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ANALES XXXIV

ELECTRON MICROPROBE MONAZITE DATING: FIRST RESULTS FOR TWO GRANITES FROM SOUTHEASTERN BRAZIL

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INTRODUCTION

Chemical dating of Th-U minerals is and old technique pioneered by A. Holmes. The interest on this systematic renewed later years as the result of both instrumental and micro-analytical improvements. The application of the electron microprobe (EPMA) to Th(U)-Pb minerals dating specially monazites has been explored successfully in several recent papers and appears to be a very promising technique (*e.g.*, Susuki and Adachi, 1991; Montel *et al.*, 1996; Rhede *et al.*, 1996). EPMA dating has the advantages of its non-destructive character, the high spatial resolution, short sample preparation and analytical times, and also low costs. Probers are able to see exactly what they are analyzing and can look for contrasting monazite generations within a thin section or distinct areas in a unique grain for an independent spot analysis. On the other hand, the attained precision is significantly lower compared with the isotopic methods. In this way, EPMA dating can be a great tool for preliminary geochronological and crustal evolution researches, to be refined and complemented with more elaborated isotopic work, not to replace it.

We present here a brief report on the analytical and data treatment procedures adopted at our microprobe laboratory at the very beginning as well as the first results for two selected granite occurrences.

SAMPLES AND METHODOLOGY

Selected thin polished sections of the Nazaré Paulista and Pinhal granite occurrences from São Paulo State, Southeastern Brazil, were chosen for testing the monazite EMPA dating method. The sampled granites are monazite- bearing peraluminous types with Brasiliano ages (*ca.* 580-630 Ma; see Janasi and Ulbrich, 1991, for a general review). After a preliminary petrographic study, a single section of each granite type was chosen for detailed EMPA analysis.

ANALYTICAL PROCEDURES

The analytical work was carried out with a JEOL-JXA8600 microprobe equipped with five WDS spectrometers and an NORAN-Voyager automation system at the Instituto de Geociências, Universidade de São Paulo. A fast EDS qualitative analysis was performed if needed to identify suspected monazites after the petrographic work. Backscattered electron imaging was employed to reveal compositional contrasts within the monazite grains as well as to locate beam spots for the quantitative WDS analysis.

The analytical conditions included an accelerating potential of 15kV and a probe current of 300 nA. Such a relatively low voltage seems not to be the best choice for analysis if one considers only peak/background counting ratios for most monazite-forming elements but allows a better spatial resolution and reduces the absorption corrections significantly, as our JEOL machine have a take-off angle of 40°. By using a defocused 5 nm beam we did not verify damage to a significant extent on our samples even for the long counting times used (see below).

Combining the spectrometers of our machine, one with TAP, one with LIF and the remaining with PET crystals we were able to perform almost complete monazite analysis even maintaining dedicated PET spectrometers for both U and Pb counting. X-ray spectral lines and total counting times were as follows: $K\alpha$ for Si (20s), Ca (20s), and P (20s); $L\alpha$ lines for Y (20s), La (20s), and Ce (20s); $L\beta$ for Pr (30s), Nd (20s), Sm (40s), Gd (40s), and Dy (40s); $M\alpha$ lines for Th (200s) and Pb (400s); and $M\beta$ for U (400s). Counting times were equally distributed between peak and background, an imposed constrain of our software. Careful wavelength scans over monazite samples and standards allowed the best background positioning avoiding the Th Mζ and La Lα influences on Pb Mα. The Y Lγ interference on Pb Mα was minimal for our samples with relatively low Y contents and was corrected by a simple out-of-run procedure. The matrix correction and data reduction were computed with the PROZA software included in the NORAN-Voyager system.

Wollastonite (Si, Ca), synthetic phosphates (REE and P), Y-garnet, ThO_2, UO_2 and the 95IRW Corning glass with 0.7 % wt. Pb were chosen as main standards; calibration and sample measurement results were checked in-run with the REE (Drake and Weill, 1972), and the NIST 610 and 612 glasses. Identification Limits, as defined by Ancey *et al.*, 1977 (*in* Merlet and Bodinier, 1990) as low as 70 ppm, 100 ppm and 150 ppm for Pb, U and Th respectively, could be achieved in our measurements. The deviations (2σ) due to X-ray counting statistics were always lower than 1% for Th and 4% for U and Pb.

