basalt, 11=trachyandesite, 12=trachyte, 13=trachydacite, 14=trachyrhyolite, 15=alkali rhyolite, 16=picrite, 17=tholeiite basalt, 18=andesite basalt, 19=andesite, 20=andesite dacite, 21=dacite, 22=rhyolite dacite, 23=rhyolite. Plots symbols: open squares=rhyolitic tuffs; filled circles=rhyolite sand; filled triangles=volcanic glass.

Major element values of the bentonites derived from the alteration of the rhyolites to bentonite are very similar for the set analysis (Table 5.2). Characteristic is the very high silica content ($68.10\% \pm 2.10\%$) attributable to the presence of silica phases in the bentonite mineralogy, but also to its rhyolitic precursor. The Al_2O_3 -content (10-15 wt%) and MgO-content (1.4-3.1 wt%) (Table 5.2) of the Boane bentonite are low compared to typical bentonite with Al_2O_3 (16 - 20 wt%) and MgO (3-6 wt%) (Seidov and Alizade, 1966; Altaner and Grim, 1990). The affinity of the bentonite to the silicic parent material is indicated by their similar values of the immobile element ratios Zr/TiO_2 (Fig. 5.8) and Nb/Y (Fig. 5.9) (Winchester and Floyd, 1977). These trace elements are usually considered to be immobile during near surface alteration processes. According to Winchester and Floyd (1977) the mentioned ratios can be used as indexes of differentiation and of alkalinity, respectively, to discriminate between common volcanic rock types. In Figure 5.7 plots of the chemical compositions of the rhyolite and bentonite are shown. It is clear that silica has been leached, but the Zr/TiO_2 ratio of the bentonites remains closely related to rhyolitic rocks. Furthermore, the plots of the bentonite data on the diagram Nb/Y against Zr/TiO_2 are consistent with the rhyolitic and rhyodacitic compositions of the parent rocks.

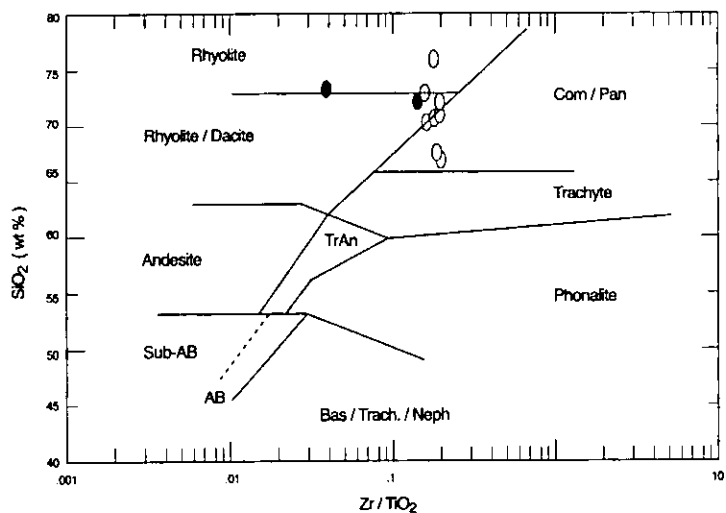


Figure 5.8: Plots of the composition of rhyolitic rocks and bentonite samples on the diagram wt%SiO₂ against the ratio Zr/TiO₂ of Winchester and Floyd (1977). Key to the symbols: Filled circles=rhyolite; inverted triangle=rhyolitic tuff and; open circles=bentonitic samples.

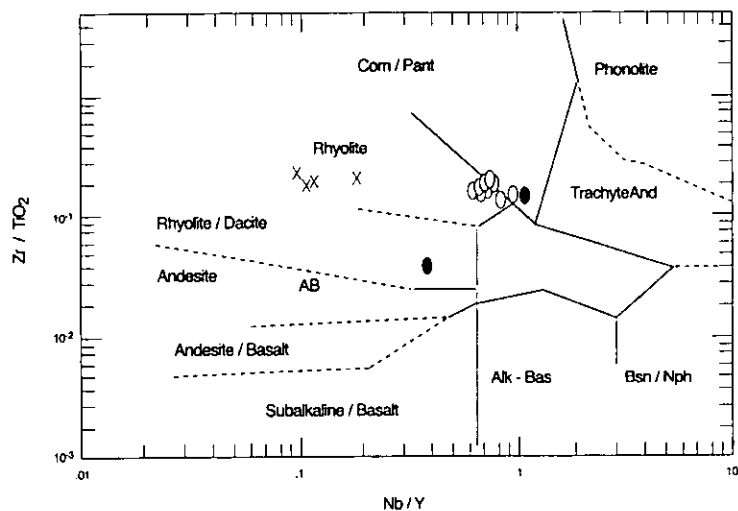


Figure 5.9: Plots of selected bentonite samples on the discrimination diagram Zr/TiO₂ versus the ratio Nb/Y of Winchester and Floyd (1977). Key to symbols: open circles=bentonite samples.

