The regional geology of the Poços de Caldas alkaline complex: mineralogy and geochemistry of selected nepheline syenites and phonolites

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ABSTRACT


The Mesozoic Poços de Caldas alkaline complex, the largest known in South America, is circular-shaped with a mean diameter of about 33 km, and developed during continental break-up and drift. It comprises a suite of alkaline volcanic and plutonic rocks (mainly phonolites and nepheline syenites) with average amounts of U, Th and rare-earth elements (REEs). The evolutionary history began with major early volcanism involving ankarketrites, phonolite lavas and volcanoclastics, followed by caldera subsidence and nepheline syenite intrusions forming minor ring dykes, various intrusive bodies and circular structures. Finally, the addition or concentration of strongly incompatible elements led to the formation of eudialyte nepheline syenites and phonolites.

Magmatic evolution included deuteritic processes indicating a volatile-rich parent magma of upper mantle origin, without appreciable crustal contamination. These processes extended over a large temperature range and resulted in the formation of pegmatitic veins and comprised mineral assemblages including rare metal silicates such as giannettite, incipient alkali exchange reactions of feldspars, various zeolites, fluorite and hematite. Geochemically, the resulting rocks are enriched in potassium when compared to global nepheline syenites and phonolites. Mobilization and concentration of U, Th and REEs did not apparently occur at this stage.

At one place (Morro do Ferro) the intermediate nephelinitic suite was affected by a possible carbonatite intrusion and the formation of a stockwork of magnetite veins.

Very intensive hydrothermal K- and S-rich alteration, associated with contemporaneous volcanic 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 stages in the evolution 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
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mine) in supergene geochemical redistribution and the formation of redox fronts sometimes related to uranium enrichments. The end of the magmatic and hydrothermal-mineralizing events is likely fixed by the Ar–Ar dating of a lamprophyre dyke at the uranium mine (76 Ma).

This study was focused towards the major rock types of the regional nepheline suite relative to those experiencing more local hydrothermal and final weathering-related alteration. In the studied intrusive, subvolcanic and volcanic nepheline syenites and phonolites, very little variation was observed. This lack of differentiation may be seen as an argument for a short emplacement history of these rock bodies. Present radiometric age measurements suggest a time span of about 10 Ma for igneous activity at the caldera.

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 amounts of U, Th and rare-earth elements (REEs) typical for these rock types. The complex initially suffered regional postmagmatic deuteritic and incipient hydrothermal alteration, resulting in widespread potassium metasomatism and zeolitization, together with minor argillation under oxidizing conditions (e.g. hematitization and hydrous ferric oxide-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 potassic metasomatism, 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 descending redox fronts associated with the supergene remobilization and precipitation of uranium concentrations that have been exploited at the Osamu Utsumi mine area (secondary mineralizing event).

The initial part of this paper reviews the regional geological evolution (summarized from selected literature). Following this, the regional reference samples of the project, later used for comparisons with the mineralized rocks with respect to their magmatic and deuteritic mineralogical and geochemical properties, are petrographically and geochemically characterized. This study forms a preliminary and highly-focused description using limited samples selected to represent the major rock types of the alkaline complex. To effect a
more complete petrologic study, more sampling and analyses would be required. For those interested in more detailed background information, an extensive bibliography has been compiled.

2. REGIONAL GEOLOGY

The Poços de Caldas alkaline complex is circular 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.

Alkaline rocks are found almost exclusively in stable intraplate tectonic settings, and 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 (Best, 1982; Fitton and Upton, 1987). The alkaline rocks of the Poços de Caldas complex are associated with the rifting of the South American and African plates.

An outline of the regional geology and geotectonics of central-east Brazil is shown in Fig. 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, with the south tract of the Atlantic Ocean opening approximately 145–125 Ma ago. 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 out-
Fig. 1. A simplified regional geological map (after Almeida, 1977) showing the locations of alkaline rocks 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) Brasília 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); (●) Infracambrian and Mesozoic alkaline rocks (Ulbrich and Gomes, 1981); (■) Mesozoic alkaline rocks with carbonatites (Ulbrich and Gomes, 1981).
Fig. 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.
standing in more than one aspect. With a surface extent of about 800 km^2, it represents the largest known alkaline complex of South America, and one of the largest in the world (Woolley, 1987). 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 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 geologically studied 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) and Montes-Lauar (1988). More detailed research, particularly with respect to nepheline syenite, was performed by Ulbrich (1984). A simplified sketch map of the Poços de Caldas alkaline complex, integrating geological and remote-sensing structural data, is shown in Fig. 2 (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 evolutionary history, according to Ellert (1959), starts with major early volcanism involving olivine nephelinites, 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 work of Bushee (1971) and the structural interpretations of Almeida Filho and Paradella (1977) (Fig. 2).

