

**GEOCHEMICAL AND Sr-Nd-O ISOTOPIC FEATURES OF THE POÇOS DE CALDAS  
ALKALINE MASSIF (SP-MG, SE BRAZIL): RELATIONSHIPS WITH THE  
SERRA DO MAR ANALOGUES**

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**Keywords:** Alkaline, syenite, phonolite, geochemistry, petrology

### INTRODUCTION

The Late Cretaceous Poços de Caldas intrusion, lying at the border between Minas Gerais and São Paulo States, extends for about 800 km<sup>2</sup>. It is the largest known alkaline complex of Brazil and one of the largest of the world.

A study of the Poços de Caldas alkaline massif has been carried out during the last decade in the framework of a Brazilian-Italian scientific cooperation, in order to characterize the mineralogical and geochemical composition of the Cretaceous-Paleogene alkaline, alkaline-carbonatite and tholeiitic complexes of SE Brazil, Paraguay and Uruguay. The results of this study indicated that the Poços de Caldas can be considered as the westernmost occurrence of the Serra do Mar Province (Thompson et al., 1998), the latter extending from the Cabo Frio area (Atlantic Ocean, SE Brazil; Bennio et al., 2002) to the southeastern end of the Alto Paranaíba Igneous Province (APIP; SE Brazil; Araújo et al., 2001; D'Amelio et al., 2003).

### GEOLOGICAL FRAMEWORK

The Poços de Caldas igneous complex forms a circular (ring) structure, about 28 km in diameter, emplaced between 78 and 76 Ma (Shea, 1992) mainly in the Guaxupé block, between the Paraná basin and São Francisco craton. The Guaxupé block separates the Brasília mobile belt from the Ribeira belt, where widespread alkaline-carbonatite and alkaline magmatism (with both potassic-ultrapotassic and sodic affinities) occurred during Late Cretaceous (Alto Paranaíba Province; 90-80 Ma; Gibson et al., 1995; Araújo et al., 2001), and Late Cretaceous to Paleogene (Serra do Mar Province; 80-54 Ma; Thompson et al., 1998), respectively.

The rock-types are potassic ( $K_2O/Na_2O$  generally  $>1$ ) phonolites (~ 80% of outcrops) and nepheline syenites (~ 14%). Pyroclastic rocks (mainly breccias), mainly found at the western margin of the massif in the Vale do Quartel, are agglomerate blocks of tephrite with subordinate ankaramite, nephelinite and phonotephrite with sodic affinity ( $K_2O/Na_2O < 1$ ; generally  $< 0.5$ ). Tephrite, trachybasalt and basaltic trachyandesite dykes

are present at the northwestern side of the complex. Mafic-ultramafic dykes of lamprophyric affinity occur within the Osamu Utsumi pit (Schorscher et al., 1991). Ultramafic lamprophyric (with alnöitic affinity) and silico-carbonatite dykes, intruding the Neoproterozoic quartz mangerites near the northern borders of the complex, are also present (Vlach et al., 1996). The presence of a carbonatite body at the Morro do Ferro mine was inferred by Waber (1992) through chemical balances on the Th-REE supergene mineralizations.

### PETROGRAPHY AND MINERAL CHEMISTRY

Phonolites are holocrystalline, aphanitic, fine-grained, and sometimes show "tinguaitic" textures. Porphyritic textures are occasionally present, with pheno- and microphenocrysts of alkali feldspar (Or 93-60 wt%), nepheline (with kalsilite content up to 30 wt%), clinopyroxene (from diopside core with mg# = 0.84 to hedenbergite and aegirine-augite rims with mg# = 0.48 and Ae up to 80 mol%), sphene and rare opaques (mostly Ti-magnetite), set in a groundmass made up of the same minerals. Common pseudoleucite (intergrowth of alkali feldspar and nepheline) and rare analcime, believed to be late metasomatic modifications, occur as phenocryst-like phase. Accessory minerals allow to distinguish peralkaline phonolites [i.e.,  $A.I.>1$ ;  $A.I. = (Na+K)/Al$ ], usually characterized by arfvedsonite, astrophyllite, eudialyte-eucolite, hainite, aenigmatite, sodalite, fluorite and other unidentified minerals (e.g., Atencio et al., 1999). Sphene and apatite are common accessories in the rare metalluminous rocks.

