SKB TECHNICAL REPORT

90-10

The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil.

H D Schorscher[1], M E Shea[2]

[1] Universidade de Sao Paulo, Instituto de Geociências, – DMP, Sao Paulo, Brazil
[2] University of Chicago, Department of Geophysical Sciences, Chicago, Illinois, USA

January 1991

SVENSK KÄRNBRÄNSLEHANTERING AB
SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO

BOX 5864 S-102 48 STOCKHOLM

TEL 08-665 28 00 TELEX 13108 SKB S
TELEFAX 08-661 57 19

NAGRA NTB 90-19
SKB TR 90-10
UK DOE WR 90-041

Poços de Caldas Report No. 1

The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil.

JANUARY 1991

An international project with the participation of Brazil, Sweden (SKB), Switzerland (NAGRA), United Kingdom (UK DOE) and USA (US DOE). The project is managed by SKB, Swedish Nuclear Fuel and Waste Management Co.

THE REGIONAL GEOLOGY, MINERALOGY AND GEOCHEMISTRY OF THE POÇOS DE CALDAS ALKALINE CALDERA COMPLEX, MINAS GERAIS, BRAZIL

H D Schorscher[1], M E Shea[2]

1 Universidade de Sao Paulo, Instituto de Geociências - DMP, Sao Paulo, Brazil
2 University of Chicago, Department of Geophysical Sciences, Chicago, Illinois, USA

January 1991

Information on SKB technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31), 1987 (TR 87-33), 1988 (TR 88-32), 1989 (TR 89-40) and 1990 (TR 90-46) is available through SKB.

The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil.

H.D. SCHORSCHER[1] and M.E. SHEA[2].

[1]Universidade de São Paulo, Instituto de Geociências – DMP, Cx. P. 20 899, São Paulo, 01498 SP. (Brazil).

[2]University of Chicago, Department of Geophysical Sciences, 5734 S. Ellis Avenue, Chicago, Illinois (USA).

Abstract

The Poços de Caldas alkaline complex, the largest in South America, is circular- shaped with a mean diameter of about 33 km. It is one of the Mesozoic alkaline occurrences of south-eastern Brazil that developed from the Upper Jurassic onwards, during continental break-up and drift. It comprises a suite of alkaline volcanic and plutonic rocks (mainly phonolites and nepheline syenites) with normal background amounts of U, Th and rare-earth elements (REEs). The evolutionary history began with major early volcanism involving ankaratrites, phonolite lavas and volcanoclastics, followed by caldera subsidence and nepheline syenite intrusions forming minor ring dykes, various intrusive bodies and circular structures. Finally, eudialyte nepheline syenites and phonolites, strongly enriched in incompatible elements, were emplaced.

Magmatic evolution included deuteric processes, indicating a volatile-rich parent magma. These processes extended over a large temperature range and resulted in the formation of pegmatitic veins and pneumatolytic and auto-hydrothermal mineral assemblages including rare metal silicates such as giannettite, various zeolites, fluorite and hematite, together with mineral alterations. These alterations developed from magmatic pseudoleucite through alkali-exchange reactions to a "clouding" of the main alkali feldspars under auto-hydrothermal conditions (with fluid inclusion formation, incipient kaolinization and hematite-hydrous ferric oxide pigmentation). Geochemically, the resulting rocks are enriched in potassium when compared to global nepheline syenites and phonolites. Mobilization and concentration of U, Th and REEs could not be detected at this stage.

At least at one location (Morro do Ferro) the intermediate nephelinic suite was affected by a carbonatite intrusion and the formation of a stockwork of magnetite veins.

Very intensive hydrothermal K- and S-rich alteration, associated with pene-contemporaneous formation of magmatic breccias, occurred locally.

These processes led to the formation of several important radioactive and REE-rich anomalies. Two of these, the Th-REE occurrence of Morro do Ferro and the U-Zr-REE-Th occurrence of the Osamu Utsumi uranium mine, comprise the study sites of the Poços de Caldas Analogue Project.

Later major evolutive stages of the Poços de Caldas complex involved the emplacement of mafic-ultramafic dyke rocks and the onset of lateritic and allitic weathering, resulting (at the uranium mine) in supergenic geochemical redistribution and the formation of redox fronts sometimes related to uranium enrichments.

The regional rock studies were focussed on the "status quo" properties of the intermediate nephelinic suite with respect to the subsequent more local hydrothermal and final weathering-related processes. They included petrographic, mineralogical, geochemical and isotopic studies, in addition to petrophysical parameters. Results showed very little variation for the studied intrusive, subvolcanic and volcanic nepheline syenites and phonolites. The lack of a major differentiated series may be seen as an argument for a short emplacement history of the intermediate nephelinic suite. Previous and present radiometric age measurements suggest a time span of about 15 Ma for emplacement, much too long if compared to modern volcanoes. The end of the magmatic and hydrothermal-mineralizing events is likely fixed by the Ar-Ar dating of an unmineralized lamprophyre dyke intrusion at the site of the uranium mine (76 Ma).

Zusammenfassung

Der kreisförmige alkalische Komplex von Poços de Caldas ist mit einem mittleren Durchmesser von 33 km der grösste in Südamerika. Er ist eines der alkalischen Vorkommen in Süd-Ost Brasilien, die sich in der Epoche ab oberem Jura im Zusammenhang mit dem Aufbruch und der Verdickung der Kontinente entwickelten. Er besteht aus einer Reihe alkalischer Eruptiv- und Intrusivgesteine (hauptsächlich Phonolite und Nephelin-Syenite) mit normalen Gehalten an U, Th, und SEE. Die Entwicklungsgeschichte begann mit frühem, starkem Vulkanismus, der zu Ankaratriten, Phonolit-Laven und Pyroklastika führte, gefolgt vom Einsinken der Caldera und der Intrusion von Nephelin-Syenit, die kleinere Ring-Gänge, verschiedene Intrusivkörper und kreisförmige Strukturen bildeten. Schliesslich wurden Eudialyt, Nephelin-Syenite und Phonolite deponiert, die an inkompatiblen Elementen stark angereichert waren.

Die magmatische Entwicklung schloss deuterische Prozesse ein, die auf ein Muttermagma, reich an flüchtigen Stoffen, schliessen lassen. Diese Prozesse erstreckten sich über ein grosses Temperaturintervall und bewirkten die Bildung von Pegmatitgängen und pneumatolytischen sowie autohydrothermalen Mineral-Ansammlungen wie SEE-Silikate (z.B. Giannettit), verschiedene Zeolite, Fluorit und Hämatit. Daneben erfolgten Mineralveränderungen, die von magmatischen Pseudoleucil durch Alkali-Austausch zu einer Häufung der wichtigsten Alkalifeldspäte unter autohydrothermalen Bedingungen führte (mit Bildung von Flüssigkeitseinschlüssen, beginnender Kaolinisierung und Pigmentierung durch Ferri-Oxyhydrate). Geochemisch sind die resultierenden Gesteine an Kalium angereichert, verglichen mit den globalen Nephelin-Syeniten und Phonoliten. Mobilisierung und Anreicherung von U, Th und SEE's konnten für dieses Stadium nicht festgestellt werden.

Zumindest an einer Stelle (Morro do Ferro) wurde die intermediäre Nephelin-Reihe durch eine Karbonalit-Intrusion und die Bildung übereinandergelagerter Magnetitgänge beeinflusst. Es fand lokal eine sehr intensive, K- und S-reiche hydrothermale Umwandlung mit autometamorpher Bildung von magmatischen Brekzien statt.

Diese Prozesse führten zur Entstehung verschiedener ausgeprägter radioaktiver und SEE-reicher Anomalien. Zwei derselben, das Th-SEE-Vorkommen von Morro do Ferro und das U-Zr-SEE-Th-Vorkommen der Osamu Utsumi Uranmine bilden die Untersuchungsorte des Poços de Caldas-Analogprojektes.

Spätere wichtige Entwicklungsstufen des Poços de Caldas Komplexes bestanden im Einbau mafischer und ultramafischer Ganggesteine und dem Beginn der allitischen und lateritischen Verwitterung, die (in der Uranmine) zu einer deszendenten geochemischen Umverteilung und zur Bildung von Redoxfronten führte, wie sie oft mit Urananreicherungen in Beziehung stehen.

Die regionalen Gesteinsuntersuchungen konzentrierten sich auf die status quo Eigenschaften der intermediären Nephelin-Reihe unter Berücksichtigung der mehr lokalen hydrothermalen Einflüsse und der abschliessenden mit der Verwitterung zusammenhängenden Prozesse. Sie umfassten petrophysikalische, petrographsiche, mineralogische, geochemische und isotopenchemische Untersuchungen. Die Resultate zeigten nur sehr geringe Variationen zwischen den untersuchten intrusiven, subvulkanischen und vulkanischen Nephelin-Syeniten und Phonoliten. Das Fehlen einer stärker differenzierten Serie kann als Argument für eine kurze Entstehungsgeschichte der intermediären Nephelin-Reihe gelten. Frühere und jetzige radiometrische Altersbestimmungen sprechen für eine Zeitspanne von etwa 15 Ma, viel zu lang im Vergleich zu modernen Vulkanen. Das Ende der magmatischen und hydrothermalen Mineralbildungszeit wird wahrscheinlich durch das Alter eines mineralisierten Lamprophyrganges in der Uranmine gegeben (76 Ma).

Résumé

Le complexe alcalin de Poços de Caldas, le plus grand en Amérique du sud, a une forme circulaire avec un diamètre moyen d'environ 33 km. Il représente l'un des gisements alcalins du Mésozoïque au sud-est du Brésil, développé à partir du Jurassique supérieur en liaison avec la rupture et la dérive continentale. Il comprend une série de roches volcaniques alcalines et de roches plutoniques (principalement des phonolites et des syénites néphélitiques) présentant des teneurs d'arrière-plan normales en U, Th et terres rares (TRs). La séquence évolutive a commencé par un jeune volcanisme majeur produisant des ankaratrites, des laves phonolitiques et des volcanoclastes, s'est poursuivie par une subsidence de la caldera et des intrusions de syénite néphélitique formant des anneaux mineurs de dykes, des corps intrusifs variés et des structures circulaires. Enfin, on trouve la mise en place de syénites néphélitiques et de phonolites fortement enrichies en éléments incompatibles.

L'évolution magmatique a inclu des processus deutériques, signalant la présence d'un magma parent riche en éléments volatils. Ces processus ont eu cours sur une large gamme de températures et ont engendré des veines pegmatitiques et des associations minérales pneumatolytiques et auto-hydrothermales comprenant des silicates à métaux rares tels que la giannettite, des zéolites variées, de la fluorite et de l'hématite, ainsi que des altérations de minéraux. Ces altérations se sont développées d'une pseudoleucite jusqu'à une palette des principaux feldspaths alcalins, par échanges d'éléments alcalins sous des conditions auto-hydrothermales (avec la formation de fluides hydrothermaux, début de kaolinisation et pigmentation par des oxides ferriques d'hématite hydratée). Du point de vue géochimique, les roches résultantes sont enrichies en potassium, par rapport à l'ensemble des syénites néphélitiques et des phonolites. Une mobilisation et une concentration en U, Th et TRs n'a pas pu être détectée à ce stade.

Au moins à un endroit (Morro do Ferro), la séquence néphélitique intermédiaire a été affectée par une intrusion de carbonatite et la formation d'un réseau de veines de magnétite. De très intenses altérations hydrothermales riches en potassium et en soufre ont été observées localement, en association avec la formation de brèches magmatiques pénécontemporaines.

Ces processus ont conduit à la formation de plusieurs anomalies radioactives importantes et riches en TRs. Deux d'entre elles, le gisement de Th-TRs à Morro do Ferro et le gisement de U-Zr-TRs-Th à la mine d'uranium d'Osamu Utsumi, font partie des sites d'étude du projet d'analogies naturelles de Poços de Caldas.

Les principales étapes ultérieures de l'évolution du complexe de Poços de Caldas comprennent la mise en place de roches filonniennes mafiques et ultramafiques, et l'apparition d'une altération latéritique et allitique, conduisant (à la mine d'uranium) à une redistribution géochimique secondaire et à la formation de fronts redox, parfois liés à des enrichissements en uranium.

Les études régionales de la roche ont été concentrées sur les propriétés de stabilité (statu quo) de la séquence néphélitique intermédiaire, en tenant compte des processus subséquents de l'hydrothermalisme local et des processus liés à l'altération. Ces études comprennent des volets pétrographique, minéralogique, géochimique et isotopique, en plus de l'examen des paramètres pétrophysiques. Les résultats ont montré qu'il y a peu de différences entre les roches étudiées, des syénites néphélitiques et des phonolites intrusives, subvolcaniques et volcaniques. L'absence de séries nettement différenciées penche en faveur d'une phase de mise en place courte pour la séquence néphélitique intermédiaire. Des datations radiométriques antérieures et actuelles suggèrent une durée de mise en place d'environ 15 millions d'années (m. a.), ce qui est beaucoup trop long si on la compare à celle des volcans actuels. La fin des événements magmatiques et de minéralisation hydrothermale est probablement déterminée par la datation Ar-Ar d'une intrusion filonienne de lamprophyre non minéralisée sur le site de la mine d'uranium (76 m. a.).

Preface

The Poços de Caldas Project was designed to study processes occurring in a natural environment which contains many features of relevance for the safety assessment of radioactive waste disposal. The study area, in the State of Minas Gerais, Brazil, is a region of high natural radioactivity associated with volcanic rocks, geothermal springs and uranium ore deposits. It contains two sites of particular interest on which the project work was focussed: the Osamu Utsumi uranium mine and the Morro do Ferro thorium/rare-earth ore body. The first site is notable in particular for the prominent redox fronts contained in the rock, while Morro do Ferro was already well-known as one of the most naturally radioactive locations on the surface of the Earth, owing to the high thorium ore grade and the shallow, localised nature of the deposit.

The features displayed by these two sites presented the opportunity to study a number of issues of concern in repository performance assessment. The four objectives set after the first-year feasibility study were:

1. Testing of equilibrium thermodynamic codes and their associated databases used to evaluate rock/water interactions and solubility/speciation of elements.
2. Determining interactions of natural groundwater colloids with radionuclides and mineral surfaces, with emphasis on their role in radionuclide transport processes.
3. Producing a model of the evolution and movement of redox fronts, with the additional aim of understanding long-term, large-scale movements of trace elements and rare-earths over the front (including, if possible, natural Pu and Tc).
4. Modelling migration of rare-earths (REE) and U-Th series radionuclides during hydrothermal activity similar to that anticipated in the very near-field of some spent-fuel repositories.