AGE CALCULATIONS

The accumulation of radiogenic Pb (Pb_{acc}) within a Th-U closed natural system as a function of time (*t*) is given by the following general equation:

$$Pb_{acc} = \frac{208 * Th}{232} * \left[\exp\left({}^{232}\lambda * t\right) - 1\right] + \\ + \frac{0.9928 * 206 * U}{238.04} * \left[\exp\left({}^{238}\lambda * t\right) - 1\right] + \\ + \frac{0.0072 * 207 * U}{238.04} * \left[\exp\left({}^{235}\lambda * t\right) - 1\right] \quad \text{(I)}$$

where the elemental concentrations are given in ppm, ${}^{232}\lambda$, ${}^{238}\lambda$, and ${}^{235}\lambda$ are the decay constants of ${}^{232}Th$, ${}^{238}U$, and ${}^{235}U$, respectively, and *t* is given in Ma. In such a form equation (I) gives us a mean Th-U-Pb *date* for that system, for instance our monazites. It can also be rearranged as an equation of a plane within the Th-Pb_{acc}-U space to give independent Th-Pb and U-Pb *dates* (Rhede *et al.*, 1996).

The resulting *dates* will have geological meaning and so the status of *ages* provided that the system remained closed, that is to say, the Th, U and Pb concentration changes were due only to radioactive decay phenomena, and that the non-radiogenic Pb contents can be considered negligible. A brief discussion of these assumptions concerning monazites as well as several good arguments for consider them valid in most common geological situations are given in Montel *et al.* (1996).

Solving equation (I) is not so straight and easy. We have developed a simple procedure with a commercial spreadsheet using the pertinent analytical data input (Th, U and Pb contents and the 95% confidence counting deviations). An approximate age is evaluated at a first step by applying the empirical formula (see also Bowles, 1990):

$$t = \frac{7550 * Pb_{acc}}{U + 0.36 * Th} \quad \text{(II)}$$

In the next step, the precise age is computed by iterating equation (I). Our results for each analytical spot include the age and its uncertainty obtained by two approaches. One (1) gives the direct *t* solution; the uncertainties being calculated by propagating the elemental content deviations on equation (1). The other solution (2) comes from Monte Carlo modeling, taking into account an expected normal random age distribution within the 95% confidence limits.

The sample age results are interpreted following the suggestions of Hurford *et al.* (1984, see also Montel *et al.*, 1996). We plot the probability density function (Y) for each analytical spot as defined by its age and the corresponding standard deviation. The sum of the *n* probability functions of the *n* spots (the *weighted histogram* of Hurford et al., 1984) allows a qualitative analysis concerning the modal character of the entire population. So one can judge if the data dispersion is consistent with a normal uni-modal age distribution (and thus one geologic event should be inferred) or some more complex situations with 2- or 3-modal distributions. The samples we study at this stage fit well the uni-modal case and we did not make any special attempt for a more rigorous quantitative population data treatment. The computed final results are a mean population age and its (95%) uncertainty as given by the classical modeling applied to a population with a normal distribution (see Montel *et al.*, 1996).

RESULTS

Representative analyses for monazites are shown in Table 1. They are Ce-monazites, which show well developed concentric or complex zoning patterns as revealed by the backscattered images; the clearest areas being mostly associated with the highest Th contents. All monazite grains shows a slight M- and H-REE contents increase towards the crystal rims. ThO_2, UO_2, and PbO % wt. values vary in the range 7.80-5.00, 8.00-5.00, and 1.150-0.110, 0.550-0.110, and 0.285-0.185, 0.210-0.175, respectively for the Nazaré Paulista and Pinhal granite samples.

Table 1. Representative monazite spot analysis for the Nazaré Paulista (NP) and Pinhal (PH) granite samples.

%Wt. Oxide	NP1 center	NP1 rim	PH2 center	PH2 rim
SiO_2	0.12	0.10	0.15	0.20
ThO_2	5.84	7.57	6.21	5.05
UO_2	0.318	0.352	0.490	0.595
Y_2O_3	0.32	0.35	0.54	0.60
La_2O_3	17.20	14.05	14.59	14.65
Ce_2O_3	31.45	29.50	30.08	30.35
Pr_2O_3	2.95	3.07	3.11	3.16
Nd_2O_3	9.54	11.01	10.74	11.54
Sm_2O_3	1.23	2.22	1.63	2.20
Gd_2O_3	0.40	0.65	0.56	0.60
Dy_2O_3	*nd*	0.30	0.30	0.35
CaO	0.45	0.50	0.89	0.76
PbO	0.170	0.238	0.205	0.174
P_2O_5	30.18	30.05	30.05	29.90
Sum	**99.87**	**100.27**	**99.54**	**99.80**

The resulting chemical monazite ages are within the 635-580 and 630-570 Ma range. The ages computed for each spot by applying the approaches (1) and (2) are almost identical and do not differ by more than 1 Ma in all cases. The 95 % confidence deviation range between 17 and 31 Ma, the Monte Carlo simulation giving a somewhat more conservative estimate 4-5 Ma higher than those derived from model (1).