Table 5.2: Major elements composition (in wt%) of bentonites and rhyolitic parent rocks from Boane district, South Mozambique.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
B21	68.41	0.36	11.11	3.30	0.03	2.20	0.47	1.17	0.33	0.03	12.56	99.97
B22	65.69	0.27	11.96	2.49	0.01	2.13	0.48	1.12	0.23	0.02	14.46	98.86
B23	70.28	0.23	10.98	2.41	0.01	2.20	0.39	0.96	0.10	0.02	13.51	101.09
B24	66.66	0.22	10.08	2.25	0.01	2.03	0.36	0.93	0.11	0.02	17.71	100.38
B25	66.46	0.25	11.35	2.54	0.01	2.16	0.37	1.01	0.15	0.02	14.36	98.68
B26	64.53	1.13	11.60	2.54	0.01	1.76	1.03	1.19	0.73	0.07	14.49	100.18
B27	66.77	0.55	11.46	3.64	0.01	2.13	0.67	1.60	0.38	0.04	12.81	99.48
B28	67.45	0.21	10.57	3.06	0.01	1.98	0.50	1.14	0.41	0.02	14.58	99.80
B29	65.53	0.23	10.09	2.93	0.01	1.91	0.39	1.02	0.28	0.02	16.40	98.56
B30	67.77	0.25	11.05	2.68	0.03	2.25	0.40	1.00	0.19	0.03	13.36	98.96
B41	68.81	0.45	11.14	2.63	0.04	2.57	0.62	1.04	0.21	0.03	10.55	99.60
B42	71.90	0.31	10.96	4.41	0.02	2.40	0.57	0.97	0.12	0.02	10.68	101.02
B43	68.49	0.31	11.57	3.07	0.02	2.64	0.58	0.97	0.12	0.02	11.04	99.16
B46	70.25	0.25	9.66	3.40	0.01	2.16	2.91	1.11	0.48	0.02	10.38	99.99
B47	66.48	0.19	10.20	2.76	0.01	2.16	4.29	1.18	0.75	0.02	11.27	98.63
B51	68.33	0.27	11.33	2.08	0.03	1.49	1.97	2.88	2.04	0.03	10.49	101.41
B52	69.08	0.25	11.49	2.55	0.02	1.36	0.67	2.77	2.15	0.03	8.72	98.92
B53	69.79	0.25	11.68	2.38	0.02	1.95	0.58	2.21	1.66	0.03	8.74	99.51
B54	69.07	0.02	11.79	2.60	0.02	1.73	0.62	2.42	1.91	0.03	9.62	99.73
B49	78.35	0.16	10.83	2.50	0.01	0.16	0.27	2.25	4.42	0.04	1.11	99.81
B58	76.15	0.17	9.56	2.51	0.01	0.75	0.34	1.28	2.85	0.02	7.17	100.83
P2A*	72.83	0.23	11.84	2.38	n.d.	2.41	0.38	0.97	0.11	n.d.	8.50	99.66
P3A*	72.05	0.26	11.46	2.88	n.d.	2.46	0.43	0.94	0.38	n.d.	8.05	98.92
P3B*	70.40	0.23	11.79	3.20	0.01	2.53	0.49	0.99	0.39	n.d.	8.12	98.14
P3C*	70.21	0.22	12.13	3.65	0.01	2.63	0.47	1.20	0.55	n.d.	8.14	99.21
S3A*	70.95	0.21	11.53	2.64	0.01	2.64	0.98	1.14	0.13	n.d.	8.32	98.56
S3B*	67.38	0.23	12.77	2.81	0.04	3.13	1.11	1.04	0.11	n.d.	9.47	98.10
SSA*	71.81	0.20	12.05	2.45	n.d.	1.98	0.44	1.02	0.62	n.d.	7.86	98.46
S5B*	66.66	0.25	14.95	4.39	0.01	2.56	0.60	0.88	0.58	n.d.	9.90	100.79
BPR*	73.49	0.77	12.51	5.36	0.01	0.47	0.156	0.17	2.04	n.d.	3.85	99.83

B49, B58 and BPR represent the rhyolitic parent rocks; n.d.=not determined

5.6. Results

In all bentonite samples smectite-type (montmorillonite) clay was found to be the main mineral component with contents ranging up to 75%. A silica phase, cristobalite, quartz and also opaline silica is always present. Samples of bentonite with 35% of cristobalite were also reported (Zúberec *et al.*, 1981; Čilek, 1986). Other mineral phases also detected in trace amounts are kaolinite, feldspars and calcite. The effects of different treatments on the clay fraction (< 2 µm) separates (Fig. 5.9) show that glycolation apparently produced little change in the XRD patterns, but the K-saturation and 500°C heat treatments produced typical effects, indicating the presence of smectite in the samples. The shapes of the (001) reflections on the patterns in the region of 7 Å suggest different degrees of crystallinity of kaolinitic minerals varying from poorly crystallized, with broad peaks to fairly good crystallized varieties.

Table 5.3: Chemical composition of two types of calcitic concretions occurring in association with bentonites in the Boane deposits.

Oxid (wt%)	BP-24	BP-25	NC-1	NC-2
SiO ₂	15.63	15.01	14.02	12.54
TiO ₂	0.09	0.05	0.08	0.04
Al ₂ O ₃	4.27	2.76	4.37	2.35
Fe ₂ O ₃	3.38	0.45	3.66	0.49
MnO	1.61	0.00	1.56	0.30
MgO	1.85	2.57	1.77	1.41
CaO	35.69	46.64	35.62	42.63
K ₂ O	0.04	0.06	0.06	0.00
LOI	35.61	30.27	36.05	38.20
Total	98.17	97.81	97.19	97.96
Traces(ppm)				
Co	13	13	-	14
V	18	14	18	14
Zn	101	28	108	28
Ba	1158	30	1028	30
Sr	134	118	129	107
Nb	37	20	39	20
Zr	172	101	190	84
Y	351	171	408	112
Ce	325	103	40	101
U	5.1	2.5	12.4	3.0
Th	27	9	6	9

The samples BP-24 and BP-25 were collected at the bottom (approx. 8m depth) of two prospecting pits located close to a open pit mine; samples NC-1 and NC-2 have been selected from the mining front/wall in a operating pit mine.

5.6.1. Calcitic concretions

Bodies of silicified calcitic concretions are frequently observed in association with bentonite. These rather hard, mostly blocky concretions are scattered in bentonitic masses or occasionally form single distinctive fragments of reduced dimensions, showing irregular distribution throughout. There are two types of concretions macroscopically differentiated by their colours. Samples BP-24 and NC-1 show darker, greyish colours, in contrast to the white colour of the samples BP-25 and NC-2. The surfaces of broken grains of the first type of calcitic concretions have also thin blackish coatings of Mn-oxides and hydroxides. Typical X-ray diffraction patterns of the calcitic concretions (Fig. 5.10), indicate calcite as the major constituent with approximately 60% and minor smectite, cristobalite and feldspars. Chemically, among the sampled calcitic concretions two types are distinguishable. There are differences in the major elements Al, Fe and Mn and, especially, in content of the trace elements Zn, Ba, Zr, Y and to some extent U, Nb and Sr (Table 5.3). Although not assessed, physico-chemical variations of conditions in microenvironments can account for the observed differences in the two sets of

samples. Moreover, chemical heterogeneity in the unaltered source rocks may have contributed to the differences in the chemical composition of the concretions.

