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Lead–Lead Method for age dating of granitic sample by LA-ICP-MS

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ABSTRACT

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is used for the direct analysis of Egyptian granite samples, which are collected from the eastern desert—Egypt for the determination of Pb isotopic ratios. The age of the samples is calculated using Lead–Lead Method. Standard Reference Material (SRM 981) is used for the mass bias correction. The probability of interferences is discussed and considered. The obtained age is found 498.56 ± 4.38 My after the mass bias correction.

1. Introduction

Lead has four naturally occurring isotopes ^{204}Pb (1.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%) and ^{208}Pb (52.3%), three of which are radiogenic decay products of either uranium or thorium. The fourth, ^{204}Pb, has a very long half-life such that it may be considered 'stable' on a geological time scale. For this reason, in geological applications, Pb isotopes are frequently ratioed to ^{204}Pb for comparative purposes.

A number of applications concerning the determination of Pb isotope ratios in geological samples have been published. Both the peak hopping and scanning modes of measurement have been used with some success. Despite the wide range, often contradictory observations are made in the literature [1].

Isotope ratios are generally determined by means of thermal ionization mass spectrometry (TIMS) because of the excellent precision attainable (RSD values <0.05%). However, the extensive sample pretreatment requirements led to some limitations in the routine use of TIMS in geochemical and archaeological research.

Another development is that an ICP ion source coupled to a magnetic sector analyzer and multi-collector is now comercially available. Compared with TIMS, this provides much better sensitivity for elements with high thermal ionization energies [2], the ion beams do not undergo progressive mass fractionation, so that a simple correction may be made for mass bias using for example Tl to correct Pb mass bias [3]. In situ, spatially resolved analysis is available using a laser to ablate sample into the plasma [4].

Since 1990, ICP-MS has also been used for lead isotope studies of archeological objects, such as various lead artefacts [5], ancient plumbic cosmetic pigments [6], brass baptismal fonts [7] and bronze or copper cast objects [8]. Although ICP-MS shows an inferior precision in comparison with TIMS, it has some important advantages, such as, its simple sample pre-treatment, higher sample throughput and simple sample introduction and its widespread availability.

In addition, previous work has shown that with a double focusing sector field ICP mass spectrometer operated at the low resolution setting [$R = 300$], isotope ratio precisions can reach the order of ≤0.05% RSD [9,10]. The improvement in precision observed with a sector field instrument operated at the lowest resolution setting can mainly be attributed to the flat-top shape of the peaks. In the framework of provenance studies, the precision obtained is sufficient to determine whether lead isotope fields show mutual overlap and is, hence, potentially useful. Finally with multiple collector ICP-MS, precision levels of 0.01% can be considered routine [3]. Precision can also be achieved with ICP-MS using multiple ion collectors (MC-ICP-MS) [11–13].

Amr et al. [14] measured the trace elements in irradiated granite samples from Hiroshima by Laser Ablation Inductively Coupled Plasma Mass Spectrometry. Imai [15] described a direct quantitative analysis method of rocks (granite, basalt, andesite, rhyorite, gabbro) by LA-ICP-MS and reported that the signal intensity was normalized either by the ablated weight or the barium signal intensity.

LA-ICP-MS is increasingly used in different fields of modern science and technology, [16] especially in geology and mineralogy, [17–19] in environmental and biological research, [20] in material research for the characterization of high purity materials [21] and for the determination of long lived radio-nuclides in non-conducting materials [21,22].

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Table 1
Experimental parameters for LA-ICP-MS.

Rf power	1200 W
Coolant gas flow rate	14 L/min
Auxiliary gas flow rate	0.3 L/min
Nebulizer gas flow rate	0.85 L/min
Frequency	20 Hz
Laser power density	7×10^{10} W/Cm^2
Number of shots in drilling mode	40 shots

Table 2
EDX analysis of granite sample.

Element	Conc. (%)	Element	Conc. (%)
O	53.04 ± 0.18	S	0.07 ± 0.02
Na	2.09 ± 0.06	K	6.4 ± 0.06
Al	6.68 ± 0.06	Fe	1.3 ± 0.05
Si	30.42 ± 0.13		

Table 3
Possible interferences with Pb isotopes and the required resolution for separation.

