GEOCHEMICAL AND Sr, Nd, AND Pb ISOTOPE SIGNATURES OF PHONOLITES AND NEPHELINE SYENITES FROM THE POÇOS DE CALDAS ALKALINE MASSIF, SOUTHEASTERN BRAZIL

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INTRODUCTION

The large Poços de Caldas alkaline massif (PC) crops out as a subcircular structure over 800 km^2 in the states of Minas Gerais and São Paulo, southeastern Brazil (Ellert, 1959; Ulbrich & Ulbrich, 1992). The main rock types are phonolites and nepheline syenites, emplaced mainly at about 79-80 Ma ago (Ulbrich et al., 2002). It is the site of U, Th, and Zr mineralization, a corollary of widespread hydrothermal alteration that lasted to around 76 Ma (Shea, 1992).

Some Sr and Nd isotopic data for regional phonolites and nepheline syenites within the massif were already presented by Shea (1992).

We report here new Rb-Sr and Sm-Nd data as well as the first Pb-Pb data for several selected samples of phonolites and nepheline syenites and draw some preliminary petrological inferences from the results.

GEOLOGY AND PETROGRAPHY

The Poços de Caldas massif is mainly constituted by subvolcanic phonolites (tinguaites), nepheline syenites (NeS), and mostly altered volcanic phonolites, in part enclosing the overlying eolian Botucatu sandstones and some Serra Geral diabases (Ellert et al., 1959; Ulbrich & Ulbrich, 1992). Related mafic and ultramafic rocks with pyroxene, analcime and olivine as the main minerals, are seen as fragments of lava flows, agglomerates, lapilli, and tuffs, within its western border, at the Vale do Quartel (VQ).

Other minor ultramafic occurrences appear in the Osamu Utsumi open pit (mainly lamprophyres), within the district, and intruding metamorphic country rocks, close to the massif´s northeastern limit (lamprophyres and associated silico-carbonatitic rocks at the Minas Pedras quarry, MP).

The NeS are mineralogically monotonous, with more K-feldspar than nepheline and lesser proportions of Na-pyroxenes, together with an assorted number of accessory rare silicates, some of which present as rock-forming minerals (*e.g.*, eudyalite in lujavrites and khibinites), constantly accompanied by late and post-magmatic phases (late aegirine, cancrinite, natrolite, fluorite, and rare minerals), a clear indication of the activity of late fluids rich in F, Fe, Na, CO_2, and rare metals. These rocks are in most cases clearly intrusive into tinguaites, appearing as discrete bodies, each characterized by a dominant petrographic facies, defined by structure, texture, and mineralogy.

The accessory mineralogy, eudialyte in particular, can be used in the field to separate agpaitic NeS (with agpaitic index over 1.1 and larger amounts of Zr, REE, Ti, U, Th, *etc*.) from intermediate and miaskitic varieties (*cf*. Ulbrich & Ulbrich, 1992).

The largest body of NeS is the Pedreira intermediate-miaskitic type, with an outcrop surface over 80 km^2, while other types are present as much smaller bodies.

GEOCHEMICAL BACKGROUND

All the NeS present rather similar whole rock chemistry for most major and minor components (own data), with the following mean values (wt. %): SiO_2: 53.55, Al_2O_3: 19.58, TiO_2: 0.52, MnO: 0.30, MgO: 0.22, CaO: 1.63, Na_2O: 7.74, K_2O: 8.31, and P_2O_5: 0.05. The larger variations are seen for K_2O and Na_2O, which are negatively correlated, and to a greater extent for $Fe_2O_3^T$ varying from 3-5 wt. % in most rocks to up to 11.2 wt. % in the mesocratic lujaurites. Usually the molar ratio Na_2O/K_2O is over 1; the agpaitic indices range from 0.98 to as high as 1.33.