The project ran for three and a half years from June 1986 until December 1989 under the joint sponsorship of SKB (Sweden), NAGRA (Switzerland), the Department of the Environment (UK) and the Department of Energy (USA), with considerable support from a number of organisations in Brazil, notably Nuclebrás (now Urânio do Brasil). The first-year feasibility study was followed by two and a half years of data collection and interpretation, focussed on the four objectives above.

This report is one of a series of 15, summarising the technical aspects of the work and presenting the background data. A complete list of reports is given below. Those in series A present data and interpretations of the sites, while those in series B present the results of modelling the data with performance assessment objectives in mind. The main findings of the project are presented in a separate summary (no. 15).

The work presented in this report is a general description of the geology, geochemistry and geochronology of the Poços de Caldas alkaline complex. This study provides a wider, regional context for interpretation of the more detailed site-specific studies presented in many of the other reports.

Poços de Caldas Project Report Series

Series A: Data, Descriptive, Interpretation

Report No.	Topic	Authors (Lead in Capitals)
1.	The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil.	SCHORSCHER, Shea.
2.	Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. I: Osamu Utsumi uranium mine.	WABER, Schorscher, Peters.
3.	Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. II: Morro do Ferro.	WABER.
4.	Isotopic geochemical characterization of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil.	SHEA.
5.	Geomorphological and hydrogeological features of the Poços de Caldas caldera and the Osamu Utsumi mine and Morro do Ferro analogue study sites, Brazil.	HOLMES, Pitty, Noy.
6.	Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	NORDSTROM, Smellie, Wolf.
7.	Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MacKENZIE, Scott, Linsalata, Miekeley, Osmond, Curtis.
8.	Natural series radionuclide and rare-earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MIEKELEY, Coutinho de Jesus, Porto da Silveira, Linsalata, Morse, Osmond.

Report No.	Topic	Authors (Lead in Capitals)
9.	Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MIEKELEY, Coutinho de Jesus, Porto da Silveira, Degueldre.
10.	Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	WEST, Vialta, McKinley.

Series B: Predictive Modelling and Performance Assessment

11.	Testing of geochemical models in the Poços de Caldas analogue study.	BRUNO, Cross, Eikenberg, McKinley, Read, Sandino, Sellin.
12.	Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	Ed: McKINLEY, Cross, Haworth, Lichtner, MacKenzie, Moreno, Neretnieks, Nordstrom, Read, Romero, Scott, Sharland, Tweed.
13.	Near-field high-temperature transport: Evidence from the genesis of the Osamu Utsumi uranium mine, Poços de Caldas alkaline complex, Brazil.	CATHLES, Shea.
14.	Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	NORDSTROM, Puigdomènech, McNutt.

Summary Report

15.	The Poços de Caldas Project: Summary and implications for radioactive waste management.	CHAPMAN, McKinley, Shea, Smellie.

Contents

page

Abstract i

Preface vii

1. Introduction 1

2. Regional geology and geomorphology 1
   - 2.1. Regional geology 1
   - 2.2. Alteration and mineralization 7
   - 2.3. General geomorphology 9

3. Description of regional samples 11
   - 3.1. Geology 11
     - 3.1.1. Nepheline syenites 11
     - 3.1.2. Phonolites 12
   - 3.2. Petrography and mineralogy 13
     - 3.2.1. Petrography 13
     - 3.2.2. Mineralogy 16
   - 3.3. Elemental geochemistry 18
     - 3.3.1. Major and trace elements 18
     - 3.3.2. Rare-earth elements 23

4. Final considerations: regional samples and geological evolution 29

5. Acknowledgements 31

6. References 31

1. Introduction

The Poços de Caldas complex is a ring structure of Mesozoic age comprising a suite of alkaline volcanic and plutonic rocks (mainly phonolites and nepheline syenites) containing normal background amounts of U, Th and rare-earth elements (REEs). The complex initially suffered regional postmagmatic deuteric alteration, resulting in widespread and pervasive potassium metasomatism and zeolitization, together with minor argillation under oxidizing conditions (e.g. hematitization and hydrous ferric oxide-HFO-mineral formation). At this stage no mobilization and concentration of U, Th and REEs occurred. The complex was subsequently modified by hydrothermal fluid/rock interaction of local extent (primary mineralizing event), which led to pyritization, strong potassification, and to the formation of several important radioactive anomalies. Two of these anomalies, the Osamu Utsumi uranium deposit (with subsidiary Th, REEs, Zr and Mo) and the Morro do Ferro thorium and rare-earth deposit (with subsidiary U and Zr), form the main study sites of the Poços de Caldas Analogue Project.

Subsequent major evolutive stages of the Poços de Caldas complex included the emplacement of mafic-ultramafic dyke rocks (lamprophyres) and the onset of weathering, resulting in the formation of a surface laterite horizon and extensive saprolitization of the bedrock. Coeval with these low-temperature processes was the formation of penetrating redox fronts associated with the supergene remobilization and precipitation of uranium concentrations now under exploitation at the Osamu Utsumi mine area (secondary mineralizing event).

The initial part of this report reviews the regional geological evolution (excerpted from selected literature) and geomorphology. Following this, the regional reference samples of the project, later used for comparisons with the mineralized rocks with respect to their magmatic and deuteric mineralogical and geochemical properties, are petrographically and geochemically characterized. For those interested in more detailed background information, an extensive bibliography has been compiled.

2. Regional geology and geomorphology

2.1. Regional geology

The Poços de Caldas alkaline complex is circular-shaped with a mean diameter of approximately 33 km, and is situated about 220 km north of São Paulo in south-eastern

Brazil (Figs. 1 and 2). Topographic maps (1:50,000) covering the ring structure and adjacent areas, and the geological maps of Ellert *et al.* (1959) and Ulbrich (1984), were used to help locate the studied outcrops of the regional rock types.

As discussed in Best (1982), alkaline rocks are found almost exclusively in stable intraplate tectonic settings including continental rifts. They are rarely found in tectonically active regions of plate convergence and rapid divergence such as subduction zones and oceanic rifts where geothermal gradients are high. The alkaline rocks of the Poços de Caldas complex are associated with the rifting of the South American and African plates, with the south tract of the Atlantic Ocean opening approximately 145-125 Ma ago.

An outline of the regional geology and geotectonics of central-east Brazil is shown in Figure 1 after Almeida (1977). Based on work by Ulbrich and Gomes (1981), the occurrences of alkaline rocks, including the Poços de Caldas complex, have been added. Although these alkaline rocks are observed to cut through all the major Precambrian cratonic and mobile belt structures and Phanerozoic basins, they are mostly associated with distinct provinces which can be correlated with large regional tectonic phenomena, such as arches, flexures, deep faults and rifts.

Geochronological studies since Amaral *et al.* (1967) have recognized two major age groups within the region: the Infracambrian province of southern Bahia State with radiometric ages of 560 to 670 Ma (Fujimori, 1967; Souto, 1972; Cordani *et al.*, 1974; Ulbrich and Gomes, 1981) and the far more numerous Mesozoic to subrecent occurrences of which the Poços de Caldas complex is the most prominent example. These occurrences developed from the Upper Jurassic onwards during continental break-up and drift of the South American and African plates. Alkaline magmatism in the continental area lasted from more than 140 to about 50 Ma ago, and continued in the Brazilian Atlantic Ocean islands up to subrecent times (Cordani, 1970; Bushee, 1971; Herz, 1977; Ulbrich and Gomes, 1981). Apparent regular age variations and structural arrangements comprising individual continental provinces and younger alkaline magmatism of the Brazilian islands have been interpreted as being of hot-spot and migrating lithosphere origin (Herz, 1977).

Compared to other alkaline complexes, the Poços de Caldas plateau is outstanding in more than one aspect. With a surface extent of about 800 km^2, it represents the largest alkaline complex of South America. Furthermore, there is no evidence of geotectonic control, either from local or regional structural studies or from geophysical investigations. The regional-geotectonic and genetic relationship between the Poços de

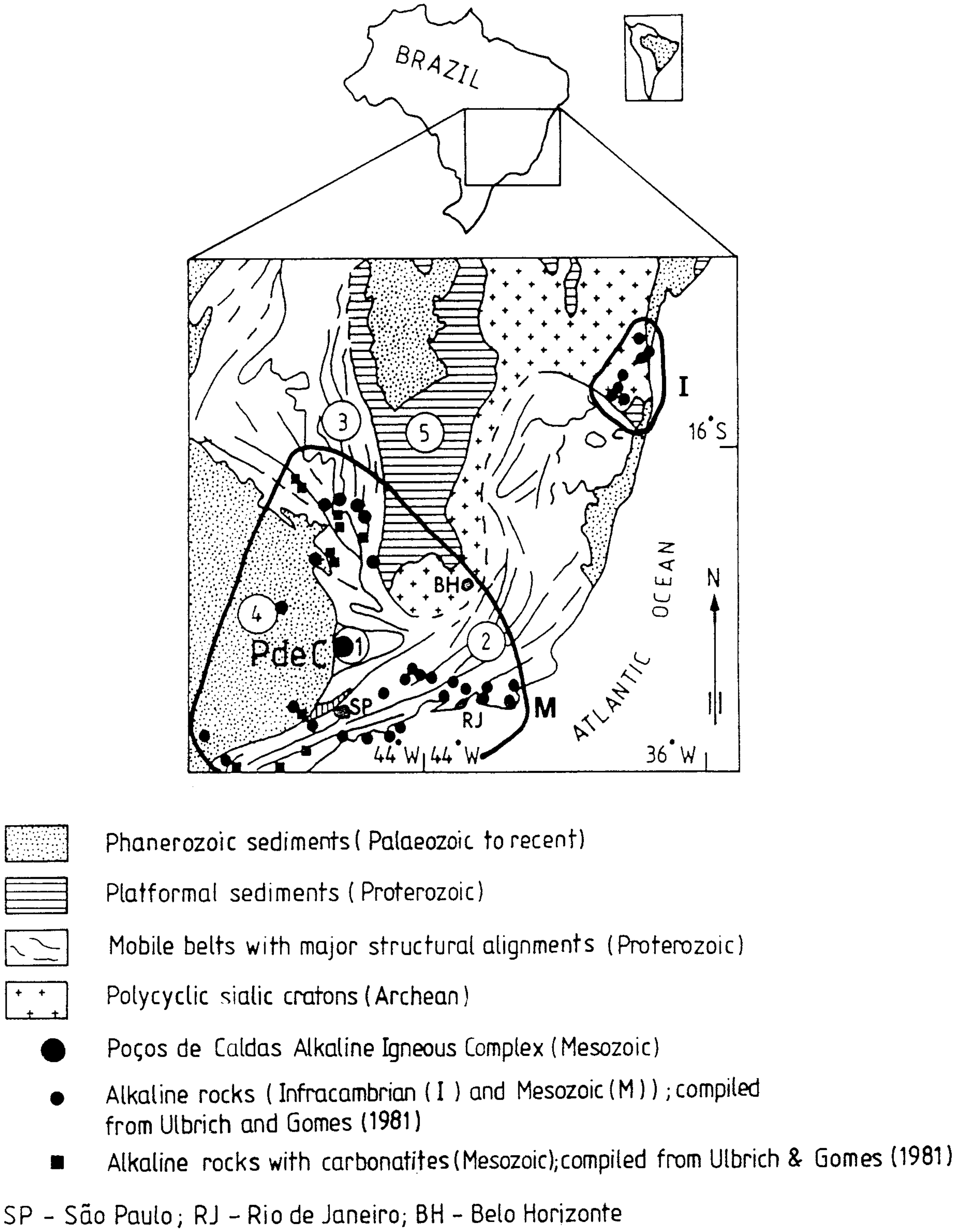


Figure 1. A simplified regional geological map (after Almeida, 1977) showing the locations of alkaline rock and the Poços de Caldas Complex (the large closed circle symbol). Tectonic subdivisions are: (1) Guaxupé Massif cratonic block (Archean); (2) Ribeira mobile belt (Proterozoic); (3) Brasilia mobile belt (Proterozoic); (4) Paraná Basin sediments and basalts (Phanerozoic) and coastal sediments (Tertiary to recent); (5) São Francisco craton (Archean) with a platformal sediment cover in the west (Proterozoic); closed circles = Infracambrian and Mesozoic alkaline rocks (Ulbrich and Gomes, 1981); closed squares = Mesozoic alkaline rocks with carbonatites (Ulbrich and Gomes, 1981).

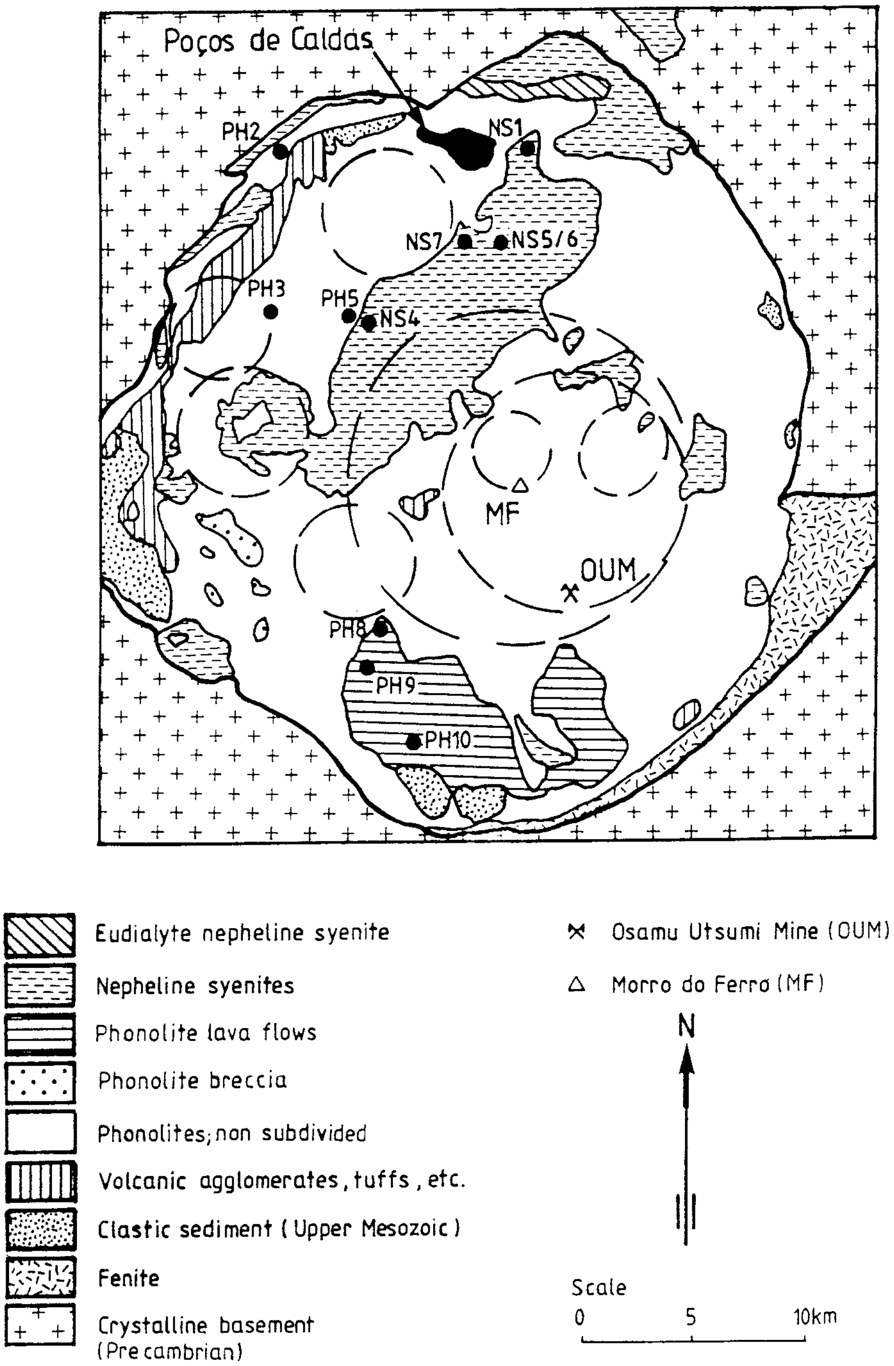


Figure 2. A simplified geological map (after Ellert et al., 1959 and Almeida Filho and Paradella, 1977) of the Poços de Caldas caldera showing the location of all the regional nepheline syenite (NS) and phonolite (PH) samples. Circular features within the caldera are mainly derived from photogeological analysis.