Nepheline syenites, phaneritic equivalent of the phonolites, in general contain less than 20 vol% of mafic minerals. Rarely, some eudialyte-rich variants (lujavrite) have up to 28 vol% clinopyroxene (Ulbrich, 1993). Medium- to coarse-grained hypidiomorphic textures are prevailing, and foyaitic (trachytic s.l.) textures are occasionally present. The main mineral assemblages are made up of alkali feldspar (Or = 83-54 wt%), nepheline (kalsilite content 15-28 wt%), clinopyroxene (from augite with mg# = 0.79 to aegirine with Ae up to 80 wt%) and occasional sodalite, amphibole (arfvedsonite) and biotite, the latter often appearing as substitution products of

clinopyroxene or as poikilitic aggregates. Zircon is an ubiquitous accessory mineral. Similar to the phonolitic rocks, accessory phases of the prevailing agpaite variants are eudialyte, hainite, rinkite, lamprophyllite and astrophyllite, that may have local importance (up to 14 vol.%, i.e. lujavrite and khibinite rocks; Ulbrich & Ulbrich, 2000). The prevailing accessories of the miaskite (metalluminous) variants are sphene, fluorite, magnetite, Ti-magnetite, ilmenite and sulphides.

Pyroclastic rocks are breccias, agglomerates, tuffites and surge deposits. Rounded to subangular blocks include ankaramite, basanite/tephrite and phonotephrite. The prevailing texture is aphanitic; the subordinate porphyritic rocks show diopsidic clinopyroxene (Wo 46-50, En 41-46) olivine (Fo 81-84), and Ti-magnetite pheno- and microphenocrysts set in a hypocrystalline groundmass made up of clinopyroxene, feldspar, biotite/phlogopite, opaques, altered olivine and analcime. Some analcime-like phenocrysts show leucite remnants at the core (Thompson et al., 1998). Variants rich in clinopyroxene megacrysts (up to 4 cm long) have been classified as ankaramites.

Dykes are usually phlogopite-rich rocks, having petrographic evidence of lamprophyric affinity (Schorscher et al., 1991; Waber et al., 1992). According to the TAS classification scheme some rock-types can be classified as basanites, trachybasalts and basaltic trachyandesites. The texture is porphyritic with mega-, macro-, pheno- and microphenocrysts of clinopyroxene (hedenbergitic core with diopside rims), phlogopite/biotite phenocrysts and olivine pseudomorphs (unaltered cores with Fo 80-75), set in a groundmass of hedenbergitic clinopyroxene, phlogopite, opaques and altered glass. In particular, ultramafic lamprophyre dykes of the Osamu Utsumi mine are characterized by high phlogopite and clinopyroxene contents (25-35 and 27-36 vol%, respectively) with some variants having up to 40-45 vol% groundmass carbonate, pointing to a carbonatitic affinity (e.g., Schorscher et al., 1991).

## GEOCHEMISTRY

Over 150 samples were analyzed by XRF and 30 most representative samples were re-analyzed by ICP-MS techniques. TAS classification clearly evidences a bimodal distribution with clusters in the phonolite-tephriphonolite and the basanite/tephrite-phonotephrite fields.

$K_2O/Na_2O$  ratio allows to distinguish a low to medium potassic affinity ( $K_2O/Na_2O$  mostly between 0.6 and 1.5) for the phonolite/nepheline syenite clan, versus the sodic affinity of the mafic blocks ( $K_2O/Na_2O < 1$ ). High-K compositions characterize the mafic-ultramafic lamprophyres ( $K_2O/Na_2O = 4.1-8.7$ ). Blocks and dykes are distinguishable from the phonolite/nepheline syenite association also on the basis of their lower A.I. (0.61 to 0.92 for blocks/dykes and 0.89-1.38 for phonolite/nepheline syenite). The Poços de Caldas samples plot in the field of the corresponding types of Serra do Mar and Trindade-Martin Vaz islands. Only some phonolite/nepheline syenite plot to the right of the

above mentioned field; these K-rich compositions can be considered the result of late stage K-metasomatism.