The trace element contents (own data), on the other hand, present a wide range, especially within the agpaitic types, as shown (in ppm): Ba 16 to 1200, Rb 92-614, Sr 410-6360, Ta ~2-273, Nb 127-1000, Hf 7.7-82.40, Zr 383-4450, Y 8-125, Th 18.70-124, U 2.78-30.60, V 30-286, Pb 0-77, Zn 101-514, La 75.60-1080, Ce 81-1450, Yb 0.93-13.40, Lu 0.12-2.00. Ni, Co, Cu, and Cr are below detection limits. This is a common feature of most large massifs with significant amounts of agpaitic rocks (*e.g.*, Khibina and Lovozero; *cf*. Kramm & Kogarko, 1994).

The tinguaites show a similar spread of values for major, minor and trace element contents, with less enrichment. Chemical data of tinguaites plot closely to those of less differentiated NeS, while more agpaitic NeS show very high abundances in trace elements, possibly indicating a post-magmatic enrichment related to fluid activity.

Chondrite-normalized REE diagrams for NeS and tinguaites show a distinct concave pattern, significantly enriched in LREE, with no Eu anomaly, La/Yb ratios varying from about 50 to up to 100.

ISOTOPE Sr-Nd-Pb DATA

Isotopic Sr-Nd-Pb data were obtained for 18 assorted Poços de Caldas rocks (10 NeS and 8 tinguaites) representatives of the main petrographic facies within the massif.

The new Sr, Nd, and Pb isotopic analyses were made at the Laboratoire de Geochimie Isotopique of the Université Libre de Bruxelles. Errors are quoted at the 95% confidence level. Previous Sr-Nd data presented for the mafic-ultramaphic samples from VQ (Thompson et al., 1998) and MP (Vlach et al., 1998) are also considered for comparison purposes. All presented initial ratios were computed for a 80 Ma reference age.

$^{87}Rb/^{86}Sr$ and $^{87}Sr/^{87}Sr$ measured values plot close to a 80 Ma reference line with an initial $(^{87}Sr/^{87}Sr)_{80}$ ratio about 0.70515 (Figure 1). The data do not fit a real isochron due to inherited $^{87}Sr/^{86}Sr$ contrasts in the magmas, or late to post-magmatic isotopic reequilibration, or both. $(^{87}Sr/^{87}Sr)_{80}$ values range from 0.70475 to 0.70552 and there is no significant difference among NeS and tinguaites.

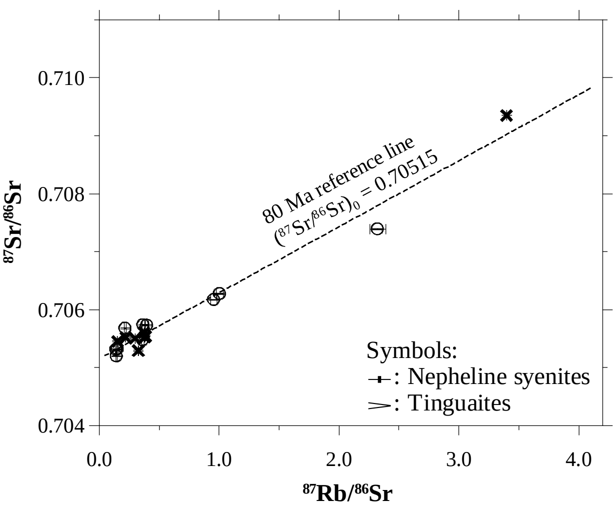

Figure 1. $^{87}Sr/^{87}Sr$ vs $^{87}Rb/^{86}Sr$ diagram for the Poços de Caldas NeS and tinguaites. Error bars at 2σ.