Caldas complex and the eastern border of the Paraná Basin (Almeida, 1983; Ulbrich, 1984) is still speculative and not supported by specific structural features.

The Poços de Caldas alkaline complex was studied geologically and mapped by Ellert (1959) and Ellert *et al.* (1959), analyzed structurally on the basis of remote-sensing by Almeida Filho and Paradella (1977) and investigated geophysically by Araujo (1980), Hamza (1982), Montes-Lauar (1988) and Montes-Lauar and Pacca (1990). More detailed research, particularly with respect to nepheline syenite, was performed subsequently by Ulbrich (1984). A simplified sketch map of the Poços de Caldas alkaline complex, integrating geological and remote-sensing structural data, is shown in Figure 2 (excerpted from Magno Jr., 1985). Known mineral deposits are of hypogene and/or supergene origin, including bauxite, clays, Zr, Zr-U-Mo, F and Th-REE (-Fe) mineralizations (Frayha, 1962; Wedow, 1967; Gorsky and Gorsky, 1974; Putzer, 1976; Santos, 1976; Magno Jr., 1985, Fraenkel *et al.*, 1985).

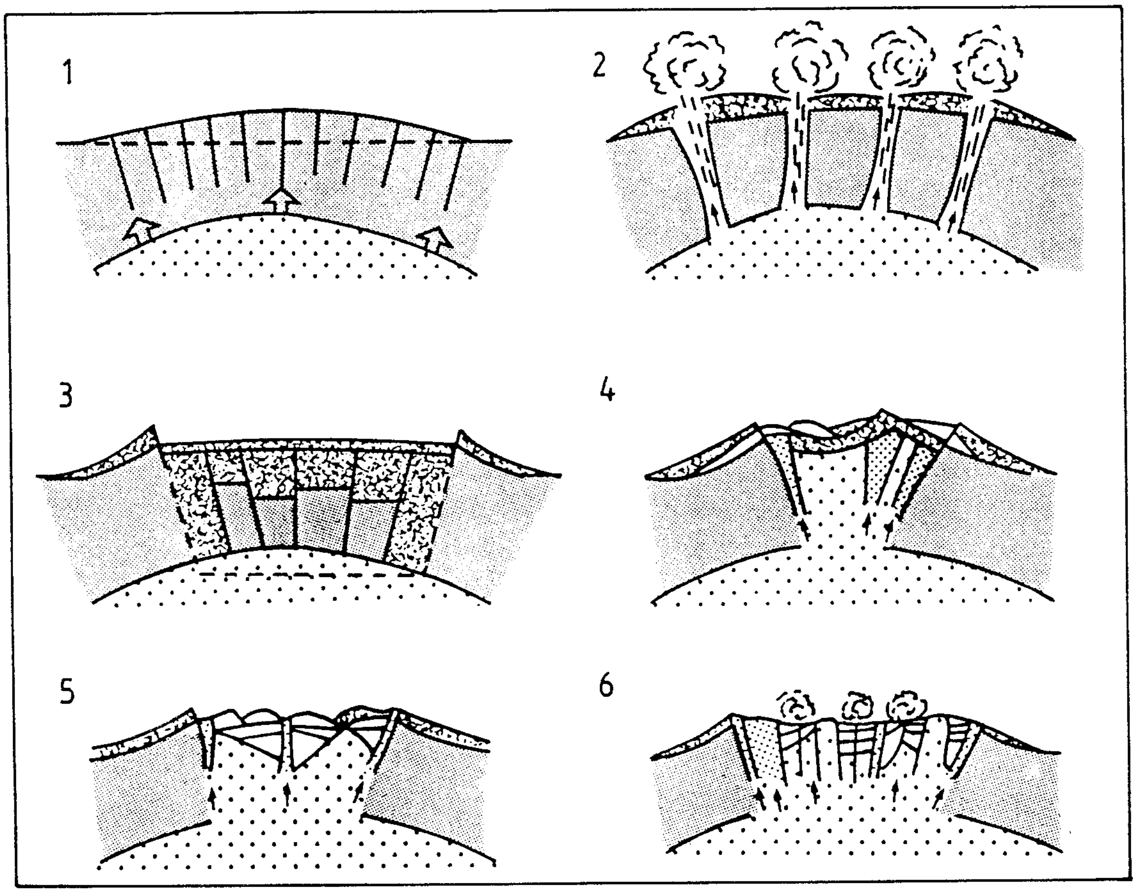
The petrographic associations of the Poços de Caldas alkaline rocks are rather complex and as yet unique in Brazil (Ulbrich and Gomes, 1981). Potassium-rich phonolites and nepheline syenites are the predominant rock types, with only minor occurrences of eudialyte-bearing nepheline syenites. The presently exposed areas of alkaline rocks (Table I) have been calculated by Ulbrich and Gomes (1981).

TABLE I

Present-day outcrop exposures and rock types of the Poços de Caldas alkaline complex (Ulbrich and Gomes, 1981).

Rock types	Outcrop exposures (area – %)
Phonolites, subvolcanic	78.0
Nepheline syenites	13.5
Phonolite lavas	5.0
Volcanoclastics	3.0
Eudialyte-bearing nepheline syenites	0.5

The evolutionary history, according to Ellert (1959), starts with major early volcanism involving ankaratrites (biotite-bearing nephelinite), phonolite lavas and volcanoclastics, followed by caldera subsidence and nepheline syenite intrusions forming minor ring dykes and circular structures and, finally, the intrusion of eudialyte-bearing nepheline syenites (Fig. 3). This early model has been partly confirmed by the geochronological



1. Basement elevation, distension, fracturing and erosion.
2. Volcanism: phonolites, volcanoclastics.
3. Caldera subsidence.

4. } Nepheline intrusions: tinguaites, phonolites, nepheline
5. } syenites, in ring dykes and minor circular structures.

6. Intrusion of lujauvites, chibinites and foyaites.

Figure 3. Evolutive model of the Poços de Caldas alkaline igneous complex (after Ellert, 1959).

work of Bushee (1971) and the structural interpretations of Almeida Filho and Paradella (1977) (Fig. 2).

Radiometric age determinations indicate that this evolution may have started some 89 Ma ago with ankaratrite (Bushee, 1971), or even earlier, producing nepheline syenites already at about 92 Ma (Kawashita *et al.*, 1984). However, the long duration of the magmatic emplacement of the Poços de Caldas complex, previously considered to be more than ca. 30 Ma (Bushee, op. cit.), is in striking contrast to the relatively short (2-3 Ma) life-span of modern volcanoes (Ulbrich, 1984). Shea (this report series; Rep. 4) has found the nepheline syenite to yield a Rb-Sr age of 78(3) Ma.

In the course of the present study, the possibility that the Morro do Ferro is a minor, strongly weathered carbonatite has been inferred (Waber, this report series; Rep. 3). Alkaline mafic and ultramafic dyke rocks (lamprophyres) of different generations are known and are thought to represent the youngest truly magmatic occurrence. Shea (op cit.) has found a lamprophyre dyke exposed at the Osamu Utsumi mine to yield an Ar-Ar age of 76(1) Ma.

2.2. Alteration and mineralization

The alkaline rocks of the Poços de Caldas complex suffered a closed system postmagmatic (deuteric) alteration. At several specific sites there also occurred additional intensive hydrothermal alterations, producing low- to medium-grade U-Th-Zr-REE-Mo-F-pyrite mineralizations.

The hydrothermal and mineralized sites were explored and investigated mainly in relation to uranium prospecting conducted under the auspices of the Comissão Nacional de Energia Nuclear - CNEN (Brazilian Atomic Energy Commission) and Urânio do Brasil (formerly NUCLEBRÁS), a governmental company (Teixeira, 1936, 1943; Oliveira, A.I. de, 1956; Frayha, 1954, 1962; Wedow, 1961, 1967; Tolbert, 1958 a,b, 1966; Oliveira, A.G. de, 1966, 1968, 1973, 1974; Fujimori, 1974; Gorsky and Gorsky, 1974; Santos, 1976; Magno Jr., 1985; Fraenkel *et al.*, 1985; IAEA, 1986; Garda, 1990). Sites typically show the combined effects of argillation and potassic alteration (kaolinite, illite and K-feldspar formation), pyritization and variable U-oxides, Mo-sulphide (jordisite), sphalerite, zircon-baddeleyite, REEs, fluorite, and pyrite mineralizations. Mineralization is either disseminated without any evident direct structural control or a vein/stockwork system associated with fractures and, in some cases, with the local formation of volcanic breccias. The Osamu Utsumi uranium mine has stockwork mineralization superimposed on disseminated ore in volcanic breccias and fractured host rocks.

The typical wall and host rock is always altered by K-metasomatism, leading to the formation of so-called potassic rocks (Frayha, 1952), i.e. hydrothermally altered phonolites and nepheline syenites with K_2O contents normally in excess of 12 wt.%. Hydrothermal mineral occurrences under exploitation include vein mineralizations of caldasite, i.e. intergrowths and mixtures of Zr-bearing minerals such as baddeleyite and zircon.

The postmagmatic history of the Poços de Caldas complex is, however, certainly much more complicated. It includes, among other features, specific hydrothermal alteration and the intrusion of lamprophyre dykes at the uranium mine (Waber *et al.*, this report series; Rep. 2). It further includes the host rocks of the alkaline caldera, mapped as fenite (Fig. 2), of which more recent studies are non-existent, and the active thermal springs presently distributed over the caldera (Cruz and Peixoto, 1989).

The relative and absolute age relationships between the different magmatic, deuteric and hydrothermal processes of the Poços de Caldas complex are largely unknown. At the Osamu Utsumi uranium mine (Waber *et al.*, this report series; Rep. 2), hydrothermal alteration and U-mineralization commenced after magmatic and deuteric alteration of the host phonolites and nepheline syenites, and were concluded before the magmatic emplacement of the 76(1) Ma old lamprophyre dyke (Shea, this report series; Rep. 4).

Similarly, the time of the onset of weathering and specific climatic conditions are not known in detail. However, during most of the Tertiary through to more recent periods, various chemical processes have prevailed and outlasted physical erosion. These include the dissolution of the alkaline rocks, the formation of residual lateritic soils and, in more restricted areas, the formation of clay deposits and bauxites, both of which are locally under exploitation.

In the areas of hydrothermally altered and U-mineralized potassic rocks, these low-temperature, weathering-related processes caused the development of spectacular redox fronts, mainly due to pyrite oxidation. Associated supergene uranium enrichment, similar to "roll-front" type mineralizations, occurred locally. One of these, the Osamu Utsumi uranium mine, was mined continuously until 1988.

2.3. General geomorphology

The Poços de Caldas alkaline caldera complex, together with those parts of São Paulo and Minas Gerais States which are bounded by the meridians 45° – 48°W and 21° – 23°S, have been geomorphologically described (on the scale 1:1 000 000) by Cavalcante *et al.* (1979). The Poços de Caldas complex forms part of the Southern Minas Gerais Highland sub-unit, bordered to the SE by an ENE-trending Precambrian mountain range (Serra da Mantiquera) which constitutes part of the Ribeira mobile belt of Proterozoic age (Fig. 1). Maximum elevations in this highly crystalline belt are around 2000 m.

To the west of the Highland sub-unit is the depression of the Paraná basin, and in between, forming the western divide, is a N-S-trending domain of old Precambrian gneisses, migmatites and granitoids of intermediate altitude, known as the northern crystalline zone of São Paulo State.

The Paraná Basin depression is constituted predominantly of Palaeozoic (Carboniferous and Permian) sediments and of minor Triassic arenites and basalts (stocks).

The Poços de Caldas caldera complex is regionally characterized by a prominent external ring wall varying between 1500 and 1700 m a.s.l., and by internal highlands of around 1300 m. The internal hills and valleys normally vary less than about 150 m from the mean altitude. If compared to the adjacent regional morphostructural units and sub-units, one observes a distinctly more homogeneous constitution of the alkaline complex with regard to both the ring wall and internal plateau. The mean altitude of the plateau is about 500 m higher than the regionally surrounding Precambrian crystalline basement (mean altitudes around and below 800 m a.s.l.). However, in the SE and NW parts of the complex, altitude differences are much less pronounced, if at all existent.

The regional geological and geomorphological conditions influence climate, vegetation and soil-type. The Poços de Caldas complex and surroundings experience a mesothermic (two-season) climate with dry winters and hot summers (October/November through March/April). The complex itself has a distinct climate of moderate-mesothermal sub-humid character (Nimer, 1979). Annual rainfall exceeds 1500 mm, two months of the year are dry and mean temperatures are lower, varying between 20° – 22° C in the summer and 18° – 20° C in the winter; occasional frosts occur.

The Poços de Caldas plateau is mainly covered by grasslands; vegetation consisting of trees and bushes (subcaducifolia, tropical pluvial, with araucaria at altitudes above 1500 m) is restricted to the headwaters and banks of rivers (Lima, 1966; Romariz, 1968).

