Research Paper

U-series dating of carbonates using inductively coupled plasma-quadrupole mass spectrometry

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ABSTRACT

We describe an analytical methodology to quantify $^{238}U-^{234}U$ and ^{230}Th using isotope-dilution systematics and inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) for geochronological purposes. This required characterization of the mass spectrometer detector performance over a large dynamic range, including a careful calibration between pulse and analogue ion-counting modes. Our methodology gives an analytical precision for $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ of 4‰ and 7‰ (2 × standard error), respectively, and yields ^{230}Th-ages with 4–5% uncertainty from 500 ng of ^{238}U. We tested our methodology by analyzing carbonate samples (corals and speleothems) which were previously dated using MC-ICPMS; excellent agreement between both techniques was obtained. Our results indicate that ICP-QMS is suitable to obtain valuable meaningful geochronological data, but it is limited to dating samples older than 1 ka, and younger than 400 ka. Our methodology thus represents an attractive alternative to obtain geochonological data to select the most interesting samples prior to high-precision analysis. Moreover, such data would also valuable to build preliminary age-models, which can be further complemented with high-precision analyses.

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1. Introduction

U–Th geochronology is one of the most powerful tools for unraveling the complex geological and climatic history of the Earth during the late Quaternary; the use of U and Th-isotope composition as proxies for a wide range of geological and environmental processes also makes them an essential tool for modern geochemical studies (Bourdon et al., 2003). Despite this, only a few laboratories worldwide have this capability, primarily because of the extremely low $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios, the inherent difficulty of detecting the low-abundance isotopes ^{234}U and ^{230}Th in the presence of high-abundance ^{238}U, and the scarcity of high-purity spikes, particularly ^{229}Th, required for the precise and accurate determination of $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ by isotope-dilution.

Because of the low activity of ^{234}U and ^{230}Th, uncertainties of several % are typically obtained during the U–Th dating of carbonates by α-spectrometry (Goldstein and Stirling, 2003). Such uncertainties, along with the large amount of sample required, were significantly diminished after the introduction of magnetic-sector mass-spectrometric methods in the 1980's (Chen et al., 1986; Edwards et al., 1987); since then, further advances in mass-spectrometry technology have improved detection limits and precision by enhancing ion-production (Houk et al., 1980), increasing detector sensitivity, reducing or controlling the sources of background (Hunter, 1994), and increasing signal stability (Bradshaw, 1989). These, along with improvements in U and Th purification methods, make possible sub-permil precision and fg/g or pg/g detection limits (Andersen et al., 2004; Potter et al., 2005a), allowing the detection of small deviations from secular equilibrium in very old samples (Andersen et al., 2008), or quantification of extremely small amounts of ^{230}Th in very young samples (McCulloch and Mortimer, 2008; Shen et al., 2008; Zhao et al., 2009). Moreover, the ability to measure instrumental mass bias for Th isotopes has also enhanced the accuracy of U-series dating (Hoffmann et al., 2007; Hoffmann, 2008). Unfortunately, the high-

precision instrumentation required for such measurements is not always available. Here we explore the feasibility of using the widely available inductively coupled plasma-quadrupole mass spectrometry (ICPM-QMS) coupled with a high-efficiency sample introduction system (APEX-Q). We show that this provides an alternative to high-precision instrumentation to quantify ^{234}U and ^{230}Th in carbonates by isotope-dilution for ^{234}U–^{230}Th geochronological purposes.

Modern ICP-QMS is an attractive, low-cost, and widely available alternative to high-precision instrumentation. It is characterized by detection limits of only few pg/g, which can be improved $\sim 10\times$ by using an efficient sample introduction system, such as a desolvators. Moreover, isotope-ratio measurements with sub-permil precision can be achieved in the most ideal cases (Bandura et al., 2000; De Muynck et al., 2008). In conjunction with laser ablation, ICP-QMS is commonly used for U−Pb dating of zircons and other accessory igneous mineral phases, with age uncertainties of only 2−4%(Horn et al., 2000; Kosler et al., 2002; Black et al., 2004; Solari et al., 2010). ICP-QMS has also been demonstrated to be useful for Rb−Sr geochronology (Vanhaecke et al., 2003), although few applications have followed suit. Moreover, most ICP-QMS are equipped with long-dynamic range electron multipliers suitable for measuring very low isotope ratios ($<10^{-4}$), such as $^{234}U/^{238}U$ and $^{230}Th/^{238}U$.

