PHLOGOPITE FROM CARBONATITIC VEINS ASSOCIATED WITH THE POÇOS DE CALDAS ALKALINE MASSIF, SE BRAZIL: MINERALOGY AND $^{40}Ar/^{39}Ar$ DATING BY THE LASER STEP HEATING METHOD

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INTRODUCTION

A large number of geochronological data (mainly K-Ar and Rb-Sr) are known for the alkaline rocks of the Poços de Caldas alkaline massif, states of São Paulo and Minas Gerais (*e.g.*, Thompson et al., 1998; Ulbrich et al., 2002), mostly from older publications. In part, the data are incompatible with geological relationships or their precision is very low, and no consensus has been reached about the best age and age interval for the emplacement of the main felsic alkaline and related ultramafic magmatic events in that district. High precision and well-constrained age determinations are needed to solve the problem.

Ultramafic rocks closely related to the main felsic Poços de Caldas magmatism crop out near the northern contact of the massif, intruding Neoproterozoic basement rocks. They comprise ultramafic lamprophyric types and silico-carbonatitic rocks with associated late carbonatitic veins.

We present in this report mineralogical data and incremental laser step-heating $^{39}Ar/^{40}Ar$ ages for a phlogopite of one of those late hydrothermal veins. The results suggest a minimum age of about 84 Ma for the phlogopite crystallization and vein formation. Possible meanings of this result are addressed in the light of the existing geological and geochronological data for the alkaline and related rocks within the Poços de Caldas massif.

GENERAL GEOLOGY AND PETROGRAPHY

The ultramafic rocks appeared in the April, 1996, mining front, as a number of sub-vertical to steeply dipping dikes up to 2m wide and a somewhat larger breccia zone (up to 15–20m), in the Minas Pedras quarry (UTM coordinates: 7592573N 331954E). They cross cut highly deformed and partially migmatitic Neoproterozoic quartz-mangerites and are closely associated with larger phonolitic dikes doubtlessly related to the Poços de Caldas felsic magmatism.

The main lithotypes are an aphanitic silico-carbonatitic rock (up to 40 % vol. carbonate), massive or with flow structure, a massive fine grained phlogopite-rich rock with abundant carbonate ocelli and pseudomorphosed macrocrysts after olivine and/or pyroxene (now phlogopite-pyroxene-amphibole-ilmenite aggregates), and a laminated medium-grained facies with alternating phlogopite-rich and carbonate-rich layers. The breccia facies contains fragments of the country rocks and silico-carbonatitic, phlogopite-rich material in variable amounts. Preliminary petrographic, chemical, and isotopic characterizations of these rocks were presented by Vlach et al. (1996, 1998) and Ulbrich et al. (1998).

The massive varieties may be somewhat younger than the phonolites, as they contain cm-sized, partially fenitized, enclaves of the latter, but these features could also be due to the very contrasting viscosities of such magmas and their emplacement could be roughly coeval.

Several late, hydrothermal, carbonatitic veins (5-20 cm wide) cut all these rocks. Some of them are made up of almost pure calcite, others contain calcite + fluorite, calcite + phlogopite + fluorite, calcite + phlogopite + magnetite + apatite, calcite + phlogopite + fluorite ± albite. Occasionally they present thorite, REE-fluorcarbonates, and other rare accessory minerals.

ANALYTICAL METHODS

Clean euhedral phlogopite crystals (*ca.* 1-2 mm diameter on basal sections) from a selected calcite + phlogopite + fluorite vein were carefully handpicked under a stereomicroscope for X-ray diffratometry (XRD), electron microprobe (EPMA), and isotopic studies at the laboratories of the Instituto de Geociências of University of São Paulo.

A XRD powder pattern was obtained in the 5-65° 2θ interval for the CuKα radiation; pure quartz was added as an internal standard. About 40 reflections were chosen for cell refinement with the LCLSQ software (Burnham, 1962). The EPMA work included electron back-scattered imaging (BSE) and chemical quantitative spot analysis (WDS). The analytical conditions were 15 keV, 20 nA and 1 (BSE) or 5 (WDS) µm for the beam accelerating voltage, current, and diameter, respectively. Minerals and synthetic compounds were used as chemical standards. Matrix effects in quantitative analysis were corrected with a PROZA procedure.

$^{40}Ar/^{39}Ar$ dating analyses by the laser step heating method were made at the Centro de Pesquisas Geocronológicas on three phlogopite grains, previously washed with pure alcohol. Analytical procedures and data treatment are described in Vasconcelos et al. (2002).