Soils are the result of regional and local interaction of climate, weathering, morphological and geological conditions. Predominant soils (Cavalcante *et al.*, 1979; Radambrasil, 1983) belong to the generic group of (tropical/subtropical) lato-soils, including 'terra roxa legítima' to true laterites, and four main types of podzol; more restricted soil-types also exist.

The specific geomorphological evolution of the Poços de Caldas alkaline complex, particularly of the caldera depression when compared to the ring wall, has been a subject of debate. Tectonic subsidence and joint-controlled weathering and erosion (Ellert, 1959) and a combination of processes including hydrothermalism, selective chemical weathering/decomposition of the hydrothermalized rocks and the (frequently torrential) activity of the drainage system (Frayha, 1971) have all been considered. Ellert (op. cit.) discerned, in addition, two morphological subdomains within the plateau. The major one is characterized by mature landscape forms and an annular drainage system and occupies the north, west and south portions of the caldera. The minor domain shows relief forms of an intermediate evolutive stage between juvenile and maturity, radial to annular mixed drainage systems, and occupies the eastern part of the caldera.

The morphological evolution of the Poços de Caldas region was further influenced by post-caldera activity, including recent tectonics. These processes caused NE- and NW-trending fracture systems and the formation of a major E-W-trending morphological 'graben' structure adjoining and separating the southern borders of the caldera from the adjacent foothills of the 'Mantiqueira' mountain range. Another major N-S tectonic boundary follows the western borders of the caldera; river diversion and capture are suspected to have occurred here, particularly in the case of the Antas river, the major river of the caldera (Ellert, op. cit.).

A recent contribution on the morphological evolution of the Poços de Caldas complex was made by Garda (1990) who considered the contrasting altitudes of the morphological and geological/stratigraphic units (cf. Ellert, 1959; Björnberg, 1959) and the patterns/assymetries both of the drainage system as a whole and of individual hydrographic basins, based on petrographic and structural data. Results show the importance of the primary magmato-tectonic structuring of the complex, of the generally very strong, but still notably differential, chemical weathering/rock dissolution and of post-caldera to neotectonic regional westward basculations associated with late stages of the Paraná Basin.

The particular geological, climatic, geomorphological and weathering conditions of the Poços de Caldas alkaline complex favoured the formation of two distinct types of bauxite and of refractory clay deposits (for additional details see Cavalcante *et al.*, op. cit.).

3. Description of regional samples

3.1. Geology

Several outcrops of the major regional rock types (nepheline syenites and phonolites) were sampled for comparative petrographic, mineralogical, geochemical and geochronological studies aimed at characterizing the magmatic and deuteric evolution and "status quo" properties of the alkaline rocks with respect to the hydrothermal (primary mineralizing) event. Samples collected were relatively large (5–25 kg) to ensure sufficient material for multiple analytical techniques and sample homogeneity. One of the major constraints of outcrop selection was the identification of relatively fresh samples free from postmagmatic alteration and weathering processes. Consequently, all the sampling sites were chosen from recent quarries and road cuts (Fig. 2). Some of these already represent classic petrographic localities of the Poços de Caldas complex, and/or "type locations" of specific lithologies.

3.1.1. Nepheline syenites

Sample NS-1 (Fig. 2) is nepheline syenite from a quarry located in the town of Poços de Caldas, i.e. representative of the predominant type-lithology. These nepheline syenites are medium- to coarse-grained and heterogeneous, locally containing abundant xenolithic enclaves of finer-grained and frequently more mafic phonolites. In addition, there occur coarse- to very coarse-grained pegmatitic nepheline syenite veins (of centimetre to decametre (dimensions) and irregular-shaped miarolitic voids (of centimetre dimensions). These contain deuteric (late magmatic to auto-hydrothermal) mineral assemblages of alkali feldspar, aegirine needles, various zeolites (mainly natrolite), fluorite, hematite, and many others. The nepheline syenites are cut by at least two younger phonolite dykes exhibiting chilled margins.

Several studies since Ellert (1959) have described this outcrop in detail characterizing the various nepheline syenite subfacies and debating the xenolithic versus autolithic nature of the more mafic phonolitic enclaves. Previous studies have detailed geochemical data (Ulbrich, 1984; Rocha *et al.*, 1986), radioisotope and geochronological data

(Kawashita *et al.*, 1984) and mineral-chemical data (Ulbrich, M., 1983; Ulbrich, M., *et al.*, 1984).

Sample NS-4 is a fine- to medium-grained porphyritic rock type, possibly representing a more rapidly cooled textural variety due to its proximity to the surrounding phonolite lavas (Fig. 2). Sample NS-5 was not studied in further detail.

Samples NS-6 and 7 are typically plutonic medium- to coarse-grained isotropic nepheline syenites.

It is important to note that all nepheline syenite samples (Fig. 2) belong to the one continuously mapped major intrusive body initially described from a quarry in the town of Poços de Caldas.

3.1.2. Phonolites

Phonolite samples PH-2A and PH-2B were collected from another classic petrographic locality called the Bortolan quarry (Fig. 2). These represent heterogeneous and inequigranular rocks of subvolcanic origin which occur in an area of poor outcrop where the magmatic stratigraphy and structural context are not well known (Ulbrich, 1984). Phonolite samples PH-3 and 5 (Fig. 2) belong to a single volcanic unit of phonolite lavas (Ellert, 1959); PH-5 is near the contact with the nepheline syenites at location NS-4. Both are very fine-grained microporphyritic rocks.

The phonolite sample sites PH-8, 9 and 10 are located in the southern part of the complex (Fig. 2). Samples PH-8 and 9 are very fine-grained volcanic rocks and the latter, in particular, shows significant evidence of fracturing and related alteration. Samples from locality PH-10 were not studied.

Little is known about the fine-grained rock types of the Poços de Caldas complex (Ellert, 1959; Ellert *et al.*, 1959; Bushee, 1971; Ulbrich, 1984). However, the volcanic phonolite samples collected for this study are thought to represent the early initial volcanic phonolites and the nepheline syenites are believed to represent the subsequent major intrusive stage of nepheline syenite magmatism. The relative age of the subvolcanics from the Bortolan quarry is uncertain.

3.2. Petrography and mineralogy

3.2.1. Petrography

Alkaline rocks typically exhibit high concentrations of the alkalis Na and K relative to silica and/or alumina. This "undersaturated" nature manifests itself mineralogically with the presence of feldspathoids and/or of alkali-rich pyroxenes and amphiboles. The studied regional rocks may be classified into four groups, based on their textural and mineralogical characteristics. These groups constitute nepheline syenites and phonolites that formed in different magmato-structural environments of the igneous complex.

Volcanic phonolites (samples PH-3, 5, 8, 9) are very fine-grained (average grain-size <0.5 mm) microporphyritic rocks, with or without evidence of igneous flow and/or layering and segregation. Evidence of rapid cooling is microscopically characterized by weak or incipient reactions with microxenoliths and microxenocrysts.

Subvolcanic phonolites (samples PH-2A, 2B) are inequigranular, very fine- to medium-grained (grain-size <5 mm) porphyritic rocks, with mean groundmass dimensions about 10 times coarser than the volcanic phonolites. They show variable textural and mineralogical properties due to advanced reactions with abundant microxenoliths, microxenocrysts and enclaves.

Hypabyssal (shallow-plutonic) nepheline syenites (samples NS-1, 4) are similarly grained to the subvolcanic phonolites, but with a more equigranular-aplitic texture. Phenocrysts are less frequent to absent; xenoliths may be present and locally frequent.

Plutonic (abyssal) nepheline syenites (samples NS-6, 7) are typically coarse-grained, isotropically structured and idiomorphically textured rocks. Xenoliths are locally present.

All of the studied alkaline rocks are leucocractic (Table II), with the total volume of mafic minerals ≤35 percent. From a petrographic viewpoint, all the phonolites and nepheline syenites are typical of the rock type, with nepheline as the predominant feldspathoidal mineral. Somewhat different is phonolite sample PH-9B which shows a micro-ocellar texture comprising >10 volume percent of pseudomorphosed groundmass leucites. It is the only rock with two significant feldspathoids (Table II).

Alkaline rocks typically exhibit a late magmatic crystallization of their mafic rock-forming minerals, in the present case represented by aegirine-augite. This holds true for all the studied regional phonolites and nepheline syenites. Exceptions are

TABLE II

Qualitative and quantitative mineralogical compositions [volume %] of regional phonolites and nepheline syenites from the Poços de Caldas complex.

Minerals	PH-2A	PH-2B	PH-3	PH-5	PH-8	PH-9B	NS-1	NS-4	NS-6	NS-7
Titanite -1	tr.	tr.	tr.	–	tr.	tr.	–	–	–	–
Ore mins -1	–	–	tr.	–	tr.	–	–	–	–	–
Nosean-1	–	–	tr. ≤ 1	–	–	–	–	–	–	–
Pseudoleucite(plc)-1	2-4	2-4	tr.	tr.	1-2	≤ 1	tr.	–	–	–
Orthoclase-1	3	2	≤ 1	≤ 1	≤ 1	tr.	–	–	–	–
Aegirine-augite-1	1	tr.	tr.	tr.	tr.	tr.	tr.	–	–	–
Zircon-2	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Titanite-2	tr.	tr.	1	tr.	1-2	2	≤ 1	≤ 1	1	≤ 1
Ore mins-2	tr.	1	2	tr.	tr.	tr.	1-2	1-2	1-2	1-2
Apatite-2	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Aegirine-augite-3	10-12	20	20-35	20-25	28-32	23-35	16-20	17-21	7-10	10-15
Nepheline (ne)-3	22-25	15-20	20	20-25	20-25	5-10	20-25	23-27	20-25	25-30
Orthoclase-3	–	–	–	–	–	–	47-51	16-23	55-60	45-50
Sanidine-3	35-40	35	35-40	50-55	35-40	30-40	–	25-30	–	–
Ab-rich plagioclase-3	tr.	3-5	tr.	1-2	tr.	tr.	tr.	tr.	tr.	tr.
Pseudoleucite-3	–	–	–	–	≤ 1	10-12	1	2-3	3-5	3-4
Sodalite-3	2	1	–	–	–	–	2-3	tr.	1	1
Analcite-3	2	3	–	–	–	–	≤ 1	tr.	tr.	tr.
Sodalite (in plc)-4	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Analcite (in plc)-4	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Cancrinite (in ne)-4	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Giannettite-5	2-4	3	3	2-3	2-3	–	2-3	1-2	–	–
Unid. rare mins-5	tr.	tr.	tr.	≤ 1	tr.	–	tr.	tr.	tr.	tr.
Zeolites-6	tr.	2-4	tr.	tr.	tr.	tr.	2	tr.	3-5	5-7
Clay mins-6	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Ore mins-6	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Carbonate-6	–	tr.	–	tr.	–	tr.	tr.	tr.	tr.	tr.
Microxenoliths Enclaves	~20	~3	≤ 1	–	~3	1-2	–	–	–	–

1: Magmatic pheno- and/or xenocryst
2: Early magmatic accessory mineral
3: Magmatic (main) mineral
4: Late to postmagmatic replacement mineral
5: Pneumatolytic minerals
6: Postmagmatic, (auto-) hydrothermal replacement minerals and latest interstitial fillings
–: Not detected
tr.: Trace amounts (< 1 vol. %)
mins: Minerals

the early magmatic, more augitic (non-pleochroic) nuclei of zoned clinopyroxenes. Zoned clinopyroxenes occur in small amounts as phenocrysts and/or xenocrysts in most of the volcanic to hypabyssal rock types, but as major mafic minerals in the plutonic nepheline syenites. In the volcanic phonolites, grain-sizes and textures indicate that crystallization occurred rapidly with almost simultaneous crystallization of the major magmatic rock-forming minerals.

All the studied regional rocks show important evidence of late- and postmagmatic (deuteric) phenomena, documenting pegmatitic, pneumatolytic and (auto-) hydrothermal stages. The particular mineral phases and reaction stages are listed in Table II. Structural and mineral-chemical changes and neomineralizations include a) pseudoleucite formation, b) the transformation and pseudomorph replacement of the sodalite group minerals, c) alkali feldspar structural changes and exsolution, d) the formation of (micro-) pegmatitic veins and/or enclaves and of progressively more aegirine-rich clinopyroxene solid solutions, e) the cancrinitization of nepheline, f) the precipitation of giannettite and other rare metal silicates, g) alkali ion substitution (Na by K) of alkali feldspars, and h) hydrous ferric oxide (HFO) formation, argillation and zeolitization.

All these petrogenetic processes occurred in magmas and rocks which from the outset were heterogeneous. This was caused by contamination with substantial amounts of partially assimilated xenocrysts and xenoliths, as might occur through magma mixing. However, all admixtures are of alkali-magmatic, i.e. most probably of consanguineous, origin. Xenoliths or xenocrysts of sensu lato granitic rocks which constitute most of the Precambrian surroundings and the pre-existing basement of the Poços de Caldas complex (Figs. 1 and 2) were not found.

The measured petrophysical properties of the regional rocks included total (Hg-) porosity and bulk and mineral/grain density (Table III). The values obtained appear to be normal for these types of leucocratic alkaline rocks.

TABLE III

Petrophysical properties of regional nepheline syenites and phonolites.

	Bulk density (g/cm^3)	Grain density (g/cm^3)	Porosity (%)
Regional nepheline syenites			
NS-1	2.55	2.64	3.2
NS-4	2.57	2.62	1.8
NS-6	2.50	2.59	3.5
NS-7	2.49	2.58	3.5
Regional phonolites			
PH-2B	2.62	2.66	1.6
PH-5	2.59	2.61	0.6
PH-8	2.59	2.64	1.9

3.2.2. Mineralogy

As discussed in Hess (1989), nepheline syenites are the phaneritic (plutonic) equivalents of nepheline phonolites. They contain subequal amounts of alkali feldspar and the feldspathoid nepheline (Sørensen, 1974). Similarly to granitoid rocks, they can be subdivided into peralkaline, peraluminous, metaluminous and subaluminous varieties. Peralkaline varieties typically contain sodic pyroxenes, amphiboles, aenigmatite and unusual Na-Zr and Na-Ti silicates. Peraluminous varieties typically contain garnet, biotite, muscovite and corundum. Metaluminous varieties commonly have hornblende and plagioclase. Subaluminous varieties bear feldspars and feldspathoids as the only minerals with essential Al_2O_3. Sphene, ilmenite-titanomagnetite, apatite and zircon are common accessories. Also possible are the Cl^-, S^{2-}, OH^- and F-bearing sodalite group minerals, as well as carbonate minerals. As will be discussed in section 3.3.1, the studied Poços de Caldas alkaline rocks range from slightly peralkaline to metaluminous. They appear to be similar to some of the hypersolvus types of nepheline syenites described by Nockolds *et al.* (1978).