Isotope	The interfere ions	Resolution
^{204}Pb	^{204}Hg	459,400
^{206}Pb	^{190}Os^{16}O	9768
^{207}Pb	^{191}Ir^{16}O	10,161
^{208}Pb	^{192}Os^{16}O	10,275

2. Granite rocks

It is an igneous rock, collected from eastern desert—Egypt, with a phaneritic texture (i.e., a relatively coarse grained rock in which the individual crystals can be distinguished with the naked eye) which is presumed to have formed at considerable depth. It is consisting essentially of quartz, alkali feldspar and plagioclase in variable amounts usually with hornblend and/or biotite.

3. Experimental

Small pieces of the Egyptian granite samples, which are collected from the eastern desert are selected and polished. The selected samples are analyzed directly using the laser ablation technique, which attached to the high resolution inductively coupled plasma mass spectrometer (JMS-PLASMAX2). Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Spectrometer (EDX) is used for the inspection of the surface and the determination of concentrations of major and minor elements in the samples. The JMS-PLASMAX2 high-resolution ICP-MS is a reversed double-focusing mass spectrometer equipped with quadrupole focusing system is capable for obtaining the resolution of 12,000. With this resolution, masses of interference and element ions can be separated from each other. A 40.68 MHz high-frequency power supply and an automatic ignition system are used in the ICP ion source to obtain stable plasma. Ions introduced into the mass analyzer from the plasma through the plasma interface can be adjusted to form a high-intensity ion beam. The masses of the ion beam entering the double-focusing mass spectrometer are separated and detected by the post-accelerator analogue detector. The optimized experimental parameters for the LA-ICP-MS for the determination of Pb isotopic ratios are shown in Table 1.

Table 4
^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb before and after the mass bias correction.

Sample	Before mass bias correction		After mass bias correction	
	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb
G1	7.83	7.50	9.63	8.68
G2	8.60	8.73	10.58	10.10
G3	9.26	9.37	11.39	10.84
G4	11.01	10.22	13.54	11.82
G5	11.37	10.90	13.98	12.61
G6	13.78	12.47	16.94	14.42
G7	14.14	13.28	17.39	15.36
G8	14.68	13.90	18.05	16.07
G9	14.99	15.22	18.43	17.61
G10	16.56	16.71	20.36	19.33

4. Results and discussions

SEM and EDX are used for measuring the concentrations of the major and minor elements in the sample as shown in Table 2. Lead does not show a signal in the major or minor concentrations, therefore is detected as trace element in the laser ablation technique.

The possibilities of interferences in lead are the isobaric interference with ^{204}Hg and the interferences with the oxide formations especially ^{190}Os^{16}O with ^{206}Pb, ^{191}Ir^{16}O with ^{207}Pb, and ^{192}Os^{16}O with ^{208}Pb. These interferences depend on the matrix elements. The possible interferences in the ICP-MS spectra with Pb isotopes and the required resolution for separation are presented in Table 3.

The interferences of Pb isotopes come from the presence of ^{190}Os^{16}O which interfere with ^{206}Pb and it must be corrected by measuring of ^{190}Os^{16}O/^{190}Os in standard samples, according to the equation:

$$^{206}\mathrm{Pb}_{cor} = {}^{206}\mathrm{Pb}_{meas} - {}^{190}\mathrm{Os}_{meas}\,({}^{190}\mathrm{Os}^{16}\mathrm{O}/{}^{190}\mathrm{Os}), \tag{1}$$

by the same way in the case of ^{191}Ir^{16}O which interfere with ^{207}Pb, it must be corrected by measuring ^{191}Ir^{16}O/^{191}Ir in a standard samples, and using the equation:

$$^{207}\mathrm{Pb}_{cor} = {}^{207}\mathrm{Pb}_{meas} - {}^{191}\mathrm{Ir}_{meas}\,({}^{191}\mathrm{Ir}^{16}\mathrm{O}/{}^{191}\mathrm{Ir}) \tag{2}$$

In our case Ir and Os are not detected so no interfere occur due to the presence of Os and Ir.

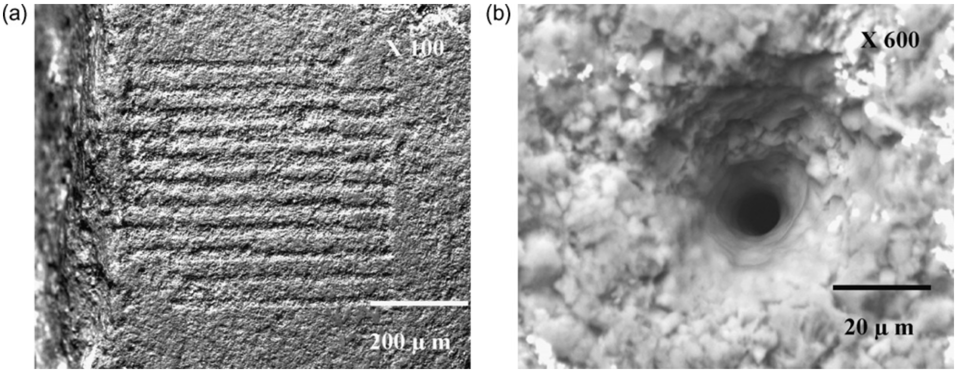

Fig. 1. SEM photo for ablated granite sample: (a) raster mode (b) drilling mode.

