

STUDY OF THE APPLICATION OF INDUCTIVELY COUPLED PLASMA QUADRUPOLE MASS SPECTROMETRY FOR THE DETERMINATION OF MONAZITE AGES BY LEAD ISOTOPE RATIOS

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Keywords: Inductively coupled plasma mass spectrometry (ICP-MS), lead dating, isotope ratio, monazite

INTRODUCTION

Considering the four stable isotopes of lead, only ²⁰⁴Pb is non-radiogenic. Since the other three, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb, are end-members of the ²³²Th (²⁰⁸Pb), ²³⁵U (²⁰⁷Pb) and ²³⁸U (²⁰⁶Pb) radioactive decay chains, different minerals show different isotopic compositions according to their age and the initial Th and U contents of the source rock (Jager & Hunziker, 1979). Monazite has been proposed for dating since it is more resistant to physical and chemical change than zircon and offers the advantage of generally higher U and Th content (Machado & Gauthier, 1996).

For the purpose of lead dating, thermal ionization mass spectrometry (TIMS) using a magnetic sector mass analyzer has been the conventional method for high precision isotopic analysis with relative standard deviations (RSD) lower than 0.05% when applied to reference materials (Hoven et al., 1999; Thirwall, 2000). However, the precision values obtained for real samples are in the range of 0.1-0.3% (Pomies et al., 1998; Halicz et al., 1996; Weiss et al., 2000). Moreover, the relatively high cost of TIMS instrumentation and the (necessary) extensive chemical pre-treatment of the sample prior to analysis have imposed serious limitations on the routine use of TIMS techniques in geochemical exploration applications (Towsend et al., 1998; Wannemacker et al., 2000).

Although the quadrupole inductively coupled plasma mass spectrometry (ICP-MS) shows an inferior precision in comparison with TIMS, it has some important advantages, such as (i) simple sample pre-treatment, (ii) high sample throughput and simple sample introduction and (iii) widespread availability (Prohaska et al., 2000).

Quadrupole based ICP-MS instruments have been used in many studies to measure Pb isotope ratios. The precisions measured in reference materials are typically 0.1- 0.3% RSD (Heumann et al., 1998; Platzner et al., 1999; Becker & Dietze, 2000; Begley & Sharp, 1997), whereas for real samples, a precision in the range of 0.2 – 0.5% RSD (Halicz et al., 1996; Weiss et al., 2000; Barbaste et al., 2001; May et al., 1999) is usually obtained. Despite of the fact that quadrupole based instruments may offer a precision 100 times worse than that obtained with TIMS for reference materials, the precision values obtained for real samples are similar in comparison with that determined by TIMS (Pomies et al., 1998; Halicz et al., 1996; Weiss et al., 2000). Several

factors may be responsible for this variability, but the most important factors affecting the precision are those regarding sample matrix effects and chemical steps associated with the method other than with the instrumental technique itself (Pomies et al., 1998; Halicz et al., 1996; Weiss et al., 2000).

In the present work, the application of quadrupole ICP-MS for the determination of lead isotope ratios has been evaluated aiming its application on dating of monazites, using U-Pb, Th-Pb and Pb-Pb methods.

EXPERIMENTAL INSTRUMENTATION

A Perkin-Elmer SCIEX ELAN 6000 ICP-MS was used for the Pb isotopic measurement equipped with the original cross flow nebulizer. A peristaltic pump performed the solution aspiration. The ICP-MS instrumental operating conditions were automatically optimized by the instrument using the SIMPLEX method and were in agreement with the conditions proposed by Halicz et al. (1996). They are summarized in Table 1.

Table 1. Perkin-Elmer SCIEX ELAN 6000 ICP-MS operation conditions.

RF Power	1050W
Plasma gas flow rate	17 L min ⁻¹
Auxiliary gas flow rate	1.2 L min ⁻¹
Nebulizer gas flow rate	0.9 L min ⁻¹
Sample uptake rate	1.0 mL min ⁻¹
Scan mode	Peak hopping
Lens scanning	Enabled
Detector mode	Dual – Pulse and Analog

REAGENTS AND STANDARD SOLUTIONS

All reagents used were of analytical-reagent grade or higher purity and de-ionized water was further purified using a Millipore Milli-Q water purification system. Certified lead isotopic standard materials (SRM 981) and (SRM 982) were purchased from the National Institute of Standards and Technology (NIST, USA).