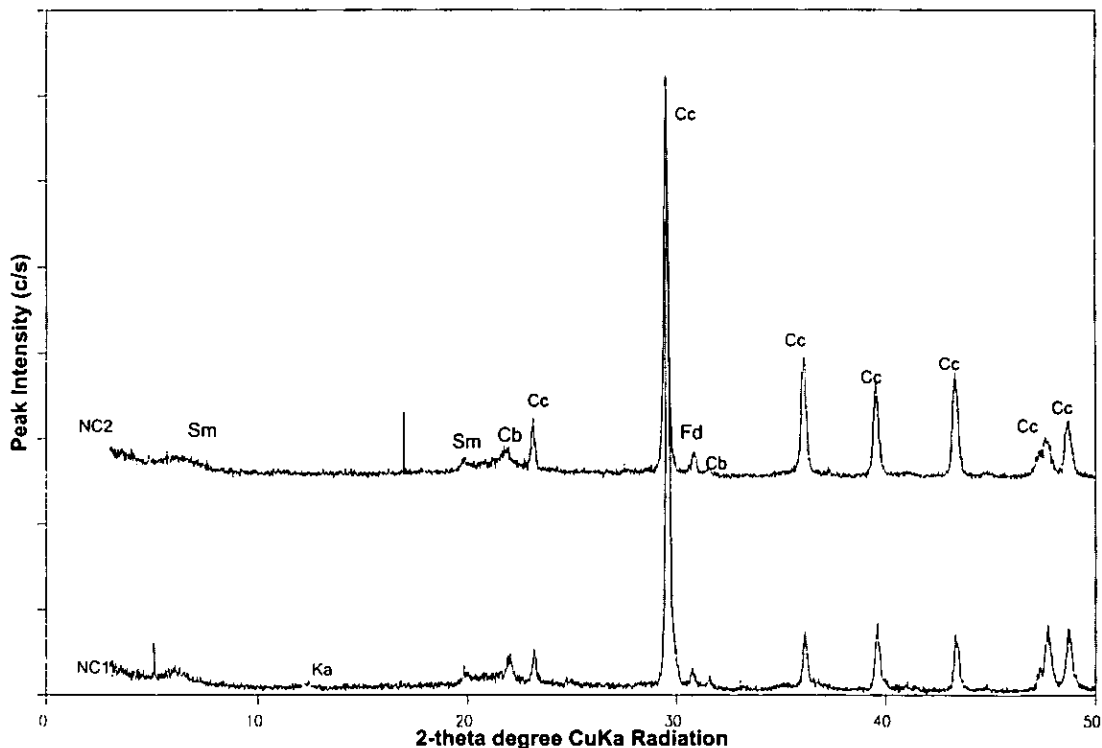


Figure 5.10: Typical X-ray diagrams of calcitic concretions that are within the bentonitic beds. Symbols: calcite, Sm=smectite, Ka=kaolinite, Cb=cristobalite, Fd=feldspar, NC=sample code.

5.6.2. Geochemistry of the bentonites

The chemical composition of the bentonites and selected rhyolitic parents is presented in (Table 5.2). There are very little differences in the major element contents of the bentonites. The high SiO_2 - (64-72 wt%) and relatively low Al_2O_3 contents (9.66 -14.95 wt%) are noteworthy, compared with typical bentonite in the literature (Seidov and Alizade, 1966; Vogt and Köster, 1978; Altaner and Grim, 1990; Pablo-Galan, 1990). The high SiO_2 percentages can be attributed to the silica phases always present in considerable amounts. Values up to 50% of cristobalite in the Boane bentonites are reported (Çilek, 1989). Furthermore, observed impurities in bentonites of unaltered silicic volcanics fragments can also cause high silica contents. In the figure 5.11 are ternary plots showing the major element composition (Al_2O_3 , Fe_2O_3 , CaO , Na_2O , K_2O and MgO in molar proportions) variation accompanying the alteration of rhyolites to bentonites. The major element concentrations in bentonite relative to the rhyolitic rocks show clearly enrichment in MgO , CaO and to a lesser extent Na_2O . Al_2O_3 and SiO_2 are the less mobile components followed by Fe_2O_3 , TiO_2 and P_2O_5 , which are relatively depleted in the altered rhyolites.

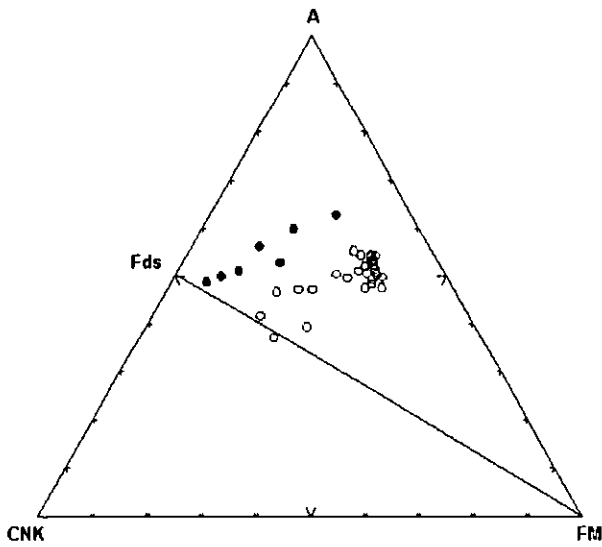
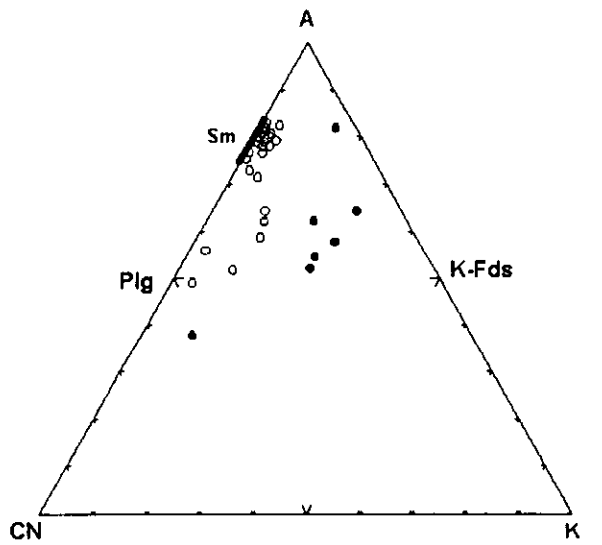


Figure 5.11: Plots of the rhyolitic parent rocks and their altered products on the A-CN-K and A-CN-K-FM diagrams (on molar basis). Key to the symbols: filled circles=rhyolitic parent rocks, open circles=bentonites, Sm=smectite, Plg=plagioclase feldspar, K-fds=potassium feldspar.