The emplacement of the alkaline complex fenitized two main areas of country rock (Fig. 2). Ellert (1959) described the metasomatism of the western fenites as comprising color alteration, reduced quartz content, feldspar blastesis and the formation of sodic amphibole.

Radiometric age determinations indicate that igneous activity 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). The K–Ar results of these earlier studies likely reflect post-emplacement alterations (Ulbrich, 1984; Shea, 1992). The long duration of the magmatic emplacement of the Poços de Caldas complex, previously considered to be more than ca. 30 Ma (Bushee, 1971), is in striking contrast to the relatively short (2–3 Ma) typical life-span of modern volcanoes (Ulbrich, 1984). Shea
(1992) found the nepheline syenite to yield a Rb-Sr age of 78 (3) Ma, which suggests that igneous activity may have persisted for approximately 10 Ma.

In the course of the present study, the possibility that the Morro do Ferro is a minor, strongly weathered carbonatite has been inferred (see Waber, 1992). Alkaline mafic and ultramafic dyke rocks (lamprophyres) of different generations are known and are thought to represent the youngest truly magmatic occurrence. Shea (1992) has found a lamprophyre dyke exposed at the Osamu Utsumi mine to yield an Ar-Ar age of 76 (1) Ma.

2.1. Alteration and mineralization

The alkaline rocks of the Poços de Caldas complex suffered widespread post-magmatic deuteric alteration. At several specific sites there also occurred additional intensive hydrothermal rock/meteoric water 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, jordisite (MoS₂), sphalerite, zircon-baddeleyite (ZrO₂), REEs, fluorite, and pyrite mineralizations. Mineralization can be disseminated without any evident structural control, or is associated with either fractured vein/stockwork systems, or local volcanic breccias, through which copious quantities of meteoric water were heated and transported (Cathles and Shea, 1992). 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 K₂O contents normally in excess of 12 wt.%. Hydrothermal mineral occurrences under exploitation include vein mineralizations of caldasite (integrowth of Zr 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., 1992). It further includes the alteration of host rocks of the alkaline caldera which have been 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., 1992), 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, 1992).

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 for-
mation 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 Fe oxyhydroxide 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 deposit, was mined until 1988.

3. DESCRIPTION OF REGIONAL SAMPLES

3.1. Geology

Several outcrops of the major regional alkaline rock types (nepheline syenites and phonolites) were sampled for comparative petrographic, mineralogical, geochemical and geochronological studies aimed at characterizing the magmatic and deuteric alteration and “status quo” properties of the alkaline rocks, all 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, which led to the relatively low number of samples, was the scarcity of relatively fresh sample sites 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, and is representative of the predominant type-lithology and the main stage of nepheline syenite plutonism of the alkaline complex. This nepheline syenite is 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 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 types. Previous studies have detailed geochemical data (Ulbrich, 1984), geochronological data (Kawashita

Sample NS-4 is a fine- to medium-grained porphyritic rock type, (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 of the studied nepheline syenite samples belong to the one continuously mapped major intrusive body (Fig. 2). Among those nepheline syenites not sampled but included in this study are the eudialyte nepheline syenites (lujavrites and chibinites) from the northern border of the caldera, which represent late stage intrusions. They are discussed further by Ulbrich (1984) and Rocha et al. (1986).

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 which predate the major intrusion of nepheline syenite. The relative age of the subvolcanics from the Bortolan quarry is uncertain, but probably younger than the main nepheline syenite.

3.2. Petrography and mineralogy

3.2.1. Petrography

Alkaline rocks typically exhibit high concentrations of the alkalies 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 three 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 equigranular, 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.

Plutonic nepheline syenites (samples NS-1, 4, 6, 7) range from medium to typically coarse-grained, isotropically structured and idiomorphically textured rocks. Xenoliths are locally present; phenocrysts are infrequent to absent.

