A new method for U–Th–Pa–Ra separation and accurate measurement of 234U–230Th–231Pa–226Ra disequilibria in volcanic rocks by MC-ICPMS

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ABSTRACT

A new method for the chemical separation and MC-ICPMS measurements of U–Th–Pa–Ra disequilibria in volcanic samples from a single sample aliquot is presented. The accuracy and precision of our techniques is assessed by replicate analyses of the synthetic U and Th isotope standards IRMM-184 and IRMM-35, and the secular equilibrium rock standards BCR-2, W-2a and TML. A measure of true sample reproducibility including the errors related to sample processing and the chemical separation is obtained from analysis of multiple digestions of the rock standards. $^{234}U/^{238}U$, $^{230}Th/^{238}U$, $^{231}Pa/^{235}U$ and $^{226}Ra/^{230}Th$ activity ratios on ten separate dissolutions of USGS rock standard BCR-2, for example, reproduce to 0.4%, 1.4%, 1.1% and 2.4% (2 SD), respectively. All elements (U–Th–Pa–Ra) are separated from a single spiked sample aliquot and the elemental concentrations are measured on the same solutions as the isotopic compositions. Analytical artefacts from determination of elemental and isotopic concentrations on different sample aliquots due to sample heterogeneity are therefore avoided. In addition, our new chemical separation protocol is time-efficient and allows for rapid processing of volcanic samples with less than 25 fg of Pa and Ra.

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1. Introduction

U-series disequilibria provide important constraints on the time scales and rates of a wide range of geological processes and are applied in diverse fields including oceanography, paleoclimatology and volcanology (Bourdon et al., 2003). In volcanic rocks, U-series disequilibria between the long lived parent isotopes ^{238}U and ^{235}U and their short-lived daughter isotopes ^{230}Th, ^{226}Ra and ^{231}Pa have been used to study magma chamber residence or differentiation times (e.g. Allègre and Condomines, 1976; Volpe and Hammond, 1991; Bourdon et al., 1994; Lowenstern et al., 2000; Condomines et al., 2003; Reid et al., 2003; Asmerom et al., 2005; Schmitt, 2006; Yokoyama et al., 2006; Snyder et al., 2007; Touboul et al., 2007), as well as magma transfer times and mantle melting rates (e.g. McKenzie, 1985; Goldstein et al., 1989; Cohen and O'Nions, 1993; Spiegelman and Elliott, 1993; Bourdon et al., 1996; Elliott, 1997; Turner et al., 1997; Lundstrom et al., 1998; Sims et al., 1999; Stracke et al., 1999; Condomines and Sigmarsson, 2000; Stracke et al., 2003; Bourdon et al., 2005; Stracke et al., 2006; Prytulak and Elliott, 2009).

Owing to the minute quantities of Ra and Pa in volcanic samples (e.g. typical concentrations of [^{231}Pa] and [^{226}Ra] for Icelandic basalts are less than 100 fg/g), mass spectrometric analyses of U–Th–Pa–Ra disequilibria in volcanic rocks are analytically challenging, and demand clean chemical separation of the elements with high yields. The extreme ratios between the daughter and parent isotopes in volcanic rocks (e.g. $^{232}Th/^{230}Th \sim 1-2 \times 10^5$ or $^{238}U/^{234}U \sim 1.8 \times 10^4$) pose further analytical challenges. Measuring these isotope ratios by mass spectrometry requires the use of ion counting systems in conjunction with Faraday cups. This involves: (1) determination of the dead time and (non)linearity of the ion counting systems; (2) the inter-calibration of SEM and Faraday detectors; and (3) a correction for tailing of the high abundance onto the low abundance beams, especially in the case of ^{232}Th and ^{230}Th.

Although numerous studies have previously reported U-series disequilibria measurements in silicate rocks, a well documented method for the chemical separation and mass spectrometric analysis of U–Th–Pa–Ra on a *single* sample aliquot has not been published. In several previously published methods the Ra and or Pa concentrations were determined on separate sample digestions from the parent Th and U concentrations (Chabaux and Allègre, 1994; Bourdon et al., 1998; Claude-Ivanaj et al., 1998; Lundstrom et al., 1998; Bourdon et al., 1999b; Sims et al., 1999; Turner et al., 2000; Dosseto et al., 2003; Lundstrom et al., 2003; Stracke et al., 2006). The chemical separation of all four elements from a single aliquot is important because sample heterogeneity can contribute significantly to the error of parent–daughter ratios if measured on separate sample splits. In addition, a method using a single aliquot is more time-efficient than previously reported methods.