By bentonite formation with or without zeolites from rhyolitic parent rocks Christidis (1998) reported migration of alkalis and Si and gains of Mg, Fe and Ca, while Al and Ti are immobile. Depletion of the components K_2O and MnO is substantially much larger. Remarkable is the strong MgO enrichment and K_2O depletion both representing extreme cases (Fig. 5.12). The elements Mg, Fe and Ti are generally fixed during bentonite formation by structural incorporation in clays or in secondary oxides and hydroxides (Zielinski, 1982; Christidis, 1998). Ca most probably is ion-exchanged and occupies interlayer positions in the clays or is incorporated in calcite or other Ca-containing mineral phases not detected by X-ray analysis (Vogt and Köster, 1978; Christidis, 1998). Removal of the soluble ions by leaching is the main mechanism causing depletion.

The highly soluble alkaline element K is easily released during rhyolitic rocks alteration and if it is occupying interlayer sites in montmorillonite it is readily ion-exchanged for dissolved Ca^{2+} (Zielinski, 1982). H^+ is also mentioned as a probable interchanger of Na^+ and K^+ during silicic rocks dissolution (White and Claasen 1980; White, 1983; Nesbitt *et al.*, 1980). Silica also forms a mobile element during rhyolite alteration. White (1983) reported release mechanisms for Si during dissolution of glassy rocks. Its removal is related to silicate matrix destruction rather than ion exchanging. Similar mechanism may have caused the release of U during alteration of rhyolites in oxidizing alkaline conditions as documented by Zielinski (1982). The behaviour of Si depends on the chemistry of the parent rock (Christidis, 1998).

The formation of smectite witnesses the fact that both the silica concentrations and $(Na^+ + K^+)/H^+$ activity ratios of the solutions were moderate. Dissolution of acidic volcanics produces smectites only when the system is well flushed (Christidis *et al.*, 1995; Christidis and Dunham, 1997).

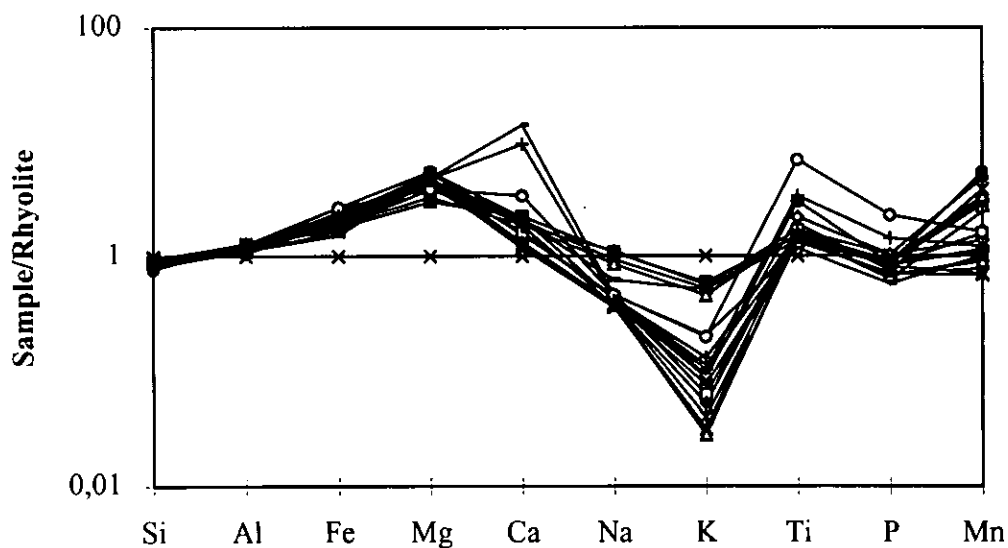


Figure 5.12: Major element variations in bentonites from Boane relative to the parent rhyolites.

Trace element composition in bentonite is presented in Table 5.4. Their pattern behaviour is much more heterogeneous than that observed with the major elements and besides that, for some elements, the variation ranges of concentrations are much larger.

This strong variability in traces may probably indicate different alteration degrees of the weathered materials. The data indicate that as much as three different situations can be considered to describe the trace-elements distribution in the bentonites (Figures 5.13 and 5.14). Firstly elements such as Co, Ba, Rb and Cs appear to be in general depleted in the altered rhyolites; especially Rb and Ba are strongly leached to almost the extent as K_2O . In alteration profiles of volcanics Sr and Rb are lost, while Zr, Nb, V and Ni are immobile and enriched in the products of alteration (Christidis, 1998).

Table 5.4: Trace elements concentrations (in ppm) of selected bentonites and rhyolitic parent rocks (B49, B55) from Boane District, Mozambique.

Sample	Ba	Be	Co	Cr	Cu	Li	Ni	Pb	Sr	V	Y	Zn	Zr
B22	547	5.6	9	4	15	5.2	9	18	48	15	128	209	400
B23	241	4.4	6	5	10	4.5	7	44	53	13	101	148	393
B24	709	4.9	8	5	13	3.4	8	18	38	9	114	167	365
B25	243	6.3	3	5	14	4.7	9	32	35	13	134	160	377
B27	220	11.9	7	7	23	7.6	12	40	64	37	273	202	387
B28	365	7.8	4	2	12	3.6	8	20	39	17	193	219	396
B29	104	8.1	6	3	12	3.8	7	22	35	19	183	199	374
B41	655	7.9	15	14	22	10.8	17	18	60	42	225	150	381
B43	263	6.3	10	7	15	7.8	10	30	45	20	185	159	389
B44	229	7.4	13	15	24	8.6	11	46	53	41	244	173	383
B45	414	5.7	9	4	21	8.6	9	76	83	21	264	173	304
B47	154	7.8	5	3	14	12.2	6	46	42	11	277	224	360
B48	229	8.3	6	2	15	14.0	7	52	37	23	242	221	403
B51	904	6.7	10	7	20	11.7	10	35	184	27	203	114	394
B53	883	7.8	11	5	21	15.9	7	33	111	22	195	134	413
B49	504	6.8	16	5	13	6.47	5	53	25	16	264	57	367
B55	1100	10.5	15	3	7	3.0	14	23	73	18	213	79	305