The subvolcanic phonolites and nepheline syenites are frequently and sharply cut by nepheline syenite pegmatites.

All of the studied alkaline rocks are leucocratic (Table 1), with the total volume of mafic minerals ≤35 %. 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 vol. % of pseudomorphosed groundmass leucites. It is the only rock with two significant feldspathoids (Table 1).

All the studied regional rocks show evidence of an evolving fluid-phase and deuteric alteration. The particular mineral phases and reaction stages are listed in Table 1 and described more fully below. These petrogenetic processes occurred in magmas and rocks which from the outset were heterogeneous. This was caused by substantial amounts of partially assimilated xenocrysts and xenoliths and/or by 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 2). The values obtained appear to be normal for these types of leucocratic alkaline rocks.

3.2.2. Mineralogy

As discussed in Hess (1989), nepheline syenites are the phaneritic (plutonic) equivalent of 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 and amphiboles, aenigmatite (Na<sub>2</sub>Fe<sub>5</sub>TiSi<sub>6</sub>O<sub>20</sub>) and unusual
### TABLE 1

Qualitative and quantitative mineralogical compositions [visually estimated volume%] of regional phonolites and nepheline syenites from the Poços de Caldas complex listed in order of crystallization

<table>
<thead>
<tr>
<th>Minerals</th>
<th>PH-2A</th>
<th>PH-2B</th>
<th>PH-3</th>
<th>PH-5</th>
<th>PH-8</th>
<th>PH-9B</th>
<th>NS-1</th>
<th>NS-4</th>
<th>NS-6</th>
<th>NS-7</th>
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<td>Titanite-1</td>
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<td>Ore mins-1</td>
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<td>Nosean-1</td>
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<td>Pseudoleucite (plc)-1</td>
<td>2-4</td>
<td>2-4</td>
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<td>1-2</td>
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<td>Orthoclase-1</td>
<td>3</td>
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<td>≤1</td>
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<td>Aegirine-augite-1</td>
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<td>Zircon-2</td>
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<td>Titanite-2</td>
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<td>Ore mins-2</td>
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<td>Apatite-2</td>
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<td>Orthoclase-3</td>
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<td>47-51</td>
<td>55-60</td>
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<tr>
<td>Na-rich plagioclase-3</td>
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<td>3-5</td>
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<td>Pseudoleucite-3</td>
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<td>≤1</td>
<td>10-12</td>
<td>1</td>
<td>2-3</td>
<td>3-5</td>
<td>3-4</td>
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<td>Sodalite-3</td>
<td>2</td>
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<td>Analcite-3</td>
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<td>Sodalite (in plc)-4</td>
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<td>Analcite (in plc)-4</td>
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<td>Cancrinite (in ne)-4</td>
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</tr>
<tr>
<td>Giannettite-5</td>
<td>2-4</td>
<td>3</td>
<td>3</td>
<td>2-3</td>
<td>2-3</td>
<td>2-3</td>
<td>1-2</td>
<td>1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Unid. rare mins-5</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
<td>≤1</td>
<td>tr.</td>
<td>—</td>
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</tr>
<tr>
<td>Zeolites-5</td>
<td>tr.</td>
<td>2-4</td>
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<td>—</td>
<td>tr.</td>
<td>3-5</td>
<td>5-7</td>
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<tr>
<td>Clay mins-5</td>
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<td></td>
</tr>
<tr>
<td>Ore mins-5</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
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<tr>
<td>Carbonate-5</td>
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<td>tr.</td>
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<tr>
<td>Microxenoliths</td>
<td>~20</td>
<td>~3</td>
<td>≤1</td>
<td>—</td>
<td>~3</td>
<td>1-2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

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

Petrophysical properties of regional nepheline syenites and phonolites

<table>
<thead>
<tr>
<th>Region</th>
<th>Bulk density (g/cm$^3$)</th>
<th>Grain density (g/cm$^3$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regional nepheline syenites</td>
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<tr>
<td>NS-1</td>
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<td>2.64</td>
<td>3.2</td>
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<td>2.62</td>
<td>1.8</td>
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<tr>
<td>NS-6</td>
<td>2.50</td>
<td>2.59</td>
<td>3.5</td>
</tr>
<tr>
<td>NS-7</td>
<td>2.49</td>
<td>2.58</td>
<td>3.5</td>
</tr>
<tr>
<td>Regional phonolites</td>
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<td></td>
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<td>1.6</td>
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<tr>
<td>PH-8</td>
<td>2.59</td>
<td>2.64</td>
<td>1.9</td>
</tr>
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</table>