The regional phonolites and nepheline syenites are mineralogically quite complex, but not essentially different in overall composition. Major differences are of a quantitative rather than a qualitative mineralogical nature. Table II summarizes the mineralogical data of the studied phonolites and nepheline syenites.

Early magmatic stages of crystallization are best preserved in the fine-grained rocks. The corresponding mineral phases are titanite, Fe-Ti oxides, nosean, pseudoleucite, alkali feldspar and clinopyroxene phenocrysts or xenocrystals, all showing reactions with the enclosing magma. The clinopyroxenes were sodic augites at this stage; alkali feldspar was a more sodium-rich high-temperature solid solution type, and pseudoleucites may have formed either from high-temperature K-analcites or Na-rich leucites, or both.

Apatite, zircon and, in the fine-grained rocks, a second generation of titanite and Fe-Ti ore minerals formed later under apparently stable conditions as early magmatic accessory constituents.

The main magmatic crystallization of nepheline in the coarser-grained rocks was possibly preceded by minor leucite (later transformed to pseudoleucite) and followed by microperthitic orthoclase; some high-temperature plagioclase formed coevally. The orthoclase crystallization outlasted nepheline and was followed by the main aegirine-augite formation. Sodalite and analcite were the last minerals to form.

In the volcanic phonolites the minerals of the main magmatic crystallization were nepheline, sanidine (instead of orthoclase), in one case (sample PH-9) associated with groundmass leucite and aegirine-augite. The crystallization in these phonolites was almost penecontemporaneous due to more rapid cooling.

Pneumatolytic down to hydrothermal crystallization has resulted in the formation of giannettite and other rare metal silicates, the final clinopyroxene (almost pure aegirine), cancrinite, zeolites (thomsonite and natrolite) and, more rarely, minor sulphides (chalcopyrite and pyrite). This stage is less well developed in the volcanic phonolites. Clay minerals (kaolinite and minor sericite/illite), carbonates, hematite and HFO minerals, fluorite and zeolites (mainly natrolite) have resulted from hydrothermalism and occur as alteration products and mineralizations in miarolitic voids and fractures.

The pneumatolytic/hydrothermal fluids were rich in Na and K, first forming K-feldspar by exchange reactions with former albite/perthites and some aegirine, and later kaolinite, some illite/sericite and natrolite. The fluids were also CO_2- and F-bearing, resulting in the formation of minor carbonate and fluorite, and oxidizing, resulting in the precipitation of hematite and HFO minerals.

From the petrographic and mineralogical data it can be stated that the regional nepheline syenites and phonolites were not affected by the hydrothermal event that caused the primary U-mineralization at the Osamu Utsumi mine, although deuteric alteration, including the (auto-) hydrothermal stage, has occurred.

Mineral chemistry (microprobe) has not been investigated and practically nothing is known about the phonolites. Nepheline syenite minerals have been studied by Ulbrich,

M. (1983) and Ulbrich, M. *et al.* (1984) using X-ray diffraction and microprobe methods. K-feldspars from most of the nepheline syenites showed within individual grains the association of high triclinicity to maximum microcline with orthoclase. Particularly interesting are the mineral chemical compositions of nepheline syenites from the Poços de Caldas quarry. The K-feldspars show high Sr contents (SrO up to 1.40 wt.%), which differs from the other nepheline syenites where Sr is present in much lower amounts. Furthermore, the K-feldspars show zoning with internal portions richer in Na, Ca and Sr, and significant Fe-contents ($Fe_2O_3 \cong 0.50$ wt.%) are always present. Nephelines generally show moderate K_2O contents in the range of 5–8 wt.% and Fe_2O_3 contents of ≤ 2 wt.% that vary inversely with Al_2O_3. The clinopyroxenes are continuously zoned with Na-augitic cores to almost pure aegirine rims enriched in Ti and Zr. These characteristics are more common in the clinopyroxenes of miaskitic nepheline syenites, being less pronounced or even absent in others, particularly in the intermediary and agpaitic rocks (see below). The mineral chemical data of Ulbrich, M. (1983) and Ulbrich, M. *et al.* (1984) are important in understanding the elemental geochemistry of the regional nepheline syenites (and phonolites) and of the hydrothermal processes.

3.3. Elemental geochemistry

The petrographically studied regional rocks were analyzed by X-ray fluorescence (XRF) for major and common trace elements and by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the REEs.

3.3.1. Major and trace elements

The chemical classification of alkaline rocks is based on the degree of peralkalinity, traditionally expressed as the molecular ratio of the oxides $(Na_2O + K_2O)/Al_2O_3$. It separates peralkaline (agpaitic) from peraluminous (miaskitic) rocks with ratios that are respectively > 1 and < 1. Some authors consider the correct values for peralkaline rocks as ≥ 1.2 and distinguish a third group of alkaline rocks, termed intermediary (metaluminous), with ratios > 1 but < 1.2. Peralkaline alkaline rocks should have, in addition, Na > K, being normally lower in Ca, Mg, CO_2 and higher in H, Li, Be, C, F, Na, Al, P, S, Cl, K, Ca, Ti, Fe, Zn, Rb, Y, Zr, Nb, Ba, REEs, Th and U than the peraluminous types (see discussions in Sørensen, 1974; Bailey, 1987).

The analytical results and the recalculated and normalized major elements are shown in Table IV. Selected major element analyses were normalized (to 100 wt.%) and recalculated as equivalent cations (ppm). Figure 4 shows the degree of peralkalinity of the regional nepheline syenites and phonolites based on the normalized values.

The mineralogy of the Poços de Caldas alkaline rocks does not strictly conform to a classical peralkaline alkaline mineral suite. This appears to further support an intermediary or metaluminous tendency in these rocks.

In general, one may observe that the studied regional nepheline syenites and phonolites (n=10; Table IV) of the Poços de Caldas plateau show relatively small variations in K_2O (range 7.73 – 8.54 wt.%) and Na_2O (range 5.66 – 8.00 wt.%). The mean K_2O / Na_2O ratio is ~1.2. The variability of the other elements is also very restricted; petrographically, distinct rock types were indistinguishable by major element geochemistry.

More recent mineralogical and petrochemical studies of the Poços de Caldas alkaline rocks include analyses of different nepheline syenite types and generations. The data for the non-agpaitic nepheline syenites of Ulbrich (1984), which stressed the mineralogical and major element consistency of the nepheline syenites, are in general agreement with present studies. It seems that this characteristic may also be extended to include at least some of the occurrences of the early volcanic phonolites.

General comparisons show that the studied rocks of Poços de Caldas (Table IV) are strongly K_2O-enriched with respect to global nepheline syenite and phonolite values (Le Maitre, 1976). This maybe due to primary magmatic perpotassic tendencies of the original alkaline silicate melts, together with deuteric alteration. Using a TAS (total alkalis versus silica) diagram (Le Maitre, 1984), all the regional samples plot in the phonolite field.

Trace element data, including semi-quantitative analyses of some of the REEs, are shown in Table V. Elements such as U, Cr, Ni, Cu and Sc show very low values, near or below the analytical detection level. The other trace elements are present, if the whole analyzed sample population (n=11) is considered, in amounts normal for leucocratic alkaline rocks, i.e. neither U nor Th or the REEs show any enrichment (Goldschmidt, 1954; Sørensen, 1974; Wedepohl, 1978).

The volcanic phonolites show significant homogeneity for most of the considered elements, including F, Ba, Nb, REEs (La, Ce, Nd), Y, Zr, V, Zn and Hf, despite their occurrence as two distinct geological provenances.

The nepheline syenite samples show a much higher variability despite the fact that they represent one geologically continuous intrusive body (Fig. 2). This is probably

TABLE IV

Selected major element data from regional nepheline syenite (NS) and phonolite (PH) recalculated to normalized equivalent cations (ppm).

OXIDE CONCENTRATION [wt.%].

Sample	SiO_2	TiO_2	Al_2O_3	Fe_{tot}	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LIL	Total wt.%
Molec. wt.	60.06	79.90	101.96	159.69	70.94	40.31	56.08	61.98	94.20	141.97		
Nepheline syenites												
NS-1	54.78	0.79	19.93	4.43	0.28	0.44	1.99	6.48	8.26	0.12	1.23	98.73
NS-4	54.83	0.87	20.20	4.34	0.25	0.51	1.99	6.48	8.23	0.13	1.88	99.71
NS-6	54.52	0.91	20.17	4.35	0.27	0.52	1.90	5.66	7.95	0.14	3.46	99.85
NS-7	52.58	0.70	19.66	3.77	0.26	0.27	1.46	7.60	7.73	0.08	3.17	97.28
Phonolites												
PH-2A	53.13	0.51	19.84	4.09	0.21	0.19	1.78	7.77	8.54	0.06	1.06	97.18
PH-2B	54.96	0.56	20.21	4.25	0.26	0.24	1.82	6.95	8.43	0.06	1.89	99.63
PH-3	55.61	0.58	20.63	3.88	0.25	0.31	1.57	6.87	8.41	0.06	1.36	99.53
PH-5	53.21	0.55	19.75	3.72	0.24	0.21	1.52	8.00	7.94	0.06	1.82	97.02
PH-8	53.92	0.59	19.83	3.81	0.24	0.24	1.58	7.30	8.53	0.06	0.96	97.06
PH-9B	53.80	0.57	19.78	3.78	0.25	0.22	1.57	7.40	8.40	0.06	1.20	97.03

ELEMENTAL CONCENTRATION in ppm {(normalized oxide wt.% / molecular wt.% / elem. prop. total) · 1 000 000}.

	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P
Nepheline syenites										
NS-1	656833	7120	140765	19978	2842	7861	25554	75291	63146	609
NS-4	655082	7813	142162	19502	2529	9079	25463	75022	62692	657
NS-6	661874	8304	144238	19862	2775	9406	24703	66584	61535	719
NS-7	652213	6527	143651	17588	2730	4990	19395	91352	61134	420
Phonolites										
PH-2A	647096	4669	142340	18735	2165	3448	23218	91703	66316	309
PH-2B	657842	5038	142494	19132	2635	4280	23330	80611	64333	304
PH-3	661575	5187	144571	17361	2518	5495	20003	79198	63791	302
PH-5	651762	5064	142501	17137	2489	3833	19940	94955	62008	311
PH-8	655418	5391	141986	17418	2470	4347	20569	85985	66108	309
PH-9B	655503	5220	141963	17322	2579	3994	20487	87369	65254	309

Analyses performed at the University of Bern by XRF.
LIL – Large Ion Lithophile

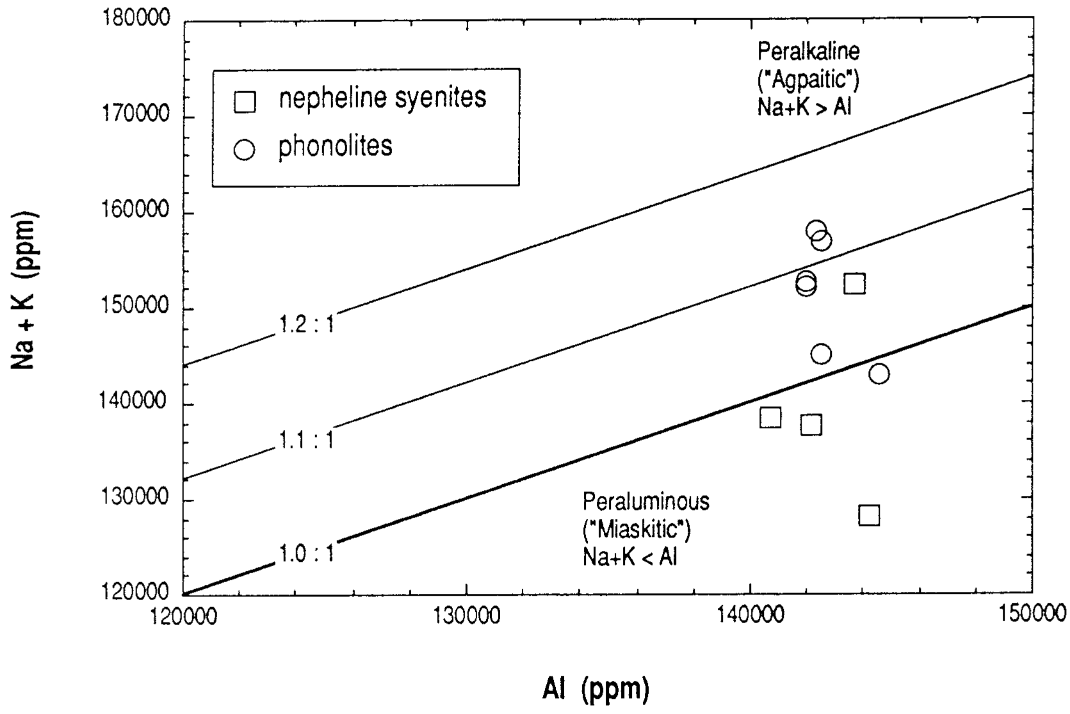


Figure 4. Degree of peralkalinity of the regional nepheline syenites and phonolites.

TABLE V
Trace element data of selected regional nepheline syenite (NS) and phonolite (PH) samples, Poços de Caldas complex.

PDC-sample		NS-1	NS-4	NS-6	NS-7	PH-2A	PH-2B	PH-3	PH-5	PH-8	PH-9B
F	ppm	2670	1766	1216	1335	2199	n.a.	1578	1490	1703	1472
Ba		261	479	502	339	371	217	44	45	60	50
Rb		148	146	138	147	173	175	143	147	165	161
Sr		2019	2709	2750	2096	1944	1974	1252	1265	1607	1559
Pb		8	6	12	12	3	23	b.d.	4	2	1
Th		14	9	17	22	6	30	1	7	6	4
U		b.d.	b.d.	b.d.	b.d.	b.d.	12	b.d.	b.d.	b.d.	b.d.
Nb		287	239	260	290	185	195	251	262	267	262
La		320	265	245	245	235	172	257	266	310	284
Ce		422	357	335	341	275	266	355	369	400	391
Nd		125	110	93	86	53	77	99	99	108	93
Y		53	44	44	52	27	39	37	42	44	39
Zr		1112	932	1156	1208	827	1004	931	891	859	858
V		69	72	51	40	72	71	63	61	78	84
Cr		b.d.	b.d.	b.d.	b.d.	b.d.	9	b.d.	b.d.	b.d.	b.d.
Ni		b.d.	b.d.	b.d.	b.d.	b.d.	3	b.d.	b.d.	b.d.	b.d.
Co		7	11	8	6	9	9	7	8	13	9
Cu		b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Zn		181	165	180	201	140	195	162	169	165	164
Hf		14	14	18	16	10	22	9	11	10	11
Sc		b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	1	b.d.
S		987	764	878	545	1689	1496	1288	630	782	651
total	ppm	8697	8088	7903	6981	8218	5989	6477	5766	6580	6093

Analyses performed at the University of Bern by XRF.

b.d. = below detection limit
n.a. = not analyzed

indicative of the primary geochemical inhomogeneity of the crystal mushes during their emplacement.