In the form of Co^{2+} , Cobalt goes into solution easily during weathering (Wedepohl, 1970, Brookins, 1988). Along with other alkaline elements Rb and Cs, after breakdown of alkali-feldspars, go readily in solution and are removed. Barium does not display enrichment as do the other alkaline earth elements Mg, Sr and Ca. This may indicate that the smaller cations (Na, Sr and Ca) are preferentially installed in the clays (Kronberg et al., 1987). A different case is shown by the elements Zn, Cu, Li, Sr and Sc, which are markedly enriched in comparison to the parent rock. A rather inconsistent behaviour is observed with Cr, Ni, Pb and V. As described for the major elements, fixation of Zn, Ni should be attributed to structural incorporation in clay minerals (Vogt and Köster, 1978; Brindley, 1984). Li^+ is the only monovalent cation likely to be structurally incorporated and occupy octahedral sites of the montmorillonite structure for Mg^{2+} and Fe^{2+} (Brindley, 1984). The elements Sc and Cr, to some extent, probably can also be present in montmorillonite (Zielinski, 1982). The other trace elements, particularly Zn, Cu, Pb and Sr are either adsorbed or ion-exchanged like Ca (Vogt and Köster, 1978; Zielinski, 1982). The relatively immobile elements, behaving similarly as Al, are Hf, Zr, Ta, Th and Ga. Their distribution broadly suggests mildly aggressive environmental conditions, which allowed their residual concentrations in bentonites.

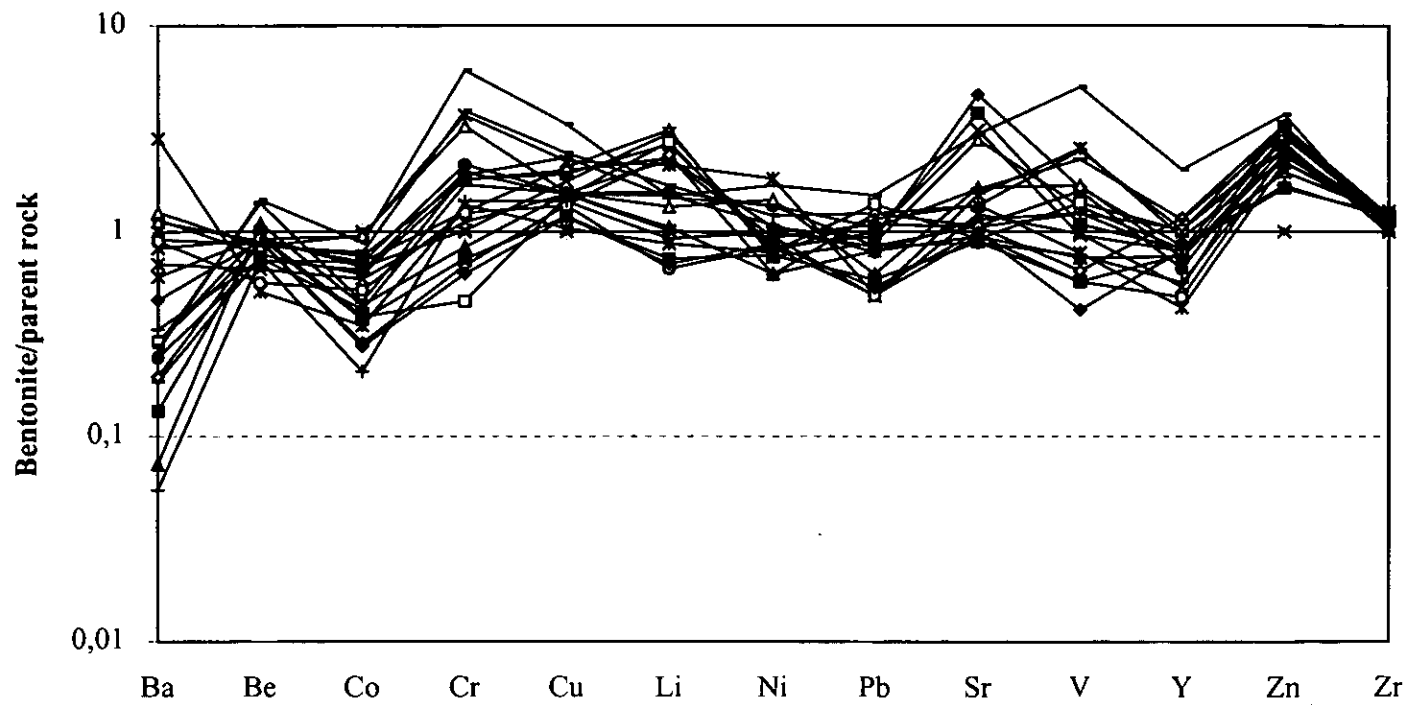


Figure 5.13: Relative enrichment or depletion of major and trace elements in bentonites in relation to the rhyolitic parent rocks.