Na–Zr and Na–Ti silicates (e.g. eudialite = Na$_4$ (Ca, Fe, Cl, Mn)$_2$ Zr Si$_6$O$_{17}$ (OH, Cl)$_2$). 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$_2$O$_3$. 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 discussed below, the studied Poços de Caldas alkaline rocks range from slightly peralkaline to metaluminous. They appear to be similar to some of the hyper-solvus types of nepheline syenites described by Nockolds et al. (1978).

The regional phonolites and nepheline syenites are mineralogically complex, but essentially equivalent in overall composition. Major differences are of a quantitative rather than a qualitative mineralogical nature. Table 1 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 xenocrysts, 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 and sanidine (instead of orthoclase), associated in one case (sample PH-9) with groundmass leucite and aegirine–augite. The crystallization in these phonolites was almost contemporaneous due to more rapid cooling.

Deuteric crystallization has resulted in the formation of giannettite (~Na₃Ca₃Mn(Zr,Fe)TiSi₆O₂₁Cl with significant amounts of REEs and Sr) 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 mairiolitic voids and fractures.

Changes in mineral structure and chemistry were driven mainly by fluid–rock interactions. This included pseudoleucite formation, the transformation and pseudomorph replacement of sodalite group minerals, alkali feldspar lattice changes and exsolution, the cancrinitization of nepheline, alkali feldspar ion substitution and exchange reactions (Na by K). The alkali feldspar reactions were accompanied by incipient kaolinization, fluid inclusion formation, and precipitation of finely disseminated iron oxides. The mineral assemblages of the mairiolitic voids include aggregates of fine aegirine needles, albite, analcite, natrolite, fluorite, calcite, and hematite. The above observations indicate that the pneumatolytic fluid (oxidizing and containing appreciable CO₂ and F) decreased in temperature and evolved, via feldspar exchange reactions, from originally K-rich to Na- and Ca-rich.

Judging from the petrographic and mineralogical data, the caldera 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 has occurred.

Mineral chemistry (microprobe) studies have not been performed on the phonolites. Nepheline syenite minerals have been studied by Ulbrich, M. (1983) and Ulbrich, M. et al. (1984) using X-ray diffraction and electron microprobe methods. K-feldspars from most of the nepheline syenites showed within individual grains the association of high triclínico 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 differ from the other nepheline syenites where Sr is present in much lower amounts. Further-
more, the K-feldspars show zoning with internal portions richer in Na, Ca and Sr, and significant Fe-contents (Fe$_2$O$_3$ $\cong$ 0.50 wt.%) are always present. Nephelines generally show moderate K$_2$O contents in the range of 5–8 wt.% and Fe$_2$O$_3$ in the range of 0.3–2 wt.% that vary inversely with Al$_2$O$_3$. The clinopyroxenes are continuously zoned with Na-augitic cores to almost pure aegirine rims enriched in Ti and Zr (REEs appear to be coupled with 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 (University of Bern), and by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the REEs (SURRC*). The uncertainties for the XRF analyses are: major elements $\pm$ 1%, minor elements $\pm$ 20% (10s ppm) and $\pm$ 5% (100s ppm), and LOI** $\pm$ 5%. The uncertainty for the ICP analyses (semi-quantitative) is $\leq$ $\pm$ 3% (Date and Jarvis, 1989).

3.3.1. Major and trace elements

The chemical classification of alkaline rocks is typically based on the degree of peralkalinity.

Sørensen (1974) favored the use of the molecular ratio (Na$_2$O+K$_2$O)/Al$_2$O$_3$, also known as the Agpaitic Index (AI), to separate nepheline syenites into agpaitic (AI $>$ 1), miaskitic (AI $<$ 1) and ill-defined intermediate types (AI $\geq$ 1).

Here, the classification of Shand (1951) for alkaline rocks (see Hess, 1989) was used. According to this system, two molecular ratios are used: (Na+K)/Al (equivalent to the AI) and (Ca+Na+K)/Al, such that

$$(\text{Na} + \text{K})/\text{Al} > 1 \quad \equiv \text{peralkaline}$$

$$(\text{Ca} + \text{Na} + \text{K})/\text{Al} > 1 \quad \equiv \text{metaluminous}$$

$$(\text{Ca} + \text{Na} + \text{K})/\text{Al} < 1 \quad \equiv \text{peraluminous}$$

In this scheme, peralkaline is equivalent to agpaitic, and peraluminous is similar to miaskitic.