The geochemistry of these rock types is presented in Figures 5 to 7. Figures 5 and 6 show the limited geochemical variability of the studied samples and the low degree of differentiation. Some minor differentiation, which may represent an initial stage, is suggested from the lower Th, Pb and Ba contents of the volcanic phonolites as illustrated in Figure 6. Figure 7 indicates that the incompatible elements are typically enriched for this type of alkaline leucocratic rock.

A very preliminary interpretation of the elemental geochemical data could support the conclusion that the studied volcanic phonolites may represent one cogenetic period of eruption. However, the Rb-Sr isotopic data of the samples do not define an isochron, and the Sm-Nd isotopic data do not conform to any possible model isochron, both observations due to these rocks having different initial isotopic values and/or open system behaviour (Shea, this report series; Rep. 4). For the Sm-Nd data this is also due to the very long half-life of ^{143}Sm. It is interesting to note that the matrix pseudoleucite-bearing rocks (sample PH-9) are geochemically indistinct from the other volcanic phonolites. Similarly, the nepheline syenite data support a cogenetic origin with localized slightly variable degrees of differentiation, thus supporting the results of earlier geological mapping and mineralogical/geochemical work (Ellert, 1959; Ellert *et al.*, 1959; Ulbrich, 1984). The nepheline syenites intruded the volcanic phonolites of the northern body that hosts the sampling points PH-3 and PH-5.

The similarities between the volcanic phonolites and nepheline syenites are considerable, especially regarding those elements insensitive to short-lived magmatic differentiation and fractionation. It is most likely that both of these groups had a common magmatic origin, where the nepheline syenites represent the original melt after minor incipient differentiation and the volcanic phonolites represent a still less differentiated early volcanic eruption.

The origin of the subvolcanic rocks of the Bortolan quarry site may be considered somewhat different from the nepheline syenite and of the volcanic phonolite rocks.

3.3.2. Rare-earth elements

The rare-earth element (REE) data are presented in Table VI and graphically represented in Figure 8; the rock values have been normalized to ordinary chondrite values. The total REE contents (sum of REEs in ppm) show a general positive

TABLE VI

Rare-earth element geochemistry of the regional nepheline syenites and phonolites (ppm).

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Nepheline syenite														
NS-1	151.99	405.45	33.72	108.33	14.86	3.95	11.70	1.55	7.78	1.56	4.20	0.58	3.44	0.49
NS-4	147.61	355.34	35.92	122.19	17.39	4.91	13.93	1.79	18.96	1.57	4.35	0.55	3.36	0.52
NS-6	214.96	451.92	46.84	149.64	20.41	6.05	18.00	2.17	10.11	1.71	5.18	0.68	3.66	0.54
NS-7	115.63	272.92	21.34	65.71	8.43	2.47	7.25	0.93	4.55	0.86	2.51	0.35	2.28	0.32
Phonolite														
PH-2A	115.09	236.80	22.60	64.45	7.40	2.18	6.66	0.96	4.81	0.93	3.10	0.42	2.95	0.41
PH-2B	164.72	310.67	29.36	82.80	9.83	2.74	9.49	1.13	6.41	1.41	3.81	0.59	3.31	0.56
PH-3	92.01	189.93	20.24	64.90	8.64	2.39	6.90	0.94	5.0	0.98	2.76	0.38	2.38	0.34
PH-5	132.02	323.02	29.79	93.36	12.07	3.18	9.29	1.35	6.70	1.28	3.45	0.49	3.06	0.41
PH-8	112.29	295.41	25.45	80.11	10.23	2.84	8.12	1.13	6.03	1.13	3.34	0.46	2.79	0.39
PH-9B	112.14	244.16	26.17	79.75	9.79	2.72	8.14	1.17	6.14	1.19	3.46	0.49	2.89	0.41
Normalized to ordinary chondrite														
Norm coeff.	0.2974	0.7643	0.1129	0.5732	0.1864	0.071	0.2491	0.046	0.3075	0.0704	0.2013	0.0306	0.2059	0.0308

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Nepheline syenite														
NS-1	511.07	530.49	298.65	188.98	79.74	55.73	46.96	33.69	25.28	22.09	20.89	19.00	16.69	15.87
NS-4	496.33	464.93	318.12	213.17	93.30	69.24	55.91	38.86	29.14	22.31	21.59	17.96	16.30	17.00
NS-6	722.78	591.29	414.86	261.07	109.52	85.30	72.26	47.20	32.89	24.25	25.74	22.25	17.79	17.65
NS-7	388.80	357.08	189.03	114.64	45.22	34.84	29.10	20.11	14.81	12.28	12.47	11.56	1.105	10.49
Phonolite														
PH-2A	386.97	309.83	200.16	112.43	39.69	30.68	26.73	20.86	15.64	13.20	15.41	13.88	14.33	13.22
PH-2B	553.85	406.48	260.06	144.45	52.74	36.68	38.09	24.64	20.85	20.06	18.93	19.42	16.07	18.07
PH-3	309.37	248.50	179.28	113.22	46.38	33.68	27.69	20.47	16.25	13.92	13.69	12.40	11.56	10.97
PH-5	443.91	422.64	263.84	162.88	64.78	44.78	37.30	29.28	21.80	18.23	17.16	16.14	14.88	13.23
PH-8	377.56	386.51	225.43	139.77	54.89	39.96	32.59	24.47	19.60	16.00	16.58	15.14	13.56	12.70
PH-9B	377.06	319.46	231.79	139.14	52.51	38.37	32.66	25.40	19.98	16.92	17.21	15.93	14.04	13.45

ICP-MS analyses were performed at the Scottish Universities Research and Reactor Centre (SURRC).

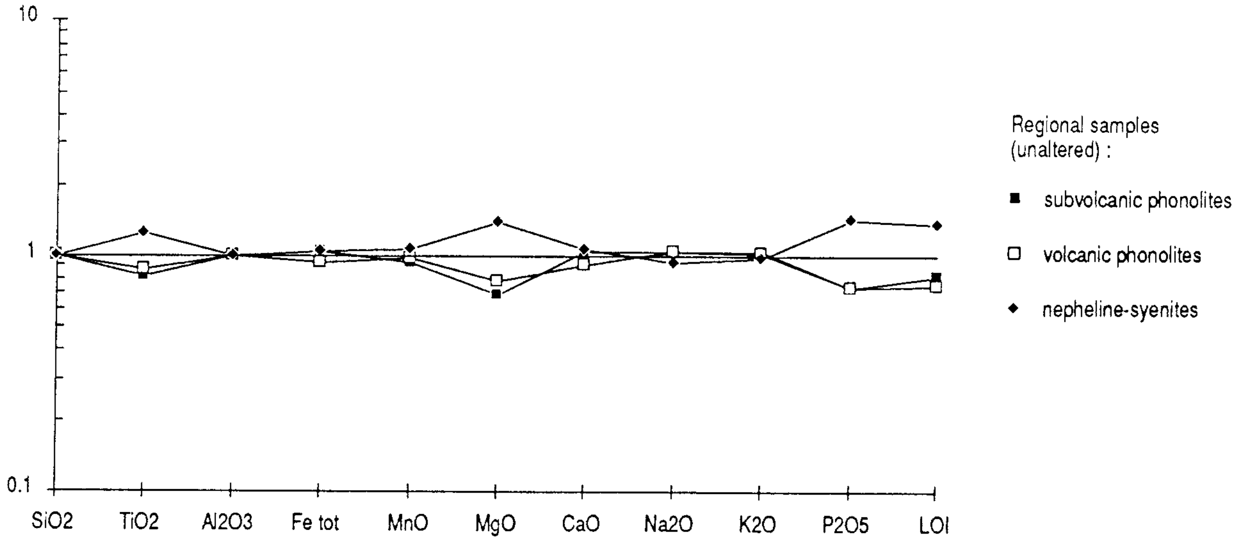


Figure 5. Major element distributions for unaltered regional outcrop samples normalized to their average value.

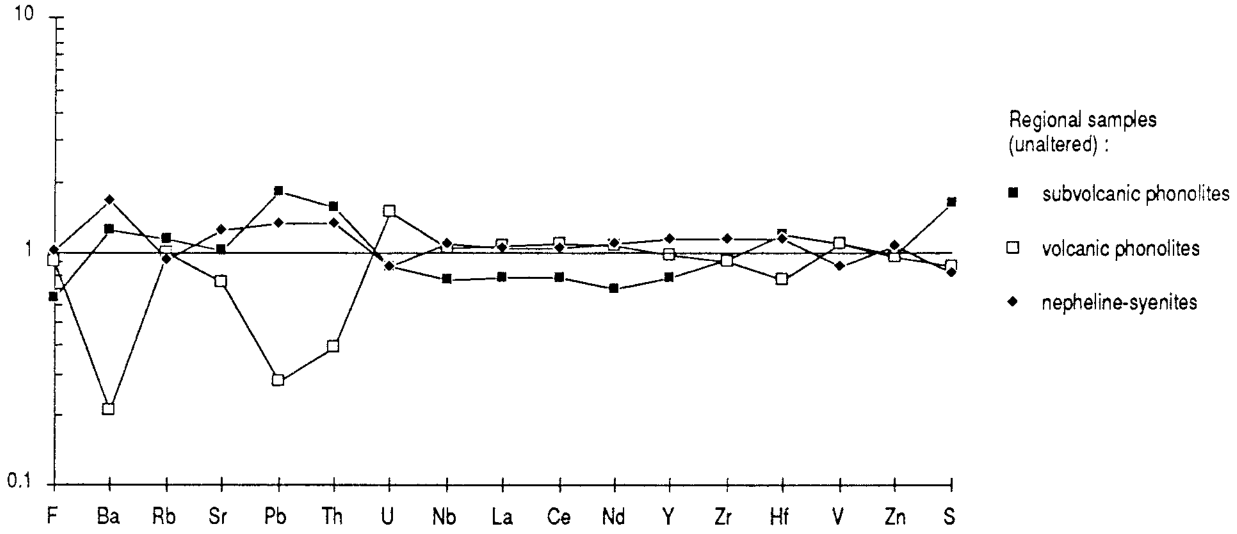


Figure 6. Trace element distributions for unaltered regional outcrop samples normalized to their average value.

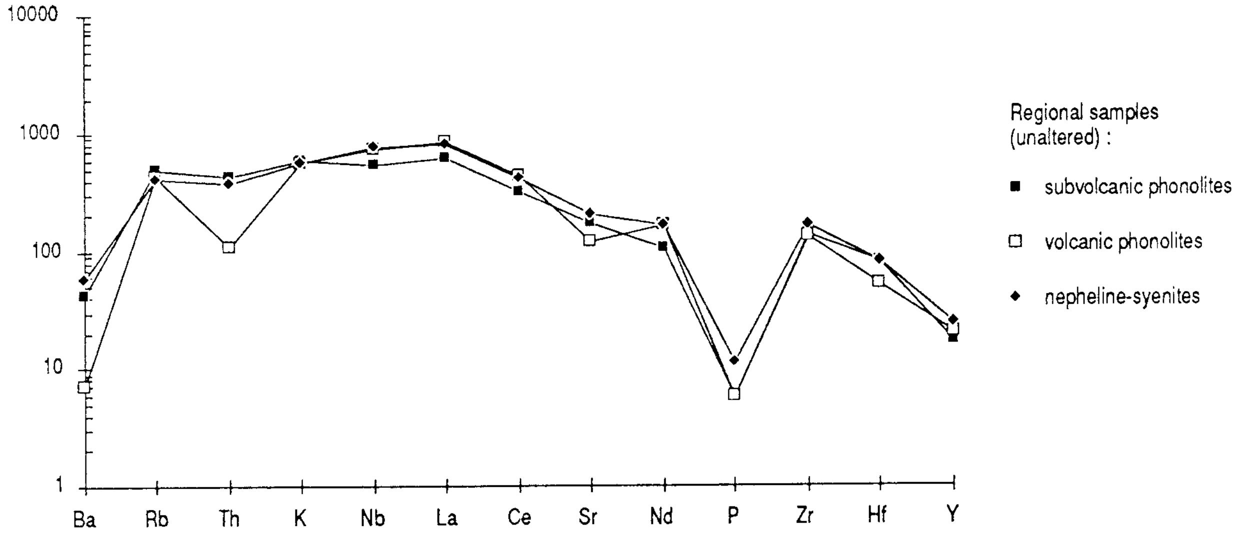


Figure 7. Distribution of incompatible elements for unaltered regional outcrop samples normalized to chondrite and primitive mantle (normalization factors after Thompson, 1982).