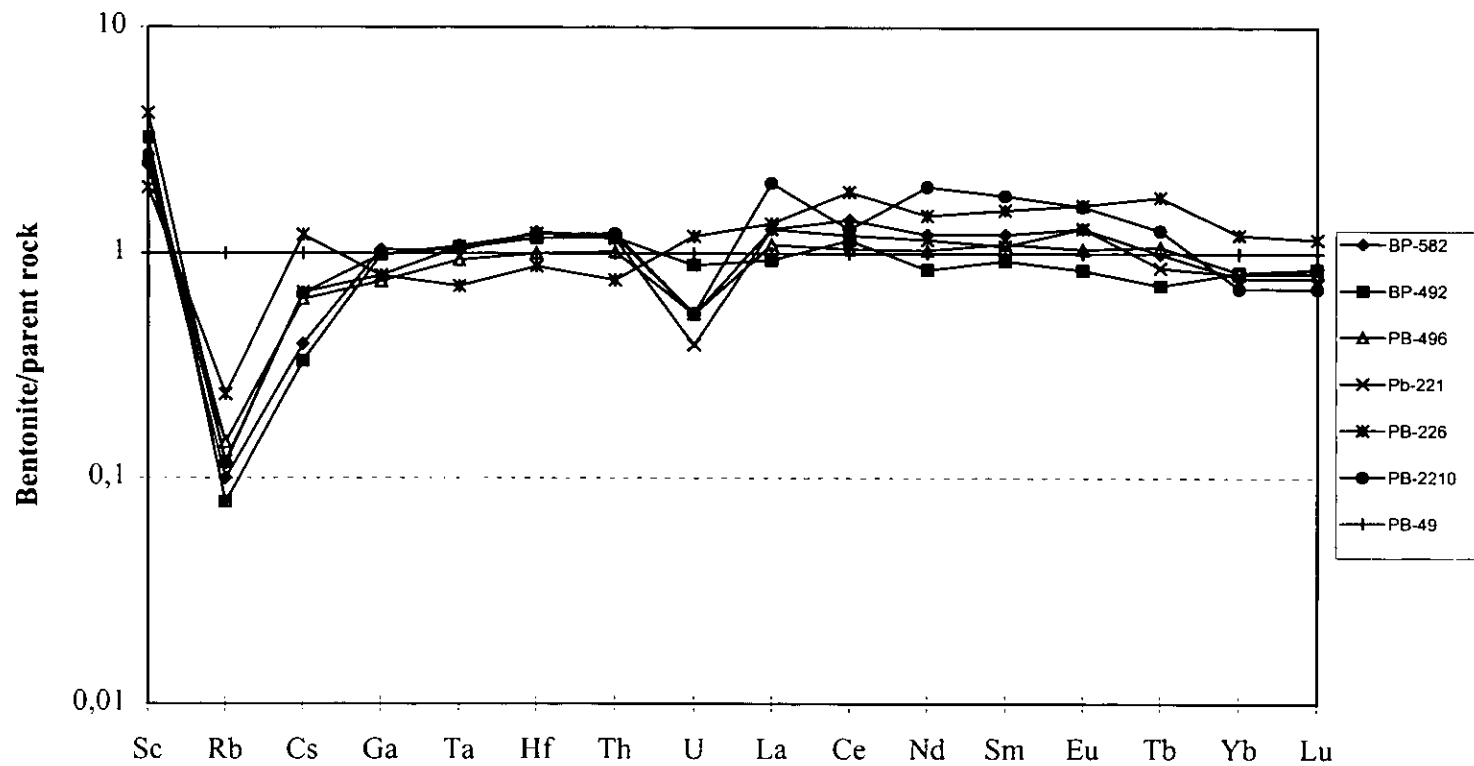


Fig. 5.14: Relative enrichment or depletion of REE and selected trace elements in bentonites in relation to the parent rhyolitic volcanics.

Particularly interesting is the way in which rare earth elements (REE) and Y appear to be developing during bentonitization (Table 5.5). It is already known that the behaviour of REE during alteration of rocks is a function of the parent rocks characteristics and of the physicochemical conditions of the alteration environment (Ronov et al., 1967; Nesbitt, 1979). As indicated by the REE and Y contents in the bentonites there exists evidence of preferential enrichment in light rare earth elements (LREE) e.g. La, Ce, Nd and Sm whilst in heavy rare earth elements a slight impoverishment is observed (Fig. 5.13). These tendencies of the REE may be due to the fact that under alkaline conditions the stability of the HREE complexes is greater than that of the LREE, so that a fractionation process LREE-HREE occurs (Ronov et al., 1967). In this case a preferential accumulation of LREE is observed. Considering the chondrite-normalized patterns of the REE redistribution in bentonites and comparing them with the REE abundances in unaltered volcanics, a relatively small shift is indicated by the total amount of these elements in both kinds of samples. This suggests that a generally little degree of mobilization or fractionation of these elements took place during the alteration process (Fig. 5.14). The REE distribution in bentonites can be compared to the tendencies of the elements Al, Ta, Th Ga and also Hf.

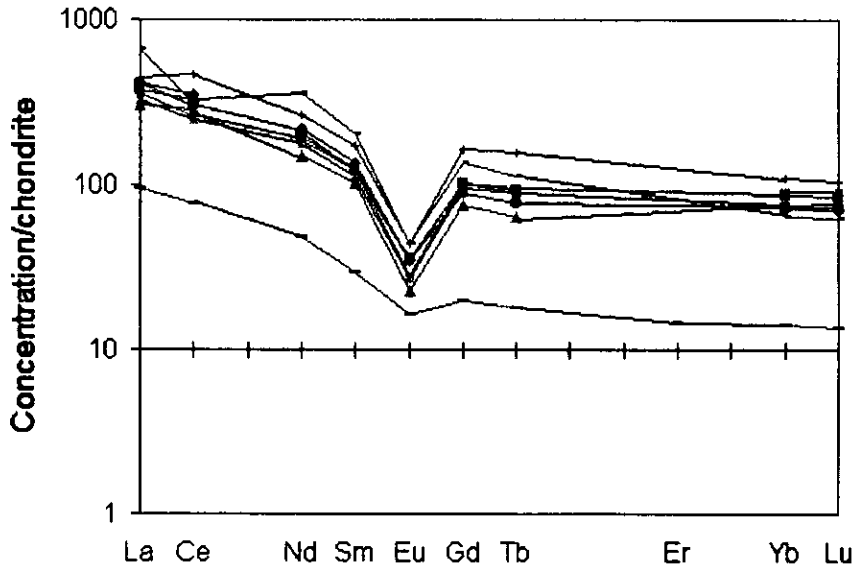


Figure 5.15: Chondrite-normalized REE abundances in Boane bentonites and the rhyolitic parent rocks. NASC (North American Shale Composite) is also showed for comparison. The chondrit values are of Nakumura (1974) in Rollinson (1993).