MINERAL DATA

In petrographic thin sections, the phlogopite crystals from the studied carbonatitic vein are very clean. They do not present any kind of alteration or inclusions, and show a weak pleochroic scheme in pale yellow (α) to orange (β ≈ γ). They present a distinct zoning pattern, with euhedral cores surrounded by also euhedral discrete rims with somewhat less intense pleochroic colours.

The computed cell parameters, in Angstroms, for the studied phlogopite are a_0 = 5.3489 (1), b_0 = 9.2560 (3), c_0 = 20.2460 (7), β angle 94.730° (1), with a cell volume = 998.96 (1) $Å^3$. These results are compatible with a $2M_1$ structural polytype.

BSE imaging of phlogopite grains shows that the crystal rims have low back-scaterred coefficients and that both cores and rims present a very weak recurrent compositional zoning. Representative WDS analytical data for core and rims appear in Table 1.

Table 1. Representative chemical phlogopite analyses (WDS). c = core, r = rim, bd = below detection limit.

Spot	**4, c**	**2, r**		**4, c**	**2, r**
Oxides			***Cations***		
SiO_2	42.63	43.75	Si	6.356	6.463
TiO_2	1.55	1.10	Ti	0.174	0.123
Al_2O_3	9.10	8.80	Al	1.596	1.531
Cr_2O_3	bd	bd	Fe^{II}	1.372	1.088
FeO	10.92	8.81	Cr	0.000	0.000
MnO	1.58	1.43	Mn	0.199	0.178
MgO	18.01	19.30	Mg	4.000	4.250
NiO	0.04	bd	Ni	0.000	0.000
ZnO	0.10	0.10	Zn	0.010	0.010
CaO	bd	bd	Ca	0.000	0.000
BaO	0.04	0.06	Ba	0.002	0.004
Na_2O	0.35	0.34	Na	0.101	0.098
K_2O	9.94	10.08	K	1.889	1.900
F	4.78	4.86			
Cl	bd	bd	Sum	15.669	15.635
(O=F)	2.01	2.05			
Sum	96.89	96.49	mg#	74.46	79.62

The phlogopite from the carbonatitic vein has more than 6 Si c.p.f.u. and low Al contents. All Al cations are in tetrahedral sites. Ti and Ba contents are relatively low, F contents and mg# numbers are in the range 4.4 – 5.1 wt. % and 74.4 (core) and 79.7 (rims), respectively.

The compositional variations depict a slightly inverse and recurrent zoning pattern in the studied crystal, and its core is somewhat richer in Ti, Al, Fe, and Mn and poorer in Mg, Ba, and F than the rims. The main chemical variations within core, intermediate zones and rims are illustrated in Figures 1A, B, and C) for that single crystal. In general, Al_2O_3 shows a negative correlation with mg# in all those zones, a positive one with FeO^T and TiO_2 in the core and intermediate zones and a slightly negative one in crystal rims.