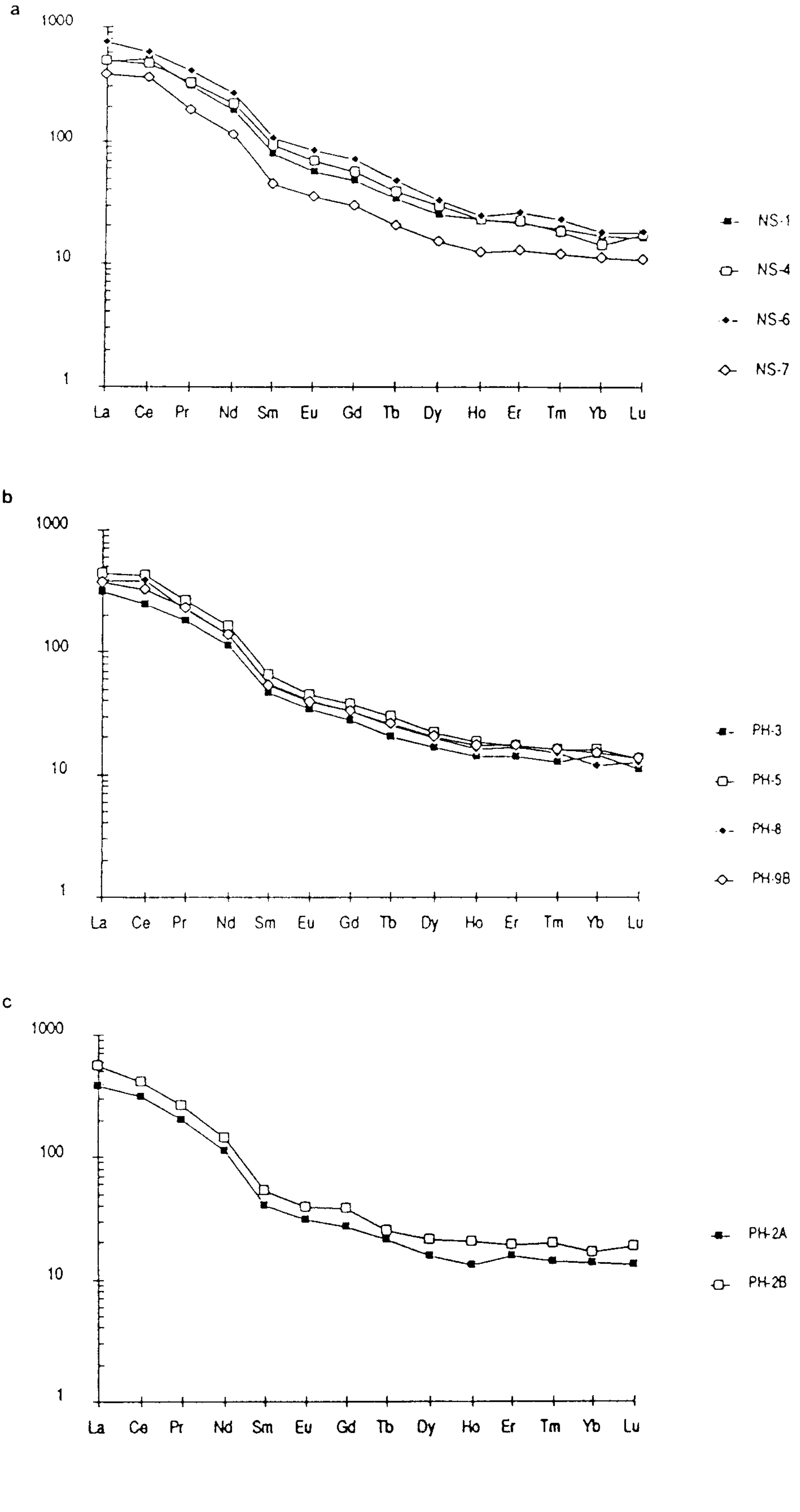


Figure 8. Distribution of rare-earth elements between regional nepheline syenites (NS) and volcanic phonolites (PH):

a) nepheline syenites
b) volcanic phonolites
c) subvolcanic phonolites.

correlation with the sum of Fe, Mg, Ti, Mn, Ca (total Fe, Mg, Ti, Ca, Mn in atomic equivalent numbers), i.e. the clinopyroxenes are the most important REE-bearing mineral phases of the studied rocks.

The REE patterns for the regional nepheline syenites (Fig. 8a) indicate a strong petrochemical correlation between the studied samples and are typical of these types of rocks (Kronberg *et al.*, 1987; Harris *et al.*, 1983; Mitchell and Platt, 1983).

Lo (1981) noted the same general pattern of light rare-earth element (LREE) enrichment for nepheline syenite from the Bancroft and Blue Mountain areas of southern Ontario, Canada. However, he also found a strong depletion in Yb and a slight negative Eu anomaly. The REE pattern for kimberlites is also very similar to those for nepheline syenites and phonolites (Hess, 1989).

The REE patterns for the regional nepheline syenites and phonolites also do not appear to show evidence of weathering. Kronberg *et al.* (1987) studied the major and trace element redistribution associated with the weathering of syenitic rocks of the alkaline massif on the island of São Sebastão, Brazil. They found that incipient weathering caused a slight negative Eu anomaly, whereas continued and intense weathering caused a marked positive Eu anomaly, along with an increase in Yb.

The REE pattern for the Poços de Caldas regional samples can be described as a light rare-earth element (LREE) enrichment relative to the heavy rare-earth elements (HREEs), with no notable Eu anomaly. The absence of an Eu anomaly suggests a primitive source, without extensive crystal fractionation, or perhaps is the signature of mantle metasomatism which enriched the source rock in Large Ion Lithophiles (LIL) and LREEs. Further, the lack of an anomaly supports the premise that these regional samples did not experience significant open-system alteration, which can possibly cause an Eu anomaly. However, the lack of an anomaly does not unequivocally establish the veracity of either of the above interpretations. There is evidence that hydrothermal alteration/metasomatism has caused a change in the REE pattern of some of the Osamu Utsumi mine F4 core samples (see discussions in Waber *et al.* and Cathles and Shea, this report series; Reps. 2 and 13).

It should also be noted that the REE profiles for the nepheline syenites lie almost entirely above those for the phonolites, with only sample NS-7 (petrographically identified as a nepheline syenite) falling into the phonolite "band". The elevation of REE concentrations for the nepheline syenites is as expected, since REE concentrations should increase with an increasing degree of differentiation.

Sample NS-7 is the most leucocratic of the nepheline syenites as evidenced by its mineralogy and major element geochemistry (Tables II and IV).

Detailed comparison of the REE distribution patterns shows that the volcanic phonolites are equivalent to the nepheline syenites (Fig. 8) and plot perfectly into the interval between the nepheline syenites NS-1, 4, 6 and 7 respectively. The two regional volcanic phonolites (Fig. 2; samples PH-3, 5, 8 and 9 respectively) show almost identical REE patterns (Fig. 8b). These REE data support the assumption that the volcanic phonolites and the nepheline syenites are cogenetic extrusive and intrusive equivalents, most probably representing separated fractions of the same original magma, produced and emplaced under restrictive time/process conditions that prevented a more effective REE fractionation.

The REE patterns of the subvolcanic, more complex alkaline rocks of the Bortolan quarry site (Fig. 8c) are almost identical to the nepheline syenites and volcanic phonolites just discussed.

In addition, the Sm/Nd ratio should decrease with increasing differentiation, due to the larger ionic radius of Nd relative to Sm. The average Sm/Nd ratio for the nepheline syenites, using the more accurate isotope dilution data from the Sm/Nd systematics analyses (Shea, this report series; Rep. 4), is 0.1343 (67). The average value for the volcanic phonolites is 0.1265 (42) and for the subvolcanics 0.1134 (28). Again, this supports the consanguinity of the nepheline syenites and phonolites, but with a somewhat larger difference for the subvolcanics which appear as the most differentiated rocks.

4. Final considerations: regional samples and geological evolution

In order to discuss and explain the Poços de Caldas complex, one has to consider not only the particular petrographic types of alkaline rocks that occur, but also the huge volumes that have been produced. There is little doubt about the general constitution of the plateau, which has resulted from erosional weathering of a continental volcanic edifice formed by a massive build-up of extrusive, volcanoclastic and intrusive rocks emplaced on a regional scale, and facilitated by structural pathways opened up during crustal subsidence and the subsequent formation of the caldera. Coeval with subsidence and volcanic activity was the intrusion and formation of ring dyke complexes marginal to the caldera (Ellert, 1959).

The overwhelming majority of the exposed alkaline rocks are leucocratic, of transitional basic to intermediate SiO_2 composition (range 50–55 wt.%) and contain normal trace element concentrations including uranium, thorium and the REEs. In contrast, mafic to ultramafic rocks are very rare.

The alkaline rocks show typical although variable textural features but are, in fact, mineralogically and geochemically very homogeneous (Ulbrich, 1984). Textural characteristics are, however, indicative of the mode and time span of emplacement and subsequent cooling. The data presented indicate clearly that the studied rocks can be considered as cogenetic with only very minor differentiation and fractionation having taken place. That which did occur produced volcanic, subvolcanic and intrusive rock associations without significant mineralogical and geochemical differences and variations. This would also support a restricted life span for the whole nepheline-alkaline magmatism that produced the Poços de Caldas complex.

No evidence of crustal remnants or contamination has been detected within the complex. The surrounding and inferred former basement rocks are part of the Precambrian polycyclic (Archean to Proterozoic) sensu lato granitic rocks that constitute the Guaxupé Massif (Fig. 1), i.e. granitic materials of very high crustal residence (Tassinari, 1988). However, such crustal basement rocks must have existed as indicated by the preserved supracrustals, i.e. Mesozoic sandstones of pre-Poços de Caldas (alkaline magmatism) age (Björnberg, 1956, 1959; Oliveira *et al.*, 1975, 1984).

All the studied regional rocks show marked deuteric alteration that occurred in the temperature/time interval corresponding from magmatic down to (auto-) hydrothermal conditions. The deuteric alterations, particularly from the intermediate to lower (pneumatolytic to auto-hydrothermal) temperature ranges, generally affected the nepheline syenites more intensively and the volcanic phonolites to a lesser extent. Again there is no significant evidence of differential geochemical alteration, i.e. no U, Th and REE mineralizations of this stage could be detected. What is notable is the total extent of the deuteric alteration (Ulbrich, 1984) and how it has affected virtually the entire complex. This strongly indicates an original magma that most probably was particularly enriched in (cogenetic) volatiles.

The present petrological/geochemical and isotopic evidence (Waber *et al.* and Shea, this report series; Reps. 2 and 4), together with the Poços de Caldas data from the literature (Ulbrich, 1984, Kawashita *et al.*, 1984), support an upper mantle derivation. This is in agreement with global occurrences of alkaline complexes (Sørensen, 1974; Fitton, 1987). The actual processes of generation of these magmas are still debatable. The identification of weathered remnants of carbonatite at Morro do Ferro (Fig. 2) may furnish additional genetic evidence (Waber, this report series; Rep. 3).

5. Acknowledgements

The authors are grateful to Prof. Tjerk Peters (Bern) for constructive comments on the script, and to Nick Waber (Bern) for many useful discussions and for supplying much of the rock analytical data and geochemical plots used in this report. The Osamu Utsumi mine geologists, in particular Luiz Barroso Magno Jr., are thanked for their continual help and logistic support.

6. References

Almeida, F.F.M. de, 1977. O Cráton do São Francisco. *Rev. Bras. Geociênc.*, 7 (4), 349-364.

Almeida, F.F.M. de, 1983. Relações tectônicas das rochas alcalinas mesozóicas da região meridional da Plataforma Sul-Americana. *Rev. Bras. Geociênc.*, 13 (3), 139-158.

Almeida Filho, R. and Paradella, W.R., 1977. Estudo do maciço alcalino de Poços de Caldas através de imagens Landsat com ênfase em mineralizações radioativas. *INPE.*, 11/2-TPT/065.

Amaral, G., Bushee, J., Cordani, U.G., Kawashita, K. and Reynolds, J.H, 1967. Potassium-argon ages of alkaline rocks from southern Brazil. *Geochim. Cosmochim. Acta*, 31, 117-142.

Araujo, R.L.C., 1980. Pesquisa geotermal na chaminé alcalina de Poços de Caldas. *31st Cong. Bras. Geol., Anais*, 2, 1059-1074 (Camboriú).

Bailey, D.K., 1987. Mantle metasomatism – perspective and prospect. In: J.G. Fitton and B.G.J. Upton (Editors), Alkaline Igneous Rocks, *Geol. Soc. Spec. Pub.*, 30, 1-13.

Best, M.G., 1982. Igneous and Metamorphic Petrology. *W.H. Freeman and Company*, New York, pp. 630.

Björnberg, A.J.S., 1956. Arenitos do bordo do Planalto de Poços de Caldas. *Anais Acad. Bras. Ciênc.*, 28 (4), 465-471.

Björnberg, A.J.S., 1959. Rochas clásticas do Panalto de Poços de Caldas. *Bol. Fac. Fil., Ciênc. Letras*, Univ. São Paulo (Geologia 18), 237, 65-123.

Bushee, J, 1971. Potassium-Argon Ages of some Alkaline Rocks from Southern Brazil. *PhD. Thesis*, University of California at Berkeley, California, pp. 145.

Cavalcante, J.C., Cunha, H.C. da S., Chieregati, L.A., Kaffer, L.Q., Rocha, J.M. da, Daitx, E.C., Coutinho, M.G. da N., Yamamoto, K., Drumond, J.B.V., Rosa, D.B., Ramalho, R., 1979. Projeto Sapucaí, Estados de São Paulo, Rio de Janeiro e Minas Gerais; Relatório Final de Geologia. DNPM/CPRM – Superintendência Regional de São Paulo (Geologia 5), *Seção Geologia Básica*, 2, pp. 299.

Cordani, U.G., 1970. Idade do vulcanismo no Oceano Atlântico Sul. Univ. São Paulo, *Bol. Inst. Geociênc., Astron. (IGA)*, 1, 9-75.

Cordani, U.G., Bernat, M., Teixeira, W. and Kanoshita, H., 1974. Idades radiométricas das rochas alcalinas do sul da Bahia. *28th Cong. Bras. Geol., Anais*, 6, 253-259 (Porto Alegre).

Cruz, W.B.d. and Peixoto, C.A.d.M., 1989. As águas termais de Poços de Caldas, MG: estudo experimental das interações água-rocha. *Rev. Bras. Geociênc.*, 19(1), 76-86.

Ellert, R., 1959. Contribuição à geologia do maciço alcalino de Poços de Caldas. *Bol. Fac. Fil. Ciênc. Letras*, Univ. São Paulo (Geologia 18), 237, 5-63.

Ellert, R., Björnberg, A.J.S., Coutinho, J.M.V., 1959. Mapa geológico do Maciço Alcalino de Poços de Caldas, Brasil. In: Ellert, R., 1959. Contribuição à geologia do Maciço Alcalino de Poços de Caldas. *Bol. Fac. Fil., Ciênc. Letras*, Univ. São Paulo (Geologia 18), 237, 5-63.

Fitton, J.G., 1987. The Cameroon Line, West Africa: A comparison between oceanic and continental alkaline volcanism. In: J.G. Fitton and B.G.J. Upton (Editors), Alkaline Igneous Rocks, *Geol. Soc. Spec. Pub.*, 30, 273-291.

Fraenkel, M.O., Santos, R.D.d., Loureiro, F.E.d.V.L. and Muniz, W.d.S., 1985. Jazida de urânio no planalto de Poços de Caldas – Minas Gerais. In: C. Schobbenhaus and C.E.S. Coelho (Editors), Principais Depósitos Minerais do Brasil Vol. 1, Recursos Minerais Energéticos. *MME, DNPM and CVRD*, Brasília, 89-103.

Frayha, R., 1952. Rochas potássicas, planalto de Poços de Caldas, Minas Gerais. *DNPM-Div. Fom. Prod. Miner., Bol. 93, Relatório da Diretoria*, Rio de Janeiro, 107-116.

Frayha, R., 1954. Importância das jazidas de minérios radioativos no Planalto de Poços de Caldas. *DNPM, Div. Fom. Prod. Miner., Bol.*, 102, Rio de Janeiro, 29-56.