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Here, we present a full description of a new chemical method to separate U, Th, Ra and Pa from a single sample aliquot and MC-ICPMS measurement techniques for accurate elemental concentration and isotope ratio determination. U-series isotope measurements on certified reference materials IRMM-184 and IRMM-35, the secular equilibrium rock sample TML, and international USGS rock standards BCR-2 and W2a, demonstrate the accuracy and precision of our method. The data set represents a true measure of reproducibility on silicate rock samples as it is obtained from multiple separate digestions of BCR-2, W-2a and TML and therefore includes the errors related to sample preparation and processing, chemical separation and mass spectrometry.

2. Experimental

2.1. Reagents and materials

Reagent grade HCl, HNO$_3$ and HF used for cleaning and chemical separation procedures were obtained from Merck Chemicals, Germany. The acids used for sample digestion and chemical separation were purified using PicoTrace™ sub-boiling cupola stills. Dilutions were done with 18.2 MΩ purified water from a Milli-Q Element Millipore system. Boric acid, 99.9995%, ascorbic acid, 99%, ammonium-thiocyanate, 98%, and hydrogen peroxide, 29–32%, were purchased from Alfa Aesar, Germany. Sample dissolution and chemical separations were carried out using PFA Teflon vials that were thoroughly cleaned with a multi-step procedure involving initial boiling in a 3% RBS-50 detergent (Carl Roth, Switzerland), followed by fluxing on a hotplate of individual vials with a mixture of ~3 N HF–3 N HNO$_3$, and subsequent boiling in 3 N HNO$_3$, 6 N HCl, and Milli-Q H$_2$O. In between all these cleaning steps beakers were rinsed with Milli-Q H$_2$O. Teflon and PP columns, pipette tips and centrifuge tubes were subject to the same cleaning procedure excluding the HF–HNO$_3$ step.

Resins used for chromatographic separation were EiChrom™ TRU-spec resin (100–150 μm), Sr-spec resin (50–100 μm), Pre-Filter material to remove organics, and Bio-Rad anion- and cation exchange resins, AG 1-X4, AG 1-X8 and AG 50W-X8, 200–400 mesh. EiChrom™ Resins were pre-cleaned with several rinses of Milli-Q H$_2$O and 1 N HCl, respectively. Bio-Rad resins were pre-cleaned by several successive rinses with 3 N HNO$_3$, Milli-Q H$_2$O and 6 N HCl.

Several rock standards and synthetic solution standards were used to evaluate the accuracy and precision of our chemical and analytical method. We have processed and measured rock standard TML (distributed by J. Gill, University of California, Santa Cruz, USA), and USGS rock standards BCR-2 and W-2a. All these rock powders are well characterised for U-series elemental concentration and were shown to be in, or close to, secular equilibrium (Hoffmann et al., 2007; Ball et al., 2008; Sims et al., 2008). The synthetic uranium and thorium reference solutions IRMM-184, IRMM-35 and IRMM-36 were obtained from the Institute for Reference Materials and Measurements, Geel, Belgium, and used to assess instrumental performance and reproducibility. IRMM-184 and IRMM-35 are especially well suited for this purpose as the ^{234}U/^{238}U and ^{230}Th/^{232}Th ratios, 5.314×10^{-5} and 1.137×10^{-5}, respectively, are similar to those of igneous rock (Richter et al., 2005; Hoffmann et al., 2007).

2.2. Spike preparation and calibration

Sample aliquots were spiked with four mono-elemental tracer solutions containing ^{236}U, ^{229}Th, ^{233}Pa and ^{228}Ra prior to dissolution. A careful calibration of individual spike concentration and isotopic composition is essential for the accurate determination of the ^{230}Th/^{238}U, ^{231}Pa/^{235}U and ^{226}Ra/^{230}Th ratios.