Fig. 1 displays the probability density (Y) function plots for the Nazaré Paulista sample. It displays the Y function for each individual age determination and the *weighted histogram* of the entire sample population. The normal uni-modal character of the data is easily deduced from the almost perfect normal distribution of the later. The diagram also shows the Y function for the population mean and its standard deviation resulting from the numerical computing. As expected, the uncertainty for the population age mean is greatly reduced: we obtain a value close to 12 Ma. Similar diagrams and conclusions were drawn for the Pinhal sample and will not be repeated in this report.

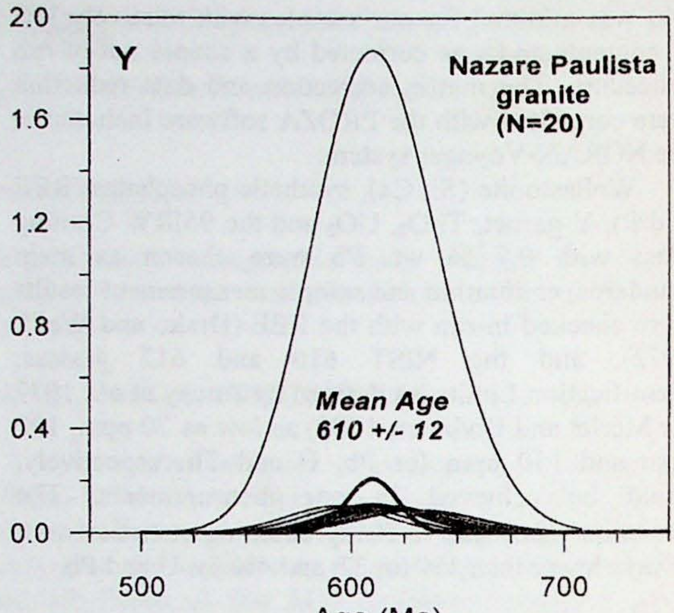

Figure 1. Representation of the probability density functions (Y) for the spot ages, the mean population age (heavy centered curve), and the corresponding *weighted histogram* for the Nazaré Paulista sample.

The final results for the Nazaré Paulista and Pinhal samples after the procedures outlined above are summarized and compared with independent isotopic age results in Table 2. Taking into account the uncertainties our results are very close to the later, reinforcing the good applicability of the EPMA dating technique for monazites.

The granite textures suggest that monazites were a relatively early precipitating phase from granite melts. The expected monazite closing temperatures are in the 600-700° C range for leucogranitic systems so our results are excellent approximations for the real granite crystallization ages, as justified also by the independent isotopic age results.

FINAL REMARKS

We presented a summary of the analytical and data treatment procedures for chemical monazite dating with the electron microprobe at the Instituto de Geociências - USP- at the very beginning. The main difference of our systematic with the previous works

Table 2. Monazite EPMA and isotopic ages for the selected granite occurrences. N is the number of individual spot determinations. The isotopic data are from V.A. Janasi (unpublished data).

Granite type	EPMA age (Ma)	Isotopic age (Ma)
Nazaré Paulista	610 +/- 12 (N = 20)	625 +/-12
Pinhal	600 +/- 10 (N = 15)	611 +/- 5

(Suzuki and Adachi, 1991; Montel *et al.*, 1996; Rhede *et al.*, 1996) is in the capability of our machine that allows almost complete in-age-run monazite analysis and as a consequence a more precise matrix correction. Identification Limits and counting deviations were also reduced to a significant extent in our measurements.

Future work will explore the method with a more systematic research on medium- to high-grade metassedimentary and associated granite belts cropping out in Southeastern Brazil. We intend also to develop a more complete and comprehensive statistical data treatment concerning discrimination within n-modal age distributions.

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