Frayha, R., 1962. Urânio e tório no planalto de Poços de Caldas. *DNPM, Bol.*, 116, pp. 75.

Frayha, R., 1971. Geologia geral e recursos minerais. In: Poços de Caldas – Plano de Desenvolvimento Integrado. *Prefeitura de Poços de Caldas, 1970/71*, 1, 141-170.

Fujimori, S., 1967. Rochas alcalinas do Sul do Estado da Bahia. *DNPM., Div. Fom. Prod. Miner.* – Notas Preliminares e Estudos, Brasília, 141, 1-11.

Fujimori, K., 1974. Minerais radioativos do Campo Agostinho, Poços de Caldas (MG). Livre-Docência Thesis, *Inst. Geociênc., Univ. São Paulo,* pp. 161.

Garda, G.M., 1990. A alteração hidrotermal no contexto da evolução geológica do maciço alcalino de Poços de Caldas, MG - SP. M.Sc. Dissertation, *Inst. Geociênc., Univ. São Paulo*, pp. 213.

Goldschmidt, V.M., 1954. Geochemistry. *Clarendon Press*, Oxford, pp. 730.

Gorsky, V.A., and Gorsky, E., 1974. Contribuição à mineralogia e petrografia do planalto de Poços de Caldas. *Com. Energia Nucl.*, Rio de Janeiro, Bull. 13, pp. 93.

Hamza, V.M., 1982. Terrestrial heat flow in the alkaline intrusive complex of Poços de Caldas, Brazil. *Tectonophysics,* 83 (1-2), 45-62.

Harris, N.B.W., Mohammed, A.E.R.O. and Shaddad, M.Z., 1983. Geochemistry and petrogenesis of a nepheline syenite – carbonatite complex from the Sudan. *Geol. Mag.*, 120 (2), 115-127.

Herz, N., 1977. Timing of spreading in the south Atlantic: information from Brazilian alkalic rocks. *Geol. Soc. Amer. Bull.*, 88, 101-112.

Hess, P.C., 1989. Origins of Igneous Rocks. *Harvard University Press*, Cambridge, pp. 336.

IAEA, 1986. Alkaline rocks and carbonatites. In: Correlation of uranium geology between South America and Africa. Chap. 7, p. 345-415. *(Tec. Rep. Ser. 270).*

Kawashita, K., Mahiques, M.M., Ulbrich, H.H.G.J., 1984. Idades Rb/Sr de nefelina sienitos do Anel Norte do Maciço Alcalino de Poços de Caldas, MG-SP. 33rd. *Cong. Bras. Geol.*, Rio de Janeiro, Resumos, 244-245.

Kronberg, B.I., Tazaki, K., and Melfi, A.J., 1987. Detailed geochemical studies of the initial stages of weathering of alkaline rocks: Ilha de São Sebastião, Brazil. *Chem. Geol.*, 60, 79-88.

Le Maitre, R.W., 1976. The chemical variability of some common igneous rocks. *J. Petrol.* 17, 589-637.

Le Maitre, R.W., 1984. A proposal by IUGS subcommission on the systematics of igneous rocks for a chemical classification of volcanic rocks based on the total alkali silica (TAS) diagram. *Austral. J. Earth Sci.*, 31, 243-255.

Lima, D.d.A., 1966. Vegetação. In: IBGE. Atlas Nacional do Brasil. *Cons. Nac. Geogr.*, Rio de Janeiro.

Lo, H.E., 1981. Geochemical investigation of some nepheline-bearing syenitic rocks from Southern Ontario, Canada. *EOS*, 62 (17), 437.

Magno, Jr., L.B., 1985. The alkaline district of Poços de Caldas. *Nuclebrás CIPC publication*, Poços de Caldas, April/85.

Mitchell, R.H., and Platt, R.G., 1983. Primitive nephelinitic volcanism associated with rifting and uplift in the Canadian Arctic, *Nature*, 303, 609-612.

Montes-Lauar, C.R., 1988. Estudo paleomagnético dos maciços alcalinos de Poços de Caldas, Passa Quatro e Itatiaio. *M.Sc. Thesis*, Inst. Astron. e Geofis., Univ. São Paulo, pp. 101.

Montes-Lauar, C.R., and Pacca, J.G., 1990. Paleomagnetism of the Poços de Caldas, Itatiaia and Passa Quatro alkaline complexes (SE Brazil) and a possible relation with hot spot tracks. (Manuscript submitted to *J. Geophys. Res.*).

Nimer, E., 1979. Climatologia da região sudeste. In: IBGE. Climatologia do Brasil, Rio de Janeiro, 265-313.

Nockolds, S.R., Knox, R.W. O'B and Chinner, G.A., 1978. Petrology for students. *Cambridge University Press*, Cambridge, pp. 435.

Oliveira, A.G. de, 1966. Aspectos geológicos de mineralização de urânio em Poços de Caldas. 20th. Cong. Bras. Geol., Resumos, *Soc. Bras. Geol.*, Rio de Janeiro, 35-37.

Oliveira, A.G. de, 1968. Urânio no planalto de Poços de Caldas. 22nd. Cong. Bras. Geol., Resumos, *Soc. Bras. Geol.*, Belo Horizonte, 30.

Oliveira, A.G. de, 1973. Perspectivas de reservas e características gerais da mineralização uranífera no setor C-09 – Poços de Caldas (Minas Gerais). 27th. Cong. Bras. Geol., B1 – Resumos, *Soc. Bras. Geol.*, Aracajú, 35-36.

Oliveira, A.G. de, 1974. Mineralização de urânio e molibdênio no planalto de Poços de Caldas – MG. 28th. Cong. Bras. Geol., Anais, V. 1 *Soc. Bras. Geol.*, Porto Alegre, 207-221.

Oliveira, A.I. de, 1956. Reservas brasileiras de tório. *Eng. Miner. Metal.*, 24(141), 163-164.

Oliveira, M.A.F. de, Alves, F.R., Coimbra, A.M., 1975. Sedimentação associada ao vulcanismo alcalino de Poços de Caldas (Divinolândia, SP). *Bol. IG-USP*, 66, 13-19.

Oliveira, M.A.F. de, Morales, N., Fúlfaro, V.J., 1984. Projeto Boa Vista. Relatório Final., Rio Claro, *SICCT-UNESP*, 1, pp. 109.

Putzer, H., 1976. Metallogenetische Provinzen in Südamerika. *Schweizerbart'sche Verlagsbuchhandlung*, Stuttgart, pp. 316.

Radambrasil, 1983. Folhas SF 23/24, Rio de Janeiro/Victória. *Levantamento de Recursos Naturais*. (Ministério das Minas e Energia / SG., Rio de Janeiro, Brasília), 32, pp. 780.

Rocha, E.B., Fujimori, K., Ulbrich, H.H.G.J., 1986. Concentrações de U, Th e K em rochas do maciço alcalino de Poços de Caldas, determinadas por espectrometria gama. - *34th Cong. Bras. Geol., Resumos*, SBG, Goiania - Go, 104.

Romariz, D.d.A., 1963. Vegetação. In: *IBGE*. Geografia do Brasil, Grande Região Sul. Rio de Janeiro, 4, 167-187.

Santos, R. (1976). Geology and mining development of the C-09 uranium deposit. *IAEA Bull.* 162/28.

Sørensen, H., 1974. Alkali syenites, feldspathoidal syenites and related lavas. In: H. Sørensen (Editor), Alkaline Rocks. *J. Wiley & Sons*, London, New York, Sydney, Toronto, pp. 622.

Souto, P.G., 1972. Geologia e petrografia da área de Potiraguá, Bahia, Brasil. *M.Sc. Thesis*, Univ. São Paulo-USP., São Paulo, pp. 65.

Tassinari, C.C.G., 1988. As idades das rochas e dos eventos metamórficos da porção sudeste do Estado de São Paulo e sua evolução crustal. *Ph.D. Thesis*, Inst. Geoc., USP, São Paulo, pp. 236.

Teixeira, E.A., 1936. Zircônio no planalto de Poços de Caldas (Minas Gerais e São Paulo). *DNPM, Div. Fom. Prod. Miner.,* Avulso 14, pp. 23.

Teixeira, E.A., 1943. Zircônio em Poços de Caldas. *DNPM. Div. Fom. Prod. Miner., Bol.* 55, pp. 63.

Thompson, R.N., 1982. Magmatism of the British tertiary volcanic province. *Scott*, J. Geol., 18, 49-107.

Tolbert, G.E., 1958a. Preliminary report on the uraniferous zirconium deposits of the Poços de Caldas Plateau, Brazil. Part I. *Eng. Min. Metal.*, 27(161), 265-269.

Tolbert, G.E., 1958b. Preliminary report on the uraniferous zirconium deposits of the Poços de Caldas Plateau, Brazil. Part II. *Eng. Min. Metal.* 27(162), 353-360.

Tolbert, G.E., 1966. The uraniferous zirconium deposits of the Poços de Caldas Plateau, Brazil. *USGS, Bull.*, 1185-C, pp. 28.

Ulbrich, H.H.G.J., 1984. A petrografia, a estrutura e o quimismo de nefelina sienitos do Maciço Alcalino de Poços de Caldas, MG-SP. *Livre-Docência Thesis*, Inst. Geosciences, Univ. São Paulo, São Paulo, 2 Vols. pp. 735.

Ulbrich, H.H.G.J., 1985. Nepheline syenite magmas: derived from asthenospheric sources? *Anais Acad. Bras. Ciênc.*, 57(1), 132.

Ulbrich, H.H.G.J. and Gomes, C.B., 1981. Alkaline rocks from continental Brazil. *Earth Sci. Rev.*, 17, 135-154.

Ulbrich, M.N.C., 1983. Aspectos mineralógicos e petrólogicos de nefelina sienitos de Poços de Caldas, MG-SP. *Ph.D. Thesis*, Inst. Geociênc., Univ. São Paulo, São Paulo, pp. 369.

Ulbrich, M.N.C., Gomes, C.B. and Ulbrich, H.H.G.J., 1984. Nefelina sienitos do maciço alcalino de Poços de Caldas, MG-SP: Caracterização mineralógica e petrológica. *33th Cong. Bras. Geol., Anais*, (Rio de Janeiro), Vol. 9, 4362-4376.

Wedepohl, K.H., 1978. Handbook of Geochemistry. Vols. II-1, II-2, II-3, II-4, II-5, *Springer*, Berlin, Heidelberg, New York.

Wedow, H. Jr., 1961. Thorium and rare earths in the Poços de Caldas zirconium district, Brazil. *USGS, Prof. Pap.*, 424-D, *Geol. Res.*, 1961 (short papers), D214-216.

Wedow, H. Jr., 1967: The Morro do Ferro thorium and rare earth ore deposits, Poços de Caldas District, Brazil. *U.S. Geol., Surv., Bull.*, 1185-D, pp. 34.

List of SKB reports

Annual Reports

1977-78
TR 121
KBS Technical Reports 1 – 120
Summaries
Stockholm, May 1979

1979
TR 79-28
The KBS Annual Report 1979
KBS Technical Reports 79-01 – 79-27
Summaries
Stockholm, March 1980

1980
TR 80-26
The KBS Annual Report 1980
KBS Technical Reports 80-01 – 80-25
Summaries
Stockholm, March 1981

1981
TR 81-17
The KBS Annual Report 1981
KBS Technical Reports 81-01 – 81-16
Summaries
Stockholm, April 1982

1982
TR 82-28
The KBS Annual Report 1982
KBS Technical Reports 82-01 – 82-27
Summaries
Stockholm, July 1983

1983
TR 83-77
The KBS Annual Report 1983
KBS Technical Reports 83-01 – 83-76
Summaries
Stockholm, June 1984

1984
TR 85-01
Annual Research and Development Report 1984
Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01 – 84-19)
Stockholm, June 1985

1985
TR 85-20
Annual Research and Development Report 1985
Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01 – 85-19)
Stockholm, May 1986

1986
TR 86-31
SKB Annual Report 1986
Including Summaries of Technical Reports Issued during 1986
Stockholm, May 1987

1987
TR 87-33
SKB Annual Report 1987
Including Summaries of Technical Reports Issued during 1987
Stockholm, May 1988

1988
TR 88-32
SKB Annual Report 1988
Including Summaries of Technical Reports Issued during 1988
Stockholm, May 1989

1989
TR 89-40
SKB Annual Report 1989
Including Summaries of Technical Reports Issued during 1989
Stockholm, May 1990

Technical Reports

List of SKB Technical Reports 1990

TR 90-01
FARF31 –
A far field radionuclide migration code for use with the PROPER package
Sven Norman[1], Nils Kjellbert[2]
[1]Starprog AB
[2]SKB AB
January 1990

TR 90-02
Source terms, isolation and radiological consequences of carbon-14 waste in the Swedish SFR repository
Rolf Hesböl, Ignasi Puigdomenech, Sverker Evans
Studsvik Nuclear
January 1990

TR 90-03
Uncertainties in repository performance from spatial variability of hydraulic conductivities –
Statistical estimation and stochastic simulation using PROPER
Lars Lovius[1], Sven Norman[1], Nils Kjellbert[2]
[1]Starprog AB
[2]SKB AB
February 1990

TR 90-04
Examination of the surface deposit on an irradiated PWR fuel specimen subjected to corrosion in deionized water
R. S. Forsyth, U-B. Eklund, O. Mattsson, D. Schrire
Studsvik Nuclear
March 1990

TR 90-05
Potential effects of bacteria on radionuclide transport from a Swedish high level nuclear waste repository
Karsten Pedersen
University of Gothenburg, Department of General and Marine Microbiology, Gothenburg
January 1990

TR 90-06
Transport of actinides and Tc through a bentonite backfill containing small quantities of iron, copper or minerals in inert atmosphere
Yngve Albinsson, Birgit Sätmark,
Ingemar Engkvist, W. Johansson
Department of Nuclear Chemistry,
Chalmers University of Technology, Gothenburg
April 1990

TR 90-07
Examination of reaction products on the surface of UO_2 fuel exposed to reactor coolant wâter during power operation
R. S. Forsyth, T. J. Jonsson, O. Mattsson
Studsvik Nuclear
March 1990

TR 90-08
Radiolytically induced oxidative dissolution of spent nuclear fuel
Lars Werme[1], Patrik Sellin[1], Roy Forsyth[2]
[1]Swedish Nuclear Fuel and waste Management Co (SKB)
[2]Studsvik Nuclear
May 1990

TR 90-09
Individual radiation doses from unit releases of long lived radionuclides
Ulla Bergström, Sture Nordlinder
Studsvik Nuclear
April 1990