MONAZITE SAMPLES

Buena monazite sample: A pure monazite concentrate sample from Buena (São Francisco de Assis county), in

the north of the Rio de Janeiro State (Brazil), was obtained from INB (Indústrias Nucleares Brasileiras).

Sugar Loaf Hill and Black Sand Beach samples: In both locations (Urca beach, Rio de Janeiro/RJ and Black Sand beach, Guarapari/ES), the area with the highest radioactivity was localized with a cintilometer and circa 5 kg sand samples taken. The monazite fraction was separated as described by Barling et al. (2000).

SAMPLE DISSOLUTION AND ANALYSIS

Three 25 mg aliquots, for each sample, were weighed, transferred to a 10 mL platinum crucible, 500 μ L of phosphoric acid added and heated to the red for a few minutes applying a Meker burner. A clear solution was observed after that and it was diluted, with 7.2M nitric acid, to 10 mL. One milliliter was taken and diluted to 50 mL with 2% nitric acid.

Using this solution, lead, uranium and thorium content were determined by ICP-MS. Lead and thorium results were also confirmed by Inductively coupled plasma atomic emission spectrometry (ICP-AES). Based on the lead content, the sample solution dilution was calculated in order to obtain a lead concentration around 20 μ g L⁻¹.

RESULTS AND DISCUSSION

ISOTOPE RATIO DETERMINATIONS

Many factors directly control the signal acquisition process on the ELAN 6000 ICP-MS. However, several ones are automatically optimized through the Simplex method. Others can be manually set-up, among them, the dwell time, the number of sweeps/replicate and the number of replicates/analysis. These three parameters were selected in this study in order to determine the best operation condition. Initially, the default operation conditions were applied and a high RSD was obtained. Considering the different isotope ratios involved, better results were achieved applying different dwell time for each isotope, higher for ²⁰⁴Pb, the least abundant, and lower for ²⁰⁸Pb, the most abundant, according Platzner et al. (1999).

Based on the ELAN 6000 operation manual (1997), the dwell time for each isotope was calculated in order to obtain 10⁶ counts/replicate, using 200 sweeps/replicate. Also based on that, it was chosen ten replicates/analyses. As the sample volume required and the time expended for each sample were too high, the same calculation was performed for 500.000 counts and 6 replicates/analyses. It was also included ²⁰²Hg, because of a potential isobaric interference of ²⁰⁴Hg, a dwell time equal to that of ²⁰⁴Pb was chosen.

A 100 mg L⁻¹ stock solution was prepared starting from the NIST SRM 981 and diluted to 1.5, 7.5, 15, 30 and 45 μ g L⁻¹. Initially, the isotope ratio was determined without a mass bias correction. Similarly, the same procedure was performed using the results of the 10 μ g L⁻¹ standard solution to correct mass discrimination. The results shown in Figure 1 demonstrate the efficiency of this procedure. Nevertheless, lead concentration cannot be higher than 20 μ g L⁻¹ in order to avoid dead time

effects as can be observed. It can be seen that, as ²⁰⁸Pb is the most abundant lead stable isotope, it is more subjected by dead time effects.

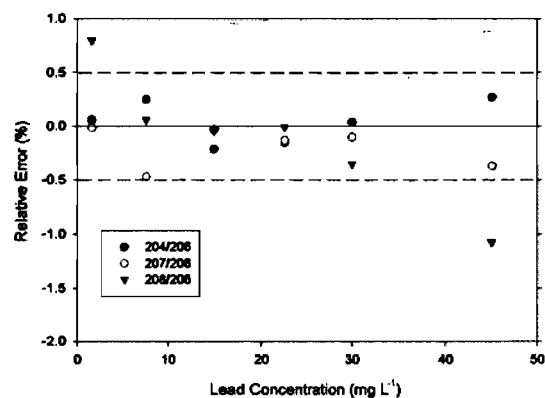


Figure 1. Relative error for Pb isotope ratios measurements after mass bias correction.