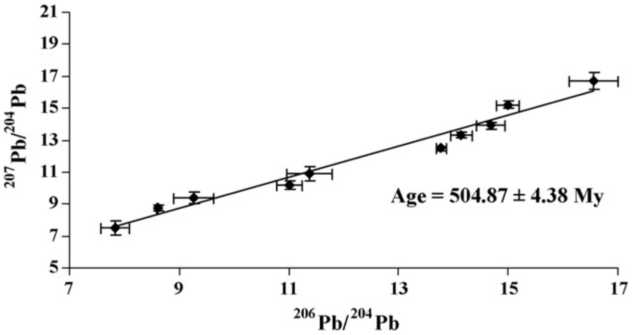

Fig. 2. Lead isochron before mass bias correction in granite samples.

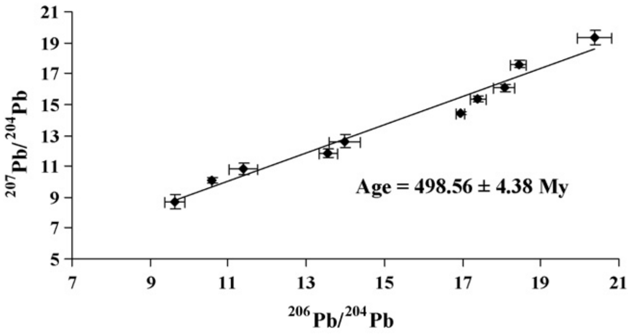

Fig. 3. Lead isochron after mass bias correction in granite samples.

Isobaric interference of ^{204}Hg with ^{204}Pb is corrected using the abundance of ^{202}Hg (if there is Hg in the samples) by the following equation:

$$I_{204\mathrm{Pb}} = I_{204} - \frac{A_{204\mathrm{Hg}}}{A_{202\mathrm{Hg}}} I_{202\mathrm{Hg}} \tag{3}$$

where ^{202}Hg isotope is free from isobaric interference, $I_{204\mathrm{Pb}}$ is the ion intensity of ^{204}Pb isotope, I_{204} is the total ion intensity at $m/z = 204$, and $A_{202\mathrm{Hg}}$ is the natural abundance of ^{202}Hg isotope.

The power low is used for the mass bias calculations following the relation:

$$\frac{R_{\mathrm{true}}}{R_{\mathrm{obs}}} = (1 + \varepsilon_{\mathrm{pow}})^{\Delta m} \tag{4}$$

this by using (SRM 981) as a standard reference material for the mass bias correction.where $R_{\mathrm{true}}/R_{\mathrm{obs}}$ is the certified to measured ratio, $\varepsilon_{\mathrm{pow}}$ the mass discrimination per mass unit and Δm is the mass difference between the isotope of interest.

Two modes of analysis by laser ablation are used namely, the raster mode where ablation is performed as a close points in a lines as shown in Fig. 1a and a drilling mode as in Fig. 1b. The two modes are used to get the good fitting of the isochron. Table 4 shows the obtained isotopic ratios before and after the mass bias correction.

To calculate the age of the rock using lead isotopic ratio measurements, the following equation is used:

$$\frac{^{207}\mathrm{Pb}}{^{206}\mathrm{Pb}} = \frac{1}{137.88}\,\frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1} \tag{5}$$

where 1/137.88 is the abundance of ^{235}U (0.72%) divided by the abundance of ^{238}U (99.2745) and the decay constant λ of ^{235}U and ^{238}U are $\lambda_{235} = 9.8485 \times 10^{-10}$, $\lambda_{238} = 1.55125 \times 10^{-10}$, respectively.

Figs. 2 and 3 show two different isochrones for the same granite samples before and after the mass bias correction. The calculated age after the mass bias correction using SRM (981) is found to be 498.56 ± 4.38 million years.

The age of the area where the sample was extracted is 489.23 ± 1.55 million years [23] which is in agreement with the present measured value of the age.

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