Table 5.5: Rare Earth Elements (REE) concentrations (in ppm) in selected bentonite samples and rhyolitic parent rocks from Boane district, Mozambique. The samples B49, B58 and BPR represent rhyolitic parent rocks

Sample	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Cs	Rb	Sc	Ga	Hf	Ta	Nb	Th	U
B52	136	339	136	27.50	2.69	4.15	15.70	2.37	13.60	126	2.39	26	16	6.73	n.d.	20.10	2.42
B42	99	293	94	21.00	1.76	3.00	16.60	2.60	0.50	126	3.16	25	15	6.89	n.d.	19.80	4.01
B46	116	252	116	25.00	2.18	4.45	16.60	2.51	0.95	23	2.60	19	13	6.13	n.d.	17.10	2.43
B21	136	280	129	24.40	2.70	3.60	16.30	2.49	1.02	19	4.06	20	16	6.98	n.d.	19.60	1.77
B26	144	450	165	35.20	3.42	7.41	24.40	3.53	1.84	38	10.90	20	11	4.68	n.d.	12.80	5.40
B30	218	327	222	40.80	3.38	5.27	14.20	2.13	1.01	19	2.64	25	16	7.06	n.d.	20.60	2.44
B49	106	254	112	22.60	2.08	4.17	20.20	3.05	1.50	160	1.00	20	13	6.54	n.d.	16.80	4.52
B58	124	324	121	2.60	2.71	4.38	19.00	2.86	1.20	150	2.00	21	12	5.00	n.d.	15.30	1.80
P1A*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	27	n.d.	n.d.	92	19.90	3.40
P2A*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	32	n.d.	n.d.	89	21.10	4.50
P3A*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.	87	21.80	3.50
P3B*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.	104	20.00	5.90
P3C*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	32	n.d.	n.d.	99	20.30	4.80
S3A*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	31	n.d.	n.d.	88	18.90	2.70
S3B*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	31	n.d.	n.d.	98	18.60	3.90
S5A*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	31	n.d.	n.d.	104	21.60	1.70
S5B*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	34	n.d.	n.d.	117	26.60	6.60
BPR*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	21	n.d.	n.d.	34	10.90	2.20

n.d.= not determined.