Major and trace element content of the Poços de Caldas products evidence an overall similarity with the correspondant rock-types of the Serra do Mar; the only exception are some K-rich phonolites and nepheline syenites that do not find any corresponding composition in the Serra do Mar products.

In primitive mantle-normalized incompatible element diagrams, phonolites and nepheline-syenites (both peralkaline and metaluminous) display parallel and overlapping patterns, similar to the analogues from Serra do Mar and Trindade-Martin Vaz. The basanite-phonotephrite-ankaramite association of Poços de Caldas shows more flattened patterns, similarly to that observed for the phonolite/nepheline-syenite association, overlapping the fields of the Serra do Mar and Trindade-Martin Vaz basic rocks. The Poços de Caldas lamprophyres show strong U, La, Nd, Eu, Y and HREE enrichment.

## Sr-Nd ISOTOPES

The Poços de Caldas data set forms almost two distinct groups: the first (phonolite/nepheline syenites, phonotephrites and lamprophyres) clusters into an intermediate position between the Alto Paranaíba and Serra do Mar basic rock-types; on the other hand, the Poços de Caldas basanite-tephrite-ankaramite group plots in the field of the Serra do Mar and Trindade-Martin Vaz basic rocks. Two samples with highest  $^{87}Sr/^{86}Sr$  values represent hydrothermal partially altered rocks, rather than contaminated magmas, considering all the geochemical parameters (e.g., Waber et al., 1992).

No systematic comparison between the Poços de Caldas rocks and the phonolite/nepheline syenite suite of the Serra do Mar province can be done due to the virtual absence of data on the latter outcrops. From the available Sr-Nd isotopic analyses a strong similarity between basanites (s.l.) and phonolite/nepheline-syenites (s.l.) of the Serra do Mar can be envisaged. This similarity is observed also among the rocks of Trindade-Martin Vaz, but not among those of Poços de Caldas. In the latter ones, samples of lamprophyric dykes show low  $^{87}Sr/^{86}Sr_{78Ma}$  (0.70323), similar to the samples from Serra do Mar.

## OXYGEN ISOTOPE COMPOSITION

Preliminary analyses on separate minerals have been performed via laser fluorination on clinopyroxenes from nepheline syenite (3), ankaramite (1), basaltic trachyandesite (1), tinguaita (1), phonolite (1) and lamprophyre (3). With the exception of two lamprophyres showing low  $\delta^{18}O$  values (down to 2.88‰), the  $\delta^{18}O_{SMOW}$  values of the analyzed clinopyroxenes are uniform ( $\delta^{18}O = 5.54 \pm 0.16\%$ ). The extremely low  $\delta^{18}O$  of the clinopyroxenes from lamprophyres are possibly related to high temperature isotopic exchange with meteoric/hydrothermal fluids that percolated along fractures or faults. Groundmass calcite of a basaltic trachyandesite breccia has been analyzed for oxygen and carbon isotopic ratios and the results ( $\delta^{18}O = 23.32$ ;

$\delta^{13}\text{C}_{\text{PDB}} = -1.75$ ) are compatible with upper crustal provenance, excluding any primary (e.g., carbonatitic) origin of the carbonate.

#### CONCLUSIVE REMARKS

The Poços de Caldas massif is a composite alkaline complex. It was formed by multiple magmatic intrusions with phonolite/nepheline-syenite composition, and by basanite-tephrite-ankaramite volcanic rocks successively intruded by phonotephritic and lamprophyric dykes.

On geochemical basis a common origin of the Poços de Caldas complex and the Serra do Mar igneous provinces can be inferred. Similar major and trace elements contents of the Poços de Caldas and the Serra do Mar and Trindade-Martin Vaz rocks suggest a similar mantle source, as formerly proposed by Thompson et al. (1998). Lithospheric and sublithospheric mantle sources may have been mobilized by the Trindade mantle plume during the westward movement of the South American plate during the Cretaceous-Eocene. However, the Sr-Nd isotope data indicate that the phonolite/nepheline-syenite rocks from Poços de Caldas are more (Sr) and less (Nd) radiogenic when compared to the Serra do Mar and Trindade-Martin Vaz analogues. The mantle sources of the Poços de Caldas products are much more homogeneous in terms of oxygen isotopic ratios. The lower  $\delta^{18}\text{O}$  of some lamprophyres can be related to meteoric/hydrothermal alteration during the late stages of consolidation of the magma.