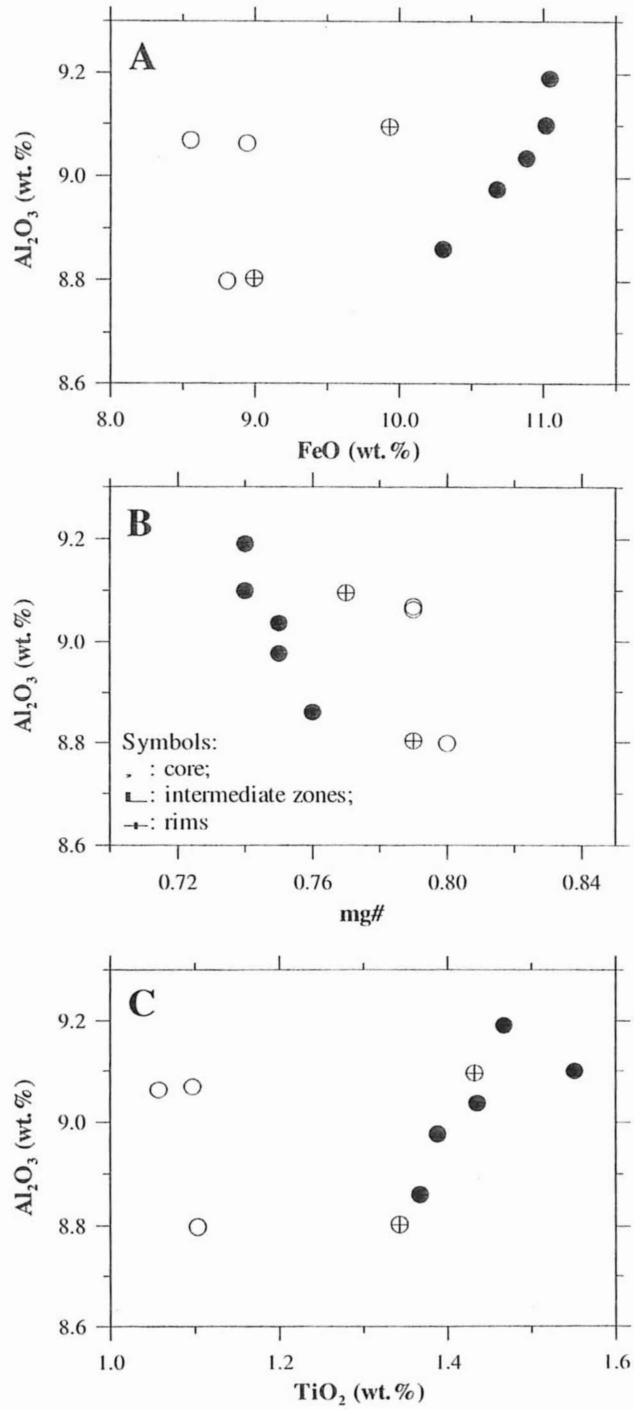

Figure 1 (A,B,C). Variation diagrams showing the main chemical trends for a single phlogopite crystal. mg# = $Mg/(Mg+Fe^{II})$, cation ratio.

$^{40}Ar/^{39}Ar$ DATING RESULTS

The dating results for the three analysed phlogopite grains are presented in Table 2. All crystals gave well-defined plateau and also integrated ages. Apparent ages for grains 1 and 2 are very concordant, in the 83.7 – 84.3 Ma range, while grain 3 yields a somewhat younger but close result, about 83.1 – 83.5 Ma.

Table 2. $^{39}Ar/^{40}Ar$ dating results for vein phlogopite.

Grain	Plateau age (Ma)	Dev. $\pm 2\sigma$	Step N	Integrated age (Ma)	Dev. $\pm 2\sigma$
1	83.8	0.2	4	84.1	0.1
	84.0	0.2	3		
2	84.3	0.2	5	84.3	0.1
3	83.5	0.2	2	83.1	0.1

The step heating ^{39}Ar release pattern from the grain 1 phlogopite, presenting two close and good plateau ages, is reproduced in Figure 2.

A summary including all data is presented in the ideogram displayed in Figure 3, which depicts a somewhat higher probability age peak at about 84.3 Ma and a minor one at 83.5 Ma. A value of 83.9 ± 0.3 (2σ), the weighted average of all measurements, is considered here as the best estimate for the age of the Ar isotopic system closure within the studied phlogopite.

DISCUSSION

Our results put some additional constraints on the geochronology of the Poços de Caldas alkaline massif and associated rocks, and also pinpoint the need for more geologically constrained geochronological work to elucidate the main age patterns within the massif.

In a recent review based on geological, paleomagnetic data, and all published ages for the Poços the Caldas rocks, Ulbrich et al. (2002) suggest a value of about 79 Ma as the best mean age for the emplacement of the main nepheline syenites and phonolites in the district. The authors suggest also a short time interval of about 1-2 Ma for the whole felsic magmatism.

Previous dating of Poços de Caldas ultramafic rocks comprise two older K-Ar results for from *ankaratrites* (*ca.* 89 and 78 Ma, whole rock, *cf.* Amaral et al., 1967) and two $^{40}Ar/^{39}Ar$ ages (75.7 ± 0.3 and 76.2 ± 0.8 Ma) for phlogopite from a fresh lamprophyric dike cutting across hydrothermally altered nepheline syenites and phonolites, the so-called "potassic rocks", in the Osamu Utsumi open pit uranium mine (Shea, 1992). A Rb-Sr isochron presented by Shea for these felsic hydrothermalized rocks gave a similar value of 76 (±1) Ma. Ulbrich et al. (2002) report also an age of 79 (±3) Ma obtained for thorite grains from another carbonatitic vein of the Minas Pedras quarry, with the Th-U-total Pb dating method by the electron microprobe.