The feasibility of measuring U-isotopic compositions using ICP-QMS, including $^{234}U/^{238}U$, has been previously demonstrated (Shaw and Francois, 1991; Mas et al., 2006) and per-mil precision can be achieved (Shen et al., 2006). Recently, deviations from secular equilibrium have been successfully measured in ancient carbonates with the aim of age-scan samples prior to high-precision U-series dating (Douville et al., 2010). Alternative methodologies for age-scanning have been proposed earlier (Potter et al., 2005b; McGregor et al., 2011). These are based on laser-ablation microsampling and, in addition to the requirement of very specialized instrumentation, significant method optimization prior to sample analysis is required. Moreover, the lack of a geological certified standards for microanalyis with known $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ is a significant conundrum that needs to be solved, usually via extensive spatial and isotopic characterization (e.g. Bernal et al., 2005), prior to routine age-scan analysis, otherwise, complex and uncharacterized matrix effects can potentially lead to incorrect geochronological conclusions. The methodology presented here is based on the same principles as the most precise methods (Luo et al., 1997; Hellstrom, 2003; Fietzke et al., 2005; McCulloch and Mortimer, 2008; Shen et al., 2008), and full implementation is possible after some instrumental characterization.

The methodology presented here required us to carefully characterize the response of the detector over its dynamic range, and developed a methodology to fully correct for the small differences in detector efficiencies between the different sections (pulse-counting and analogue). This has allowed us to determine $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ with uncertainties of 4‰ and 7‰ (2 × standard error, 2E), respectively, from ∼500 ng U aliquots, which translates into 3−5% age uncertainties for samples older than 1 ka. We assess the accuracy of our methodology by analyzing secular equilibrium standards, as well as coral and speleothem samples previously dated by MC-ICPMS.

2. Experimental

2.1. Standards, reagents and ^{229}Th and ^{233}U tracers

All samples and solutions were prepared and stored in PTFE vessels in a Class 100 laboratory under laminar-flow hoods, using triple-distilled acids diluted in Milli-Q water (18.2 MΩ). Procedural

blanks were always ≤ 12 pg/g of ^{238}U and <1 pg/g for ^{232}Th and ^{230}Th, thus corrections by blank contributions were not necessary. A solution of the U isotopic standard NIST SRM 960 was prepared from U metal. This was previously cleaned in Milli-Q water, 1:1 HNO_3, 1:3 HCl, thoroughly rinsed in Milli-Q water, and vacuum dried in a desiccator at room temperature (Cali, 1972). Once cleaned and dried, the material was dissolved in 1:1 HNO_3 and gravimetrically diluted to obtain a 10 mg/g U stock solution, from which further dilutions were prepared as required. This standard is certified for a $^{238}U/^{235}U$ composition of 137.88 (Cali, 1972), but recent and more precise measurements have concluded that such value is between 0.03% (Richter et al., 2010) and 0.08% (Condon et al., 2010) lower than the certified composition. Although this material is not certified for its $^{234}U/^{238}U$ composition, analysis by several laboratories using MC-ICPMS and TIMS yield a $^{234}U/^{238}U = (52.86 \pm 0.021) \times 10^{-6}$ (robust mean from Andersen et al., 2004), equivalent to $\delta^{234}U = -36.87 \pm 0.40‰$ ($n = 17$, MSWD 0.54, probability 0.93), which is in agreement with the recently published value by Richter et al. (2010).

The U and Th isotopes were quantified using normal isotope-dilution systematics. Samples were spiked with known amounts of ^{233}U and ^{229}Th acquired from Isotrak (AEA Technology QSA Inc, UK). The spikes were calibrated for their isotopic composition by measuring three different aliquots bracketed by SRM 960 to correct for mass bias using $^{238}U/^{235}U = 137.88$. The resulting isotopic composition for each spike is summarized in Table 2, and shows good agreement with the available data from the certificate provided by AEA Technology. We note that use of the recently published improved values of $^{238}U/^{235}U$ for SRM 960 (Condon et al., 2010; Richter et al., 2010) represent only a small change ($<0.1‰$) in the calculated isotopic compositions and ages presented here, and well within the uncertainty of our measurements. Because of the relatively low-purity of our ^{229}Th tracer ($^{229}Th/^{230}Th = 650 \pm 21$, see below), its concentration in the spiked sample was kept as low as possible to minimize its contribution upon the total ^{230}Th; resulting in $^{239}Th_{spike}/^{230}Th_{sample}$ lower than 250.

To assess the precision and accuracy of our measurements, we prepared solutions from Harwell uraninite (HU-1), which is known to be in secular equilibrium with respect to $^{234}U/^{238}U = (54.875 \pm 0.003) \times 10^{-6}$ (robust mean from data summarized in Andersen

Table 1
Summary of relevant instrumental parameters used in this work.

Forward power	1450 W
Carrier gas	0.7 l min^{-1}
Make-up gas	0.3 l min^{-1}
Sample uptake	400 µl min^{-1}
Extraction voltage 1	2.1 V
Extraction voltage 2	143 V
Omega-bias	−18 V
Omega lens	2.4 V
Detector voltages	
Pulse counting	1660 V
Analogue	1300 V
Discriminator (factory setting)	4 mV
Dwell time (s):	
^{238}U	0.7
^{235}U,	0.85
^{234}U,	1.1
^{233}U,	0.3
^{232}Th	0.2
^{230}Th,	1.0
^{229}Th	0.85
Settling time	0.001
APEX	
Heating	120 °C
Cooling	2 °C
No N_2 added.	