Using the AI (see Table 3), the Poços de Caldas alkaline rocks would be

*Scottish Universities Research & Reactor Centre.

**Loss on ignition.
### TABLE 3

Selected major element data from regional nepheline syenites (NS) and phonolites (PH): oxide concentration (wt.%)  

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe&lt;sub&gt;tot&lt;/sub&gt;</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>LOI</th>
<th>Total</th>
<th>Al</th>
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<tbody>
<tr>
<td><strong>Nepheline syenites</strong></td>
<td></td>
<td></td>
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<tr>
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<td>0.79</td>
<td>19.93</td>
<td>4.43</td>
<td>0.28</td>
<td>0.44</td>
<td>1.99</td>
<td>6.48</td>
<td>8.26</td>
<td>0.12</td>
<td>1.23</td>
<td>98.73</td>
<td>0.98</td>
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<td>0.87</td>
<td>20.20</td>
<td>4.34</td>
<td>0.25</td>
<td>0.51</td>
<td>1.99</td>
<td>6.48</td>
<td>8.23</td>
<td>0.13</td>
<td>1.88</td>
<td>99.71</td>
<td>0.97</td>
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<td>5.66</td>
<td>7.95</td>
<td>0.14</td>
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<td>0.89</td>
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<td>3.77</td>
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<td>0.27</td>
<td>1.46</td>
<td>7.60</td>
<td>7.73</td>
<td>0.08</td>
<td>3.17</td>
<td>97.28</td>
<td>1.06</td>
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<td><strong>Phonolites</strong></td>
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<td></td>
<td></td>
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<tr>
<td>PH-2A</td>
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<td>19.84</td>
<td>4.09</td>
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<td>1.06</td>
<td>97.18</td>
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<tr>
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<td>0.56</td>
<td>20.21</td>
<td>4.25</td>
<td>0.26</td>
<td>0.24</td>
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<td>6.95</td>
<td>8.43</td>
<td>0.06</td>
<td>1.89</td>
<td>99.63</td>
<td>1.02</td>
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<td>6.87</td>
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<td>0.06</td>
<td>1.36</td>
<td>99.53</td>
<td>0.99</td>
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<td>19.75</td>
<td>3.72</td>
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<td>0.21</td>
<td>1.52</td>
<td>8.00</td>
<td>7.94</td>
<td>0.06</td>
<td>1.82</td>
<td>97.02</td>
<td>1.10</td>
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<tr>
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<td>0.59</td>
<td>19.83</td>
<td>3.81</td>
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<td>0.24</td>
<td>1.58</td>
<td>7.30</td>
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<td>0.06</td>
<td>0.96</td>
<td>97.06</td>
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<td>0.22</td>
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<td>7.40</td>
<td>8.40</td>
<td>0.06</td>
<td>1.20</td>
<td>97.03</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Analyses performed at the University of Bern by XRF. Fe<sub>tot</sub>: total iron (as Fe₂O₃). LOI: Loss On Ignition. Al: Agpaitic Index.
classified as ranging from slightly miaskitic (AI = 0.89) to mildly agpaitic (AI = 1.12), and therefore intermediate (?). Using the Shand classification (see Fig. 4), the nepheline syenites, with the notable exception of NS-7, are metaluminous, and the phonolites more or less restricted to the peralkaline field.

The analytical results and the recalculated and normalized major elements are shown in Table 3. Figure 4 shows the degree of peralkalinity of the regional nepheline syenites and phonolites, plotted with the aid of TRIPLOT (Rock and Carroll, 1989).

The mineralogy of the Poços de Caldas alkaline rocks does not strictly conform to a classical (i.e. Sørensen) agpaitic mineral suite, which further supports an intermediate rock type designation. It also conforms (i.e. Hess) to a peralkaline, but not necessarily metaluminous, rock type.