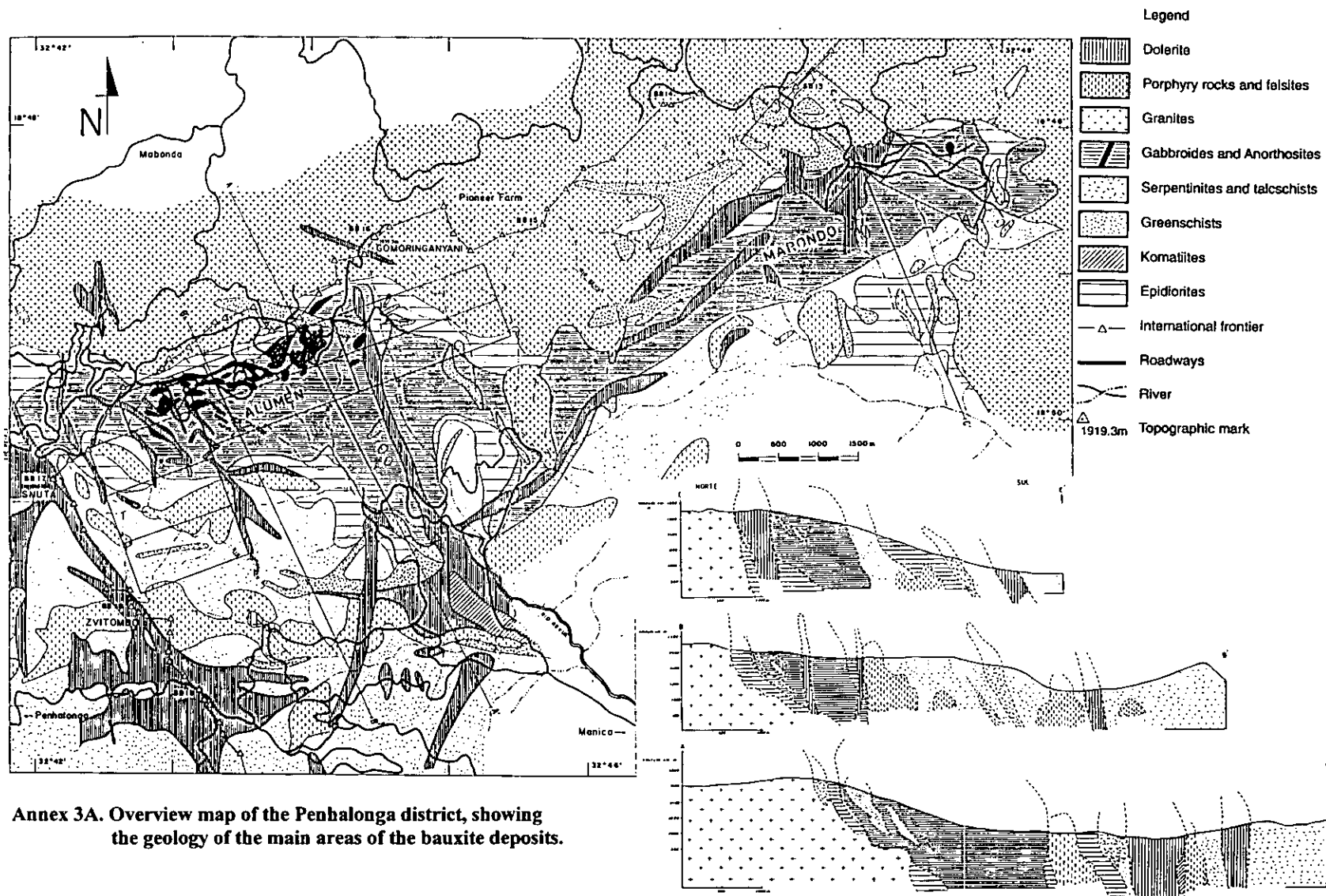
5.7. Discussion

The Little Lebombo rhyolites are associated with several occurrences of bentonite. Chemical composition in major and trace elements indicate the rhyolitic and rhyolite-dacitic character, which has undergone alteration, totally or partly to smectite rich material. Layers with cores of partially altered parent material are frequent within the bentonitic masses. This can possibly be attributed to textural heterogeneities within the parent rocks, leading to preferential sites of alteration. In some places the undulating surface boundary between the bentonite and overlying beds of sediments suggest erosion of the bentonitic bodies, prior to the deposition of colluvial and alluvial material. The bentonite is composed of a Ca-type smectite, and is always accompanied by a silica phase. There is not yet a general agreement on the alteration mechanisms of the rhyolites to bentonite. Wachendorf (1971), based on field data, considered as probable a relationship between the formation of the bentonitic masses and the vertical movements of the groundwaters interacting with the rhyolite. Through such a mechanism, in an alkaline environment, the alteration of the parent rocks was restricted from the paleo-groundwater table downwards, leaving the overlying rock horizons basically unaltered or only partially silicified (Wachendorf, 1971). The near horizontal boundary surface between the silicified rhyolitic tuff and the underlying bentonite that occurs in the Boane deposit seems to support this point of view. However, alteration caused by descending solutions can not be completely discarded. The general chemical composition variation of the MgO, CaO, Na₂O and K₂O contents both in the tuffs and bentonite have to be considered. MgO and K₂O, for example, show opposite trends, suggesting leaching of the alkalis; yet alteration in an environment rich in MgO (Tables 5.3 and 5.4). The general configuration of the deposits, with alteration decreasing with depth, suggests a supergene origin of the alteration agents (Tavares, 1973), weathering of the parent volcanics by dominantly descending meteoric waters. Grim and Güven (1978), on the basis of mineralogical associations of the bentonites, excluded any hydrothermal agents in the formation of the bentonite from Boane district and described geological similarities to those occurring in Natal Province in Zululand, South Africa, which are supposed to have originated by deuteric action. According to Grim and Güven (1978), hydrothermal alteration should have provoked mineral zoning of the deposit and surrounding country rocks, with hydrothermal phyllosilicate minerals, such as pyrophyllite and kaolinite. On the basis of the available field and analytical data the bentonite deposits from Boane appear to have been derived *in situ* from the alteration by meteoric water of rocks with mainly rhyolitic composition. The deposits may have had a complex history and may also have been affected by hydrothermal alteration, so that a mixed origin of the bentonites can be suggested. Two separate events or phases may have acted in the alteration process of the parent rocks. The geological setting and distribution of the bentonitic beds in the deposits, in places lying under fresh rhyolitic rocks, and the outcropping of insignificant pockets of bentonite inside rhyolites, may denote particular environmental conditions by the bentonite formation other than entirely supergenetic action. The bentonitic pockets are commonly found in voids of porous rhyolites, covering rhyolitic boulders of different sizes. Calcite crystals are also found filling voids in rhyolites. Furthermore, the mineralogy of the bentonites themselves, characterized by relatively high contents of silica phases, with predominantly cristobalite and opaline silica, can be an indicative of hydrothermal influences in the bentonite formation. Probably weathering, afterwards, may have imprinted the already affected rocks and led to the unusual thickness of the bentonitic deposits, through leaching of alkalis, particularly K₂O, and gain of MgO, CaO and also Fe from the permeating solutions. Despite different macroscopic aspects of the rhyolitic parent rocks, the major element composition is very similar. Chemical composition and principal minerals of the bentonite are generally uniform, suggesting similar chemical character of the parent materials. The alteration in bentonite seems to be developed in

conditions of freely leaching of the alkalis ($\text{Na}^+ + \text{K}^+$), as indicated by the differences in alkali contents in the parent rocks and bentonite. The absence of zeolitic minerals in areas of formation of bentonite deposits has been often related with moderate alkalinity in closed hydrologic systems (Zielinski, 1982; Christidis *et al.*, 1995; Christidis, 1998). No zeolitic mineral phase could be detected in the XRD analysis of the Boane bentonite. The presence of calcitic concretions associated with bentonite is likely to have resulted from micro-environmental changes: its precipitation may have acted as buffer for Ca^{++} -ions, allowing continuous leaching of rhyolite (Fritz, 1985). Furthermore this also indicates essentially alkaline conditions, which favored calcium carbonate precipitation.

5.8. Conclusions

Descriptions of the alteration of the volcanics in the Little Lebombo in Boane area have been carried out. Petrographic observations, chemical analyses of major and trace elements and X-ray determinations were applied to study unaltered rocks and bentonite samples. The chemical data suggest that the rocks of mainly rhyolitic and rhyodacitic compositions underwent different degrees of leaching in association with slightly alkaline and alkaline solutions under chemically open-system environment. The mineral assemblages and the overall behaviour of major and trace elements indicate this. Formation of montmorillonite instead of zeolites is likely to occur under moderate $(\text{Na}^+ + \text{K}^+)/\text{H}^+$ activity ratios (Zielinski, 1982; Christidis *et al.*, 1995; Christidis, 1998). Zeolitic mineral phases have not been detected by X-ray Diffraction analysis. Under this geochemical scenario the soluble alkaline elements K, Rb and Cs were clearly removed from the system and therefore are depleted in the bentonite. Silica has been also mobilized during the alteration process, whilst earth alkaline Ca, Mg, and Sr as well as some transition metals e.g. Sc, Ni, V, Cr and Ti are enriched either by structural incorporation, co-precipitation with residual and secondary mineral phases or by ion exchange and adsorption in clay minerals. Depletion in Co and Ba presents an unexplained solubility condition, which probably caused their removal. Interaction with Mg rich solutions can be viewed as a possible reason for its strong enrichment in bentonite. Insoluble elements are represented by the elements Al, Ga, Ta, Hf, Zr and Nb which are relatively immobile, similar to Th and REE. The observed redistribution of these immobile elements under supergene conditions is described to be favoured by alkaline to moderate alkaline conditions in the alteration of rhyolitic rock (Wedepohl, 1970; Christidis, 1998).



Annex 3A. Overview map of the Penhalonga district, showing the geology of the main areas of the bauxite deposits.

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**Annex 3A. Overview map of the Penhalonga district, showing
the geology of the main areas of the bauxite deposits.**

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