The ^{236}U spike was calibrated against gravimetric U reference material CRM-145b (New Brunswick Laboratory), which has a certified uncertainty of 0.03‰ (2σ) on the ^{238}U concentration

(10.6886 mg/g). The spike concentration was determined gravimetrically using mixtures of diluted CRM145b standard and ^{236}U spike with variable mixing proportions. The propagated error on the spike concentration includes weighing errors involved in dilution of the gravimetric standard as well as weighing of the spike. The spike was determined to have a ^{236}U concentration of 6.783 ± 0.015 ppb and a purity of 99.68%. The ^{229}Th spike (0.1373 ppb) was calibrated using a similar protocol against an in-house gravimetric Th standard, which was prepared by dissolving solid ultrapure (>99.999%) metal Th, to an uncertainty of 0.3%. The 233-Protactinium spike batches were prepared by neutron activation of ^{232}Th using the Swiss Spallation Neutron Source (SINQ) at the Paul Scherrer Institute (PSI), Villigen, Switzerland. ^{233}Th was produced by neutron capture on ^{232}Th, ~1 mg Th as a nitrate salt, in a sealed glass ampoule (Bourdon et al., 1999a; Aciego et al., 2009). The ^{233}Th then decays to ^{233}Pa with a half life of 22.3 min. After decay of the short-lived nuclides formed by the irradiation decay (i.e. ^{24}Na, $T_{1/2} = 15$ h; ^{28}Al, $T_{1/2}$ 2.5 min), the produced ^{233}Pa was dissolved in ~5–10 mL 9 N HCl. Separation of Pa from Th and other impurities by anion exchange was done in two steps, using an 5 mL and a subsequent 0.5 mL anion exchange column (AG1-X8, 200–400 mesh, Bourdon et al., 1999a). The 5 mL column was cleaned with 6 column volumes (cv) 9 N HCl. The Pa fraction was then eluted in 2 cv 9 N HCl + 0.1 N HF, and evaporated to ~1 mL. At this point, saturated boric acid was added to break up PaF$_7^{2-}$ complexes. This solution was loaded on the second column, previously cleaned with 3 cv 9 N HCl. The Pa fraction was then eluted in 3 cv 9 N HCl + 0.1 N HF. The second separation step was repeated until the Pa/Th ratio in the ^{233}Pa spike is greater than 1, which typically required 3 repetitions. Loss of protactinium to beaker walls or wash solutions during the purification procedure was monitored with a gamma-counter equipped with a 44-11 detector, Ludlum Measurements, INC., Texas USA, connected to a ratemeter. The loss of ^{233}Pa during the spike separation procedure was typically less than 10%.

Due to the decay of ^{233}Pa to ^{233}U with a half life of 26.967 days (Usman and MacMahon, 2000) the ^{233}Pa spike batches produced from ^{232}Th have a finite life span of approximately 5 months. Therefore, new batches of spike had to be prepared at PSI several times during this project and subsequently calibrated with the procedure described below. For each aliquot of spike, the initial ^{231}Pa/^{233}Pa was determined by MC-ICPMS, as described in Section 2.4, after chemical purification from ^{233}U using column 2 in our chemical separation procedure described in Section 2.3.

The ^{233}Pa spike was calibrated against the Long Valley rhyolite glass LV18 distributed by G. Davies, Free University Amsterdam (Bourdon et al., 1999a). LV18 was dated to have an age of 1.6 ± 0.05 Ma (OL unit in Metz and Mahood, 1985; Metz and Mahood, 1991) and is therefore expected to be in secular equilibrium. Regelous et al. (2004) showed that LV18 is heterogeneous for U and Pa concentrations. For the ^{233}Pa spike calibration, it is therefore critical to measure the U and Pa concentrations on the same digestion. The coarse-grained glassy LV18 was carefully handpicked to avoid alteration and inclusions of accessory phases that may cause the variations in U concentration. The purified fraction was ground in an agate mortar to produce a homogenous powder. Three batches of ~100 mg of LV18 spiked with varying amounts of ^{233}Pa were separated as described in Section 2.3 and analysed for uranium and ^{233}Pa spike concentrations for each individual spike calibration. Over a period of 18 months we obtained an average U concentration for LV18 of 15.02 ± 0.09 ppm ($n = 13$), significantly higher than the average of 10.47 ± 0.2 ($n = 3$) reported by Regelous et al. (2004). To check the accuracy of the Pa spike calibration, Pa concentrations and ^{235}U/^{231}Pa activity ratios of international rock standards BCR-2, TML and W-2a were compared to published values (Prytulak et al., 2008); Section 4.3. The Pa concentration (and ^{231}Pa/^{233}Pa) of the spike on the day of U–Pa separation must be calculated from its initial calibrated concentration (typically between 2000 and