In general, one may observe that the studied regional nepheline syenites and phonolites (n = 10; Table 3) of the Poços de Caldas plateau show relatively small variations in K₂O (range 7.7–8.5 wt.%) and Na₂O (range 5.7–8.0 wt.%), with a mean K₂O/Na₂O ratio of ~ 1.2. The variability of the other elements is also very restricted such that 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 of Ulbrich (1984), which stressed the mineralogical and major element consistency of the nepheline syenites, are in general agree-

![Fig. 4. Degree of peralkalinity of the Poços de Caldas regional nepheline syenites and phonolites, using the classification of Shand (1951). Triangular area encompassing data has been enlarged.](image-url)
ment 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 4) are strongly K₂O-enriched with respect to global nepheline syenite and phonolite values (Le Maitre, 1976). This is probably due to a primary magmatic perpotassic characteristic in the original alkaline silicate melts, together with deuteric alteration. Using a TAS (total alkalis versus silica) diagram (Le Maitre, 1984; Le Bas et al., 1986), 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 4. 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=10) is considered, in amounts normal for leucocratic alkaline rocks, i.e. neither U nor

### TABLE 4

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

<table>
<thead>
<tr>
<th>PDC-sample</th>
<th>NS-1</th>
<th>NS-4</th>
<th>NS-6</th>
<th>NS-7</th>
<th>PH-2A</th>
<th>PH-2B</th>
<th>PH-3</th>
<th>PH-5</th>
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<td>195</td>
<td>162</td>
<td>169</td>
<td>165</td>
<td>164</td>
</tr>
<tr>
<td>Hf</td>
<td>14</td>
<td>14</td>
<td>18</td>
<td>16</td>
<td>10</td>
<td>22</td>
<td>9</td>
<td>11</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>S</td>
<td>987</td>
<td>764</td>
<td>878</td>
<td>545</td>
<td>1689</td>
<td>1496</td>
<td>1288</td>
<td>630</td>
<td>782</td>
<td>651</td>
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</tbody>
</table>

Total  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.
Th or the REEs show any enrichment (Goldschmidt, 1954; Sørensen, 1974; Wedepohl, 1978).

The 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 distinct geological occurrence.

The nepheline syenite samples exhibit greater variability despite the fact that they represent one geologically continuous intrusive body (Fig. 2). This is likely indicative of a primary geochemical inhomogeneity.

The geochemistry of the studied samples shows limited geochemical variability and a low degree of differentiation. The only particularly noticeable differences are the lower Th, Pb, and Ba contents of the volcanic phonolites. 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 phonolite samples do not define an isochron, and the Sm–Nd isotopic data do not conform to any possible model isochron, both observations strongly suggesting that these rocks had different initial isotopic values. For the Sm–Nd data this is also due to the very long half-life of $^{143}\text{Sm}$ (Shea, 1992). It is interesting to note that the matrix pseudoleucite-bearing rocks (sample PH-9) are geochemically indistinct from the other volcanic phonolites. 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.

The origin of the subvolcanic rocks of the Bortolan quarry site may be considered somewhat different from that of 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 5 and graphically represented in Fig. 5; the rock values have been normalized to ordinary chondrite values. The total REE contents (sum of REEs in ppm) show a general positive correlation with the sum of Fe, Mg, Ti, Mn, Ca (total Fe, Mg, Ti, Ca, Mn in atomic equivalent numbers). The mineral chemistry data of Ulbrich, M. (1983) and Ulbrich, M. et al. (1984) indicate that clinopyroxene may play an important role in the REE distribution of the studied rocks.
The REE patterns for the regional nepheline syenites (Fig. 5a) 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).

The REE patterns for the regional nepheline syenite and volcanic phonolite samples 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 Sebastião, 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. Lo (1981) noted a similar pattern of 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 absence of an Eu anomaly suggests a primitive source, without extensive crystal fractionation. 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., 1992 and Cathles and Shea, 1992).