#### REFERENCES

- Araújo A.L.N., Carlson R.W., Gaspar J.C. and Bizzi L.A., 2001. Petrology of kamafugites and kimberlites from the Alto Paranaíba alkaline province, Minas Gerais, Brazil. *Contrib. to Mineralogy and Petrology* 142, 163-177.
- Atencio, D., Coutinho, J.M.V., Ulbrich, M.N.C. and Vlach, S.R.F., 1999. Hainite from Poços de Caldas, Minas Gerais, Brazil. *The Canadian Mineralogist* 37, 91-98.
- Bennio L., Brotzu P., Gomes C.B., D'Antonio M., Lustrino M., Melluso L., Morbidelli L. and Ruberti E., 2002. Petrological, geochemical and Sr-Nd isotopic features of alkaline rocks from the Arraial do Cabo Frio peninsula (Southeastern Brazil). *Period. di Mineralogia* 71, 137-158.
- D'Amelio F., Ruberti E., Gomes C.B., Lustrino M., Melluso L., Morbidelli L. and Morra V., 2003. Clinopyroxene and perovskite partition coefficients in kamafugitic rocks. *Proc. EGS-AGU-EUG Joint Assembly 2003*, Nice, France.
- Gibson, S.A., Thompson, R.N., Dickin, A.P. and Leonardos, O.H., 1995. High-Ti and low-Ti mafic potassic magmas: key to plume-lithosphere interactions and continental flood-basalt genesis. *Earth and Planetary Sci. Lett.*, 136, 149-165.
- Schorscher, H.D., Garda, G.M., Shea, M.E. and Waber, N., 1991. Lamprophyre dykes from the Osamu Utsumi uranium mine, Poços de Caldas (MG), Brazil. *International Symposium on Mafic Dykes*, São Paulo, Extended Abstracts Volume, pp. 116-124.
- Shea, M.E., 1992. Isotopic geochemical characterization of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil. *Journal of Geochemical Exploration* 45, 173-214.
- Thompson, R.N., Gibson, S.A., Mitchell, J.G., Dickin, A.P., Leonardos, O.H., Brod, J.A. and Greenwood, J.C., 1998. Migrating Cretaceous-Eocene magmatism in the Serra do Mar alkaline Province, SE Brazil: melts from the deflected Trindade mantle plume? *J. Petrology* 39, 1493-1526.
- Ulbrich, H.H.G.J. and Ulbrich, M.N.C., 2000. The lujavrite and khibinite bodies in the Poços de Caldas alkaline massif, southeastern Brazil: a structural and petrographical study. *Revista Brasileira de Geociências* 30, 615-622.
- Ulbrich, M.N.C., 1993. Mineralogy of nepheline syenites from the Poços de Caldas alkaline massif, SE Brazil: chemistry, X-ray data and microtextures of feldspars. *Revista Brasileira de Geociências* 23, 388-399.
- Vlach S.R.F., Ulbrich, M.N.C. Ulbrich, H.H.G.J. and Garda, G.A.R., 1996. Rochas de afinidades alnoíticas e silico-carbonatíticas periféricas ao maciço alcalino de Poços de Caldas (Mg-Sp). *XXXIX Congresso Brasileiro de Geologia*, Anais 2, 128-130.
- Waber, N., 1992. The supergene thorium and rare-earth element deposit at Morro do Ferro, Poços de Caldas, Minas Gerais, Brazil. *Journal of Geochemical Exploration* 45, 113-157.
- Waber, N., Schorscher, H.D. and Peters, Tj., 1992. Hydrothermal and supergene uranium mineralization at the Osamu Utsumi mine, Poços de Caldas, Minas Gerais, Brazil. *Journal of Geochemical Exploration* 45, 53-112.