The $(^{143}Nd/^{144}Nd)_{80}$ ratios show a significant range from 0.51233 to 0.51239; three NeS stand out as the more evolved rocks (Fig. 2). The VQ and MP ultramafic rocks are clearly more primitive than the NeS and tinguaites as shown by the respective initial ratio. With the exception of one VQ sample, the ultramafic rocks present also higher Sm/Nd ratios, reflecting its less fractionated REE pattern. Depleted mantle model ages (DePaolo, 1981) of the felsic rocks vary within 650-750 Ma and give an almost normal distribution with a mean of 692 ± 54 Ma (2σ), while VQ and MP samples range between 630-810 and 580-640 Ma, respectively (Fig. 3).

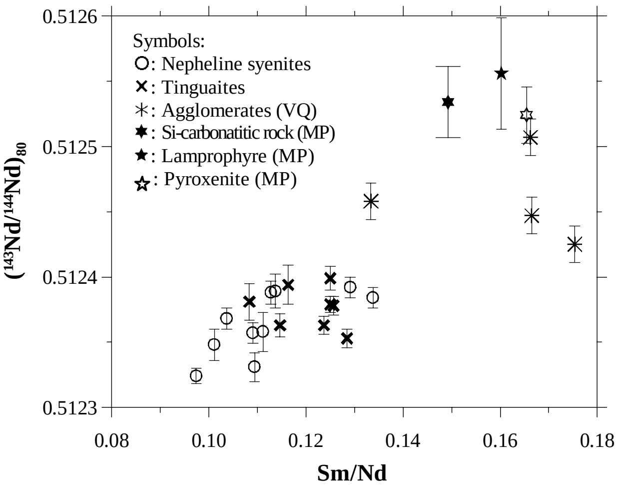

Figure 2. $(^{143}Nd/^{144}Nd)_{80}$ vs Sm/Nd plot for the Poços de Caldas NeS, tinguaites and associated VQ and MP ultramafic rocks. Error bars at 2σ.

The correlation among $(^{87}Sr/^{87}Sr)_{80}$ and $(^{143}Nd/^{144}Nd)_{80}$ ratios is depicted in Figure 4. The felsic PC rocks plot to the right of and below the Bulk Earth (BSE) value (at 80 Ma); they have similar Sr but more primitive Nd isotopic characteristics than the EMI reference reservoir, and plot at the lower limit of the OIB field (*cf.* Zindler & Hart, 1986). The Sr isotope variations in the ultramafic rocks cover the same range as the felsic samples, with the exception of the silico-carbonatitic rock from MP and one of the agglomerates from VQ. Sr and Nd isotope data for the Lovozero and Khibina massifs, emplaced at about 370 Ma in the Kola Alkaline Province (Kramm & Kogarko, 1994), are also represented for comparative purposes, showing that PC rocks have similar Nd, but greatly evolved Sr isotopic characteristics; the PC rocks plot to the right of, and Lovozero and Khibina to the left of the BSE (at their crystallization ages).

The $(^{206}Pb/^{204}Pb)_{80}$, $(^{207}Pb/^{204}Pb)_{80}$, and $(^{208}Pb/^{204}Pb)_{80}$ isotopic ratios of the NeS and tinguaite rocks are similar and range between 17.9-18.3, 15.43-15.48, and 38.10-38.55, respectively. With the exception of two NeS and one tinguaite samples, $(^{208}Pb/^{204}Pb)_{80}$ and $(^{207}Pb/^{204}Pb)_{80}$ have a good positive correlation with $(^{206}Pb/^{204}Pb)_{80}$. In the $(^{207}Pb/^{204}Pb)_{80}$ vs $(^{206}Pb/^{204}Pb)_{80}$ diagram (Fig. 5) the data array plots close to the NHRL (Northern Hemisphere Reference Line, *e.g.*, Zindler & Hart, 1986) and define a *ca*. 2.2 Ga reference line, which probably represents some kind of a mixing array. The cited tinguaite and one of the NeS plot close to the Geochron In Figure 6, a plot of $(^{87}Sr/^{87}Sr)_{80}$ against $(^{206}Pb/^{204}Pb)_{80}$, the data cluster relatively close to the EMI reference reservoir.