According to Platzner et al. (1999), it is possible to reduce RSD in isotope composition determinations using a quadrupole ICP-MS by consecutive measurements. This procedure of multiple determinations was performed employing a solution of 10 μ g L⁻¹ of SRM 981 to nine sequential determinations. For a sample containing 10 μ g L⁻¹ of lead, a sample volume around 20 mL is necessary. If nine measurements should be carried out, it would be necessary circa 200 mL of sample solution. It means that, dealing with real samples, in the future, the aliquot taken should contain 2 μ g Pb. The results obtained with the SRM 981 solution are shown in Table 2 and demonstrate that a relative error of the mean lower than 0.1% is obtained in all three-isotope ratios.

The previous procedure was repeated after calibrating the equipment regarding mass discrimination with a solution of 10 μ g L⁻¹ SRM 981 and using 10 μ g L⁻¹ SRM 982 as “unknown”, which has an isotope composition similar to the expecting isotope compositions, low Pb-204 (non-radiogenic) and Pb-206/Pb-204, Pb-207/Pb-204 and Pb-208/Pb-204 ratios similar to the expected compositions. The results obtained are demonstrated in Table 3 and show that precision better than 0.1% as well as accuracy in the range of 0.1 to 1% can be achieved.

Table 2. Reproducibility observed for a 10 μ g L⁻¹ SRM 981 solution.

	204/206	207/206	208/206
Reference value	0.059042	0.91464	2.1681
Mean value (n=9)	0.058761	0.913525	2.188593
RSD (%)	0.25	0.18	0.33
Relative error of the mean (%)	0.08	0.06	0.11
Relative bias (%)	-0.47	-0.13	0.95

Table 3. Reproducibility observed for a 10 $\mu\text{g L}^{-1}$ SRM 982 solution.

	204/206	207/206	208/206
Reference value	0.027219	0.46707	1.00016
Mean value (n=9)	0.027782	0.46550	0.997151
RSD (%)	0.39	0.12	0.19
Relative error of the mean (%)	0.13	0.04	0.06
Relative bias (%)	2.1	-0.34	-0.30

REAL SAMPLES

The lead, uranium and thorium contents of the three analyzed monazite samples are shown in Table 4 and the observed lead isotope ratio in Table 5. The observed elevated RSD, for the lead isotope ratios and for the elemental concentrations, reflect much more the sample inhomogeneity than the analytical techniques themselves. The monazite ages were calculated applying the U-Pb, Th-Pb and Pb-Pb methods and the obtained values are shown in Table 6. The agreement between the individual results for each dating method as well as among the dating methods is very good. Moreover, the obtained ages are in agreement with Brasiliano orogeny (Babinski et al., 1999; Söllner & Trouw, 1997; Leite et al., 2000). The obtained Sugar Loaf Hill U-Pb age is in agreement with the 560 My value announced during the 31st International Geological Congress (2000) using the SHRIMP method.

Table 4. Mean lead, uranium and thorium content of the analyzed monazite samples (values in g kg⁻¹).

Sample	Lead	Uranium	Thorium
Buena	1.23 (1.7%)	1.72 (0.3%)	45.2 (1.7%)
Sugar Loaf Hill*	1.45	1.83	47.4
Black Sand Beach	2.31 (3.4%)	1.20 (7.3%)	58.9 (5.4%)

*Only two aliquot analyzed

Table 5. Mean observed lead isotope ratio.

Sample	204/206	207/206	208/206
Buena	0.00264 (8.0%)	0.09786 (3.1%)	7.9320 (0.41%)
Sugar Loaf Hill	0.00420 (3.6%)	0.12072 (2.0%)	8.3067 (0.23%)
Black Sand Beach	0.000624 (29%)	0.06592 (5.8%)	15.5244 (1.9%)

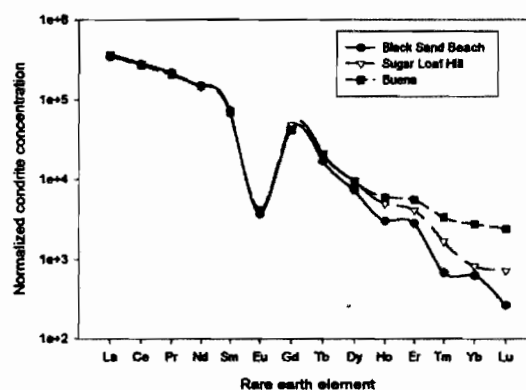
Table 6. Obtained monazite ages (values in Ma).