The contrasting results obtained for the ultramafic rocks from Osamu Utsumi and Minas Pedras need some additional discussion, since there is no clear geological argument indicating one or more ultramafic rock emplacement events in the massif. There is always the possibility that one of the $^{40}Ar/^{39}Ar$ ages, or both, reflect either Ar excess or loss in the phlogopite system, although the ^{39}Ar release patterns in our data, or in those presented by Shea (1992), do not suggest significant disturbance. This question can only be correctly addressed with independent new high-precision age determinations.

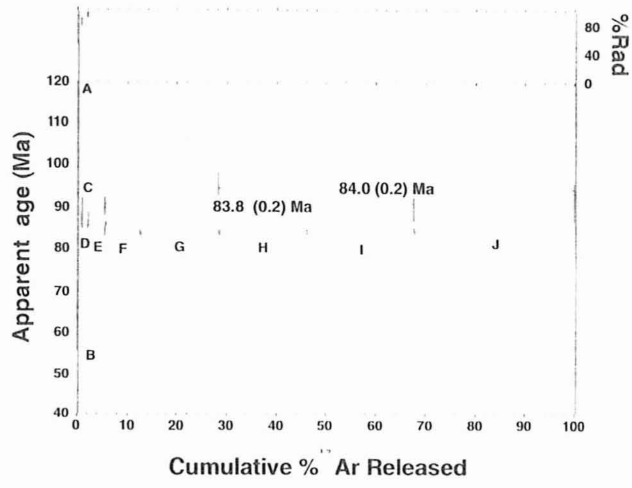

Figure 2. Step heating incremental ^{39}Ar release pattern plotted against apparent ages for the vein phlogopite (grain 1).

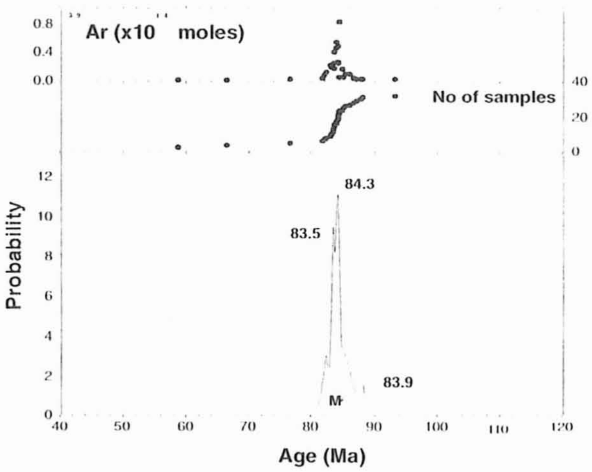

Figure 3. Ideogram showing the apparent age distributions against probability for vein phlogopite (grains 1, 2, and 3). M is the weighted average.

With these remarks in mind, the following conclusions can be reached with the data at hand:

1. Both dating results may be very close to the real phlogopite crystallization age and, therefore, of the age of vein and dike formation. In the Minas Pedras case, the phlogopite crystallized under a low-temperature hydrothermal environment, possibly not much higher than *ca.* 300-350° C, the closure temperature for the $^{40}Ar/^{39}Ar$ system and so the apparent ages should be very close to the real crystallization ages. The phlogopite in the Osamu Utsumi dike formed at a high magmatic temperature, and the measured ages will approach real ages only if the cooling down to *ca.* 300° C was fast. If this were the case, then at least two main episodes of carbonatitic-related ultramafic magmatism did occur.

The geological evidence at the Minas Pedras quarry suggests that at least some of the ultramafic rocks crystallized at the same time as the felsic phonolitic dikes. Similarly, the phlogopite-bearing rock in the Osamu Utsumi pit dated by Shea (1992) is at least coeval with the main hydrothermal event that followed the emplacement of the nepheline syenites and phonolites. If these figures are meaningful, then the Minas Pedras and Osamu Utsumi $^{40}Ar/^{39}Ar$ ages could date the beginning and the end of the magmatism in the district, in a minimum interval of about 8 Ma.

A mean age around 80 Ma for the felsic magmatism peak (Ulbrich et al., 2002), constrained by paleomagnetic data, which was considered also as a minimum reference age by Thompson et al. (1998) for the whole massif, is in this context still a good reference value, until high-precision ages will be available.

2. Despite its fresh aspect, another possibility is that the the ultramafic dike from the Osamu Utsumi open pit may have been subjected to late resetting at around 76 Ma, as hydrothermal alteration is widespread in the internal parts of the Poços de Caldas Massif. In this case, considering whole rock the Rb/Sr data, a minimum interval for the whole magmatism of about 5 Ma would fit better the available geocrhonological data.

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