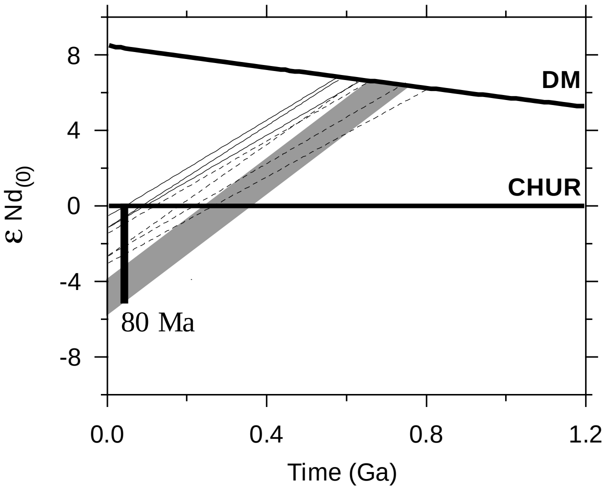

Figure 3. Isotope evolution of ε_{Nd} against time for NeS and tinguaites (dark area), VQ (dashed lines) and MP (solid lines) rocks from the Poços de Caldas Massif.

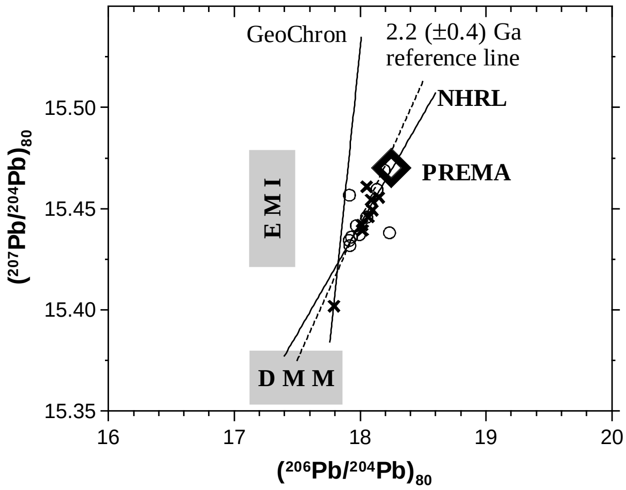

Figure 5. $(^{207}Pb/^{204}Pb)_{80}$ vs $(^{206}Pb/^{204}Pb)_{80}$ diagram showing the distribution of the NeS and tinguaites from Poços de Caldas and the present day compositions of some mantle reservoirs. Symbols as for Figure 2.

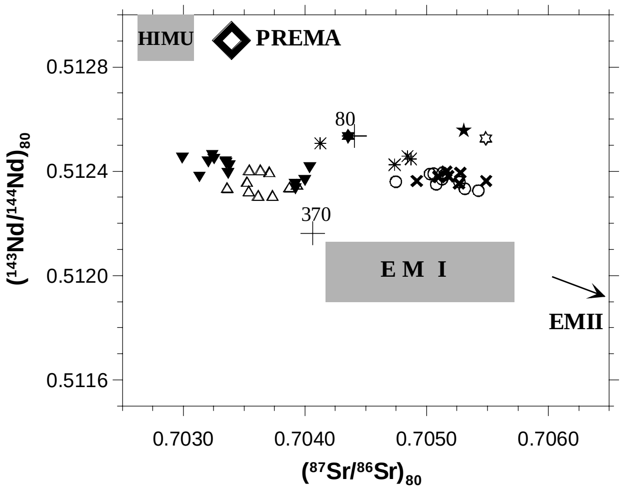

Figure 4. Sr-Nd isotope correlation diagram for the Poços de Caldas felsic and ultramafic rocks, showing also the present day compositions of typical mantle reservoirs. Symbols as for Figure 2. Inverted filled triangles: Khibina; normal triangles: Lovozero. Crosses are Bulk Earth compositions for the indicated ages.