Sample	U/Pb	Th/Pb	Pb/Pb	Mean age
Buena	(542 \pm 2)	(532 \pm 1)	(544 \pm 3)	(539 \pm 6)
Sugar Loaf Hill	(560 \pm 7)	(593 \pm 7)	(601 \pm 37)	(585 \pm 22)
Black Sand Beach	(535 \pm 13)	(544 \pm 19)	(527 \pm 50)	(535 \pm 9)

Each Black Sand beach sample aliquot was analyzed only once whereas the aliquots of the two other samples were analyzed three times, and consequently, better

isotope ratio precisions were obtained. Also, the association of a higher thorium content with a lower uranium concentration lead to a low ²⁰⁷Pb signal and to a large standard deviation related to the Pb-Pb age.

Since the lead, uranium and thorium contents are different; REE compositions were determined in order to clarify the genetic origins. The chondrite-normalized REE content is shown in Figure 2. All monazite samples have patterns with negative europium anomalies and with similar light REE compositions. The HREE are divergent, the largest difference being found for the heaviest elements.

**Figure 2.** Rare-earth elements concentration, normalized to the Chondrites, in the studied monazite samples. Chondrite values are taken from Anders & Grevesse (1989).

Finally, the method was tested with older samples. A thorianite sample from Amapá was obtained from the Brazilian Nuclear Energy Commission. Three 10 mg aliquots were taken, after total dissolution with HNO₃-HF-HClO₄, they were analyzed in the same way as the monazite samples. The Th-Pb, U-Pb and Pb-Pb ages obtained were 2152 \pm 53 My, 2032 \pm 11 My, 2044 \pm 6 My respectively, with a mean value of 2076 \pm 66 My. This value is coherent with the 2.08 \pm 0.02 Gy age of the Bacuri complex, Amapá, reported by Pimentel et al. (2002).

CONCLUSIONS

The present study showed that, it is possible to obtain useful monazite dating regarding precision and accuracy when the acquisition setting parameters of the ICP-MS Perkin Elmer-Sciex ELAN 6000 are optimized. Moreover, the use of monazite allows the direct determination of lead isotope ratios without the need of a chemical separation.

ACKNOWLEDGEMENT

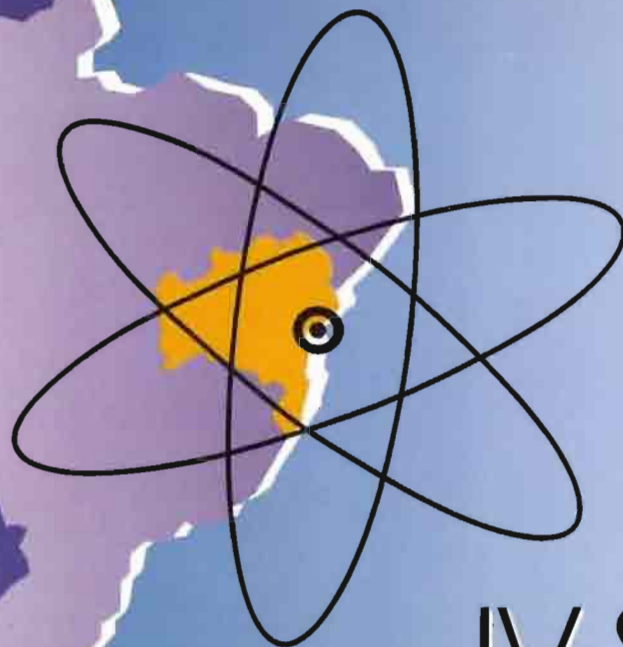
The present work was supported by FINEP (Financiadora de Estudos e Projetos) and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior). The authors wish to express their gratitude to Claudio Valeriano (UERJ) and Marcio Pimentel (UnB) for their help during different phases of the present work.

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ISSN 1679-3684



IV South American Symposium on Isotope Geology

SALVADOR-BA, BRAZIL AUGUST 24th - 27th, 2003

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Short Papers of the IV South American Symposium on Isotope Geology – IV SSAGI, Salvador, August 24th - 27th ; Maria de Lourdes da Silva Rosa et al. (Organizers). – Salvador : CBPM; IRD, 2003.

ii-xxii - 789p. : il.

Reference.

1. Isotope Geology. 2. Geology – South America. 3. Geology – International Meeting. 4. Symposium. I. Rios, Débora Correia. II. Kosin, Marília. III. Santos Pinto, Marilda. IV. Title.

CDD 551.701

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