It should also be noted that the REE profiles for the nepheline syenites lie

### Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
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<tr>
<td><strong>Nepheline syenite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NS-1</td>
<td>151.99</td>
<td>405.45</td>
<td>33.72</td>
<td>108.33</td>
<td>14.86</td>
<td>3.95</td>
<td>11.70</td>
<td>1.55</td>
<td>7.78</td>
<td>1.56</td>
<td>4.20</td>
<td>0.58</td>
<td>3.44</td>
<td>0.49</td>
</tr>
<tr>
<td>NS-4</td>
<td>147.61</td>
<td>355.34</td>
<td>35.92</td>
<td>122.19</td>
<td>17.39</td>
<td>4.91</td>
<td>13.93</td>
<td>1.79</td>
<td>18.96</td>
<td>1.57</td>
<td>4.35</td>
<td>0.55</td>
<td>3.36</td>
<td>0.52</td>
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<td>NS-6</td>
<td>214.96</td>
<td>451.92</td>
<td>46.84</td>
<td>149.64</td>
<td>20.41</td>
<td>6.05</td>
<td>18.00</td>
<td>2.17</td>
<td>10.11</td>
<td>1.71</td>
<td>5.18</td>
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<td>115.63</td>
<td>272.92</td>
<td>21.34</td>
<td>65.71</td>
<td>8.43</td>
<td>2.47</td>
<td>7.25</td>
<td>0.93</td>
<td>4.55</td>
<td>0.86</td>
<td>2.51</td>
<td>0.35</td>
<td>2.28</td>
<td>0.32</td>
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<tr>
<td><strong>Phonolite</strong></td>
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<tr>
<td>PH-2A</td>
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<td>22.60</td>
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<td>7.40</td>
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<td>310.67</td>
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<td>2.74</td>
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<td>PH-5</td>
<td>132.02</td>
<td>323.02</td>
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<td>93.36</td>
<td>12.07</td>
<td>3.18</td>
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<td>1.35</td>
<td>6.70</td>
<td>1.28</td>
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<td>3.06</td>
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<tr>
<td>PH-8</td>
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<td>10.23</td>
<td>2.84</td>
<td>8.12</td>
<td>1.13</td>
<td>6.03</td>
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<td>2.79</td>
<td>0.39</td>
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<td>PH-9B</td>
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<td>244.16</td>
<td>26.17</td>
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<td>9.79</td>
<td>2.72</td>
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<td>1.19</td>
<td>3.46</td>
<td>0.49</td>
<td>2.89</td>
<td>0.41</td>
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</table>

ICP-MS analyses were performed at the Scottish Universities Research and Reactor Centre (SURRC).
Fig. 5. Distribution of chondrite normalized rare-earth elements for the regional nepheline syenites (NS) and phonolites (PH): (a) nepheline syenites; (b) volcanic phonolites; (c) sub-volcanic phonolites.
almost entirely above those for the phonolites, with only sample NS-7 (petrographically identified as the most leucocratic of the nepheline syenites as evidenced by its mineralogy and major element geochemistry) falling into the subvolcanic 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. One would also expect an increase in the fractionation between LREEs and HREEs, but this is not particularly noticeable in the sampled nepheline syenites.

A comparison of the REE distribution patterns (Fig. 5) shows that the volcanic phonolites are analytically indistinguishable from the nepheline syenites (NS-1, 4, 6 and 7). The two regional volcanic phonolites (samples PH-3, 5, 8 and 9) show almost identical REE patterns (Fig. 5b). These REE data support the assumption that the volcanic phonolites and the nepheline syenites are consanguineous, 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. Again, however, the Rb–Sr and Sm–Nd data indicate that the phonolites, at least, are isotopically distinguishable from one another.

The REE patterns of the subvolcanic, more complex alkaline rocks of the Bortolan quarry site (Fig. 5c) are analytically 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, 1992), 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, with a somewhat larger difference for the subvolcanics which appear to be either more differentiated or were hybridized by eudialyte nepheline syenite.

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 SiO₂ 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, experiencing only very minor differentiation and fractionation, which has produced volcanic, sub-volcanic 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 basement 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 with long crustal residence times (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, M.A.F. et al., 1975, 1984).

All the studied regional rocks show evidence of deuteric alteration that occurred in the temperature/time interval corresponding from magmatic down to hydrothermal conditions. The deuteric alterations, particularly from the intermediate to lower 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 possibly indicates that the original magma was enriched in (cogenetic) volatiles. The δD and δ¹⁸O data of the regional rocks are interpreted as representing deuteric and/or post-eruptive incipient meteoric water/rock interaction (Shea, 1992).

The present petrological/geochemical and isotopic evidence (Waber et al., 1992; Shea, 1992), 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. Further study of possible weathered remnants of carbonatite at Morro do Ferro (Fig. 2) may furnish additional genetic evidence (Waber, 1992).
5. ACKNOWLEDGEMENTS

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