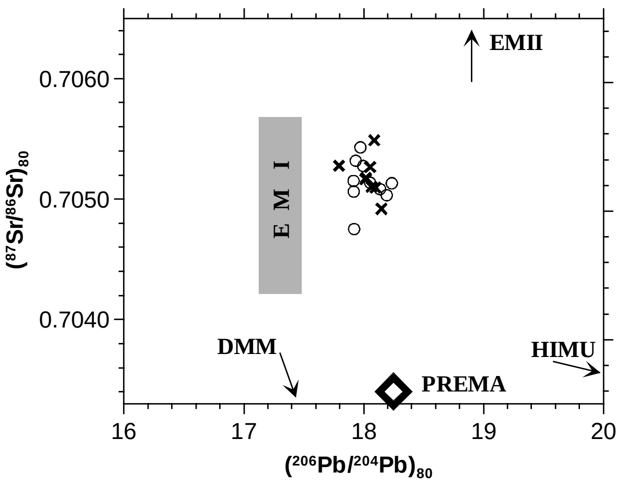

Figure 6. $(^{87}Sr/^{87}Sr)_{80}$ vs $(^{206}Pb/^{204}Pb)_{80}$ diagram showing the distribution of the Poços de Caldas NeS and tinguaites. Symbols and reservoirs as in previous figures.

PRELIMINARY DISCUSSION

The original NeS-phonolite magmas are clearly representative of end-member liquids collected in the undersaturated "low temperature valley" of the residual nepheline-kalsilite-quartz phase diagram, the data clustering around the minimum temperatures for a H_2O pressure of about 1 kbar. The absence of compatible elements (Cu, Ni, Cr and Co below d.l.) and the very low contents of MgO in almost all NeS and tinguaites strongly suggest extreme differentiation. The REE patterns are compatible with removal of clinopyroxene, titanite and/or apatite.

Three main hypotheses may account for the observed geochemical patterns: (1), a "wehrlitic" fractionation scheme trough the removal of clinopyroxene and Mg-olivine from parental ultrabasic nephelinite-like magmas; (2), low degree of partial melting of a similar alkaline ultrabasic protolith; and (3), low degree of fractional melting of an enriched mantle source followed by melt collection and homogeneization during ascent (*e.g.*, Kramm & Kogarko, 1994; Draper & Green, 1997). This latter possibility is less likely, on account of the absence of those incompatible elements and the low MgO values.

Our Sr-Nd isotope data, as well as those presented by Shea (1992) indicate contrasted sources for the VQ, MP, and the felsic rocks; the MP rocks are the most primitive in terms of the Nd isotopes. The data for NeS and tinguaites depict also some significant variations, considered at least in part as inherited features, each body of NeS and tinguaite presenting similar but proper isotope characteristics, in agreement with the petrographic and geochemical evidence (*e.g.*, Ulbrich and Ulbrich, 1992). Other variations could be acquired later during magma evolution and some of them may be related to localized felsic-ultramafic magma mixing phenomena. It is worth noting that most miaskitic NeS (the Pedreira syenites) and also some of the tinguaites contain augitic-bearing ultramafic enclaves and/or augite xenocrysts.

The isotope initial compositions of the felsic rocks do not support simple mixing relations between two or more of the typical mantle reference reservoirs in order to constrain the isotope compositions of their sources. A simple DMM-PREMA mixing relation, as suggested by the initial Pb composition variations in Figure 5, does not agree well with the observed Sr-Nd and Pb-Sr isotope initial ratios.

The enrichment in alcalies and trace elements in the NeS and tinguaites indicates that the magma generation event must have collected these elements from very large masses of mantle rocks, probably trough a preceding metasomatic episode, creating an enriched mantle source for later melting (*e.g.*, Kramm and Kogarko, 1994).

In any case, it appears that the main NeS and tinguaite bodies crystallized from discrete magma batches rather than being derived by crystal fractionation from the same parental magma.

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