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From volcanic rock powder to Sr and Pb isotope ratios: a fit-for-purpose procedure for multi-collector ICP–mass spectrometric analysis

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Abstract

Geochemical research into volcanic rocks often involves isotopic analysis of whole rock powders. The method of Deniel and Pin (Anal. Chim. Acta, 2001, 426, 95-103) for simultaneous isolation of strontium and lead using extraction chromatography via Sr spec[TM] resin was therefore adapted into a straightforward procedure for Sr and Pb isotope ratio determination by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The main focus was to reduce their rather extensive and costly cleaning procedures for resin and columns without negatively affecting data quality. It was furthermore demonstrated that non-quantitative Sr and Pb recoveries do not compromise the quality of the isotope data obtained and that no Pb isotopic fractionation occurs on the Sr spec[TM] resin. The accuracy of the analyses was assessed by monitoring rock reference materials. GSJ basalt JB-2, commonly regarded as the most homogeneous Pb isotopic rock reference material, hereby produced one anomalous Pb isotopic composition out of eight analyses, suggesting that JB-2 might also be affected by nugget contamination.

1. Introduction

Isotope ratios of Sr and Pb are used extensively in geological, geochronological and archaeological studies. [1-7] Part of our research into the geochemistry and petrology of the South Aegean arc for example, involves isotopic fingerprinting of the different sources contributing to the final geochemical signature of the arc magmas. Sr and Pb isotope ratios therefore need to be determined for a large collection of volcanic rocks, ranging from basaltic andesites to rhyodacites. Thermal ionisation mass spectrometry (TIMS) has traditionally been the reference technique for high-precision isotope ratio determination of the heavier elements. [8] However, multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS), combining a powerful ion source with a sector field mass spectrometer and an array of Faraday cups, delivers comparably precise results for Sr and Pb isotopic analysis. [9] High-precision isotope ratio determination *via* either TIMS or MC-ICP-MS requires quantitative isolation of the target element from its matrix prior to isotope ratio measurement. Common isolation techniques for Sr include the use of AG50WX8 ion exchange resin [10,11] or extraction chromatographic Sr spec^{TM} resin [12], which can also be used for Pb isolation [13]. Other commonly applied Pb separation methods involve the use of extraction chromatographic Pb spec^{TM} resin [14,15] or AG1X8 ion exchange resin [16]. The single stage isolation of both Sr and Pb on Sr spec^{TM} resin, as described by Deniel and Pin [17], has obvious advantages such as reduced laboratory time and sample handling (and hence lower contamination risk), but is still costly and time-consuming due to extensive cleaning procedures. In this paper, we present a routinely applicable method for the single-stage isolation of Sr and Pb from volcanic rock powders. Compared to previously reported procedures, this method reduces costs and laboratory time without compromising accuracy or precision of subsequent MC-ICP-MS analyses. It is furthermore studied whether or not Pb isotopic fractionation occurs on the Sr spec^{TM} resin and how a non-quantitative recovery of Sr and Pb affects the accuracy of the isotope data obtained. The problem of suitable Pb isotopic rock reference materials will also be briefly discussed.

2. Experimental

2.1. Reagents and materials

All sample handling was carried out in class 10 horizontal laminar flow hoods. *Pro analysi* nitric acid (14 M) was purchased from VWR International, Fontenay-sous-Bois, France and ultrapure nitric acid (14 M) from Fisher Scientific, Loughborough, UK. *Pro analysi* hydrochloric acid (12 M) (Panreac, Spain) was further purified by sub-boiling distillation in quartz equipment. Hydrofluoric acid (22 M, instra-analyzed) was bought from J.T. Baker Chemicals N.V., The Netherlands. Ultrapure water with a resistivity >18 MΩ cm was obtained from a Milli-Q Element system (Millipore, USA) and was used throughout this work for diluting concentrated acids. Standard solutions for quantitative analysis were prepared by diluting commercially available single element 1 g L^{-1} stock solutions (Alfa Johnson-Matthey, Germany). Certified reference materials used for method validation and assessing data accuracy were available from the National Institute for Standards and Technology, USA (NIST SRM 987 strontium carbonate, NIST SRM 981 common lead and NIST SRM 997 thallium isotopic standard), the United States Geological Survey (USGS) (andesite AGV-2 and Hawaiian basalt BHVO-2) and the Geological Survey of Japan (GSJ) (basalt JB-2). In-house standard LB43 (Ca-rich island arc basalt), previously characterised for its Pb isotopic composition *via* both TIMS (Adelaide, Australia) and MC-ICP-MS (Amsterdam, the Netherlands) [18], was used as a fourth rock reference material. Sr spec[TM] resin (particle diameter 50-100 µm) was purchased from TrisKem International, France (formerly Eichrom Environment). More information on the chemical properties of this extraction chromatographic resin and the binding properties of Sr, Pb and other elements can be found in the literature. [19,20] Biorad polypropylene 1 mL columns with an internal diameter of 6 mm were used as the container holding the chromatographic resin. Rock powder dissolution and collection of the Sr and Pb fractions during separation was carried out in flat bottom screw cap Teflon (PFA) vials (Savillex, purchased from AHF Analysentechnik, Tübingen, Germany).

Since low blanks are essential for the application of Pb isotope ratios to geology, but can be rather difficult to achieve, special care was taken to clean all lab material thoroughly before use. Every lab

tool was hereby cleaned with acid(s) of similar strength as the one(s) it would come in contact with when used during dissolution, separation or dilution of the samples. This way, contamination that could potentially come from the lab material was already leached out during cleaning. The cleaning procedures involved a four-step protocol for cleaning all Teflon recipients, starting with boiling them for 2 hours in 6 M *pro analysi* HNO_3, and repeating this step with 6 M *pro analysi* HCl. The Teflon vials were then filled for about one third with a 4 to 1 mixture of 14 M *pro analysi* HNO_3 and ultrapure 22 M HF, thoroughly closed and left on a hotplate at 110°C for 24 hours. After subsequent emptying and rinsing the vials with Milli-Q water, this third step was repeated with 6 M subboiled HCl. Pipette tips were cleaned by keeping them in 6 M subboiled HCl for at least one week after which they were rinsed with Milli-Q water and dried. Micro-centrifuge tubes were cleaned by filling them with ultrapure HNO_3, 7 M if they were to be used for centrifuging or 1.5 M if they would be used for the final MC-ICP-MS dilution. When cleaning with 7 M HNO_3, the centrifuge tubes were emptied after 24 hours, rinsed with Milli-Q water and dried; centrifuge tubes filled with 1.5 M HNO_3 were emptied and rinsed after one week. Separation columns were first kept in 7 M ultrapure HNO_3 for 24 hours, then rinsed with Milli-Q water, then kept in subboiled 6 M HCl for up to one week and finally stored in subboiled 1 M HCl. Cleaning and storing the columns in 1 M HBr was omitted to reduce laboratory time, costs and the risk of contamination that comes with the introduction of an additional chemical compound.

One week prior to separation, Sr spec[TM] resin was dispersed in Milli-Q water, left 15 minutes to settle down after which the supernatant was poured off and replaced with fresh Milli-Q water. This was repeated until the water above the settled resin was clear (approximately 4 to 5 times) and the resin was then stored in Milli-Q water. The necessity of pre-cleaning our Sr spec[TM] resin with 6 M ultrapure HCl as described in Deniel and Pin [17] was assessed in a first series of analyses. Hereby, 4 mL of Sr spec[TM] resin was packed into a 10 mL Biorad polypropylene column and the resin was further washed with 250 mL of 6 M subboiled HCl and subsequently stored in 6 M subboiled HCl. The blanks and Sr and Pb isotope ratios obtained using the HCl pre-cleaned resin on the one hand and the H_2O-rinsed resin on the other hand, were compared afterwards.

2.2. Sample digestion and chemical separation

Approximately 100 mg of powdered rock samples and reference materials were weighed into 15 mL flat bottom Teflon (PFA) screw cap vials for dissolution. 1 mL of 14 M HNO_3 and 2 mL of 22 M HF were added and the closed vials were left on a hotplate at 110°C for 24 hours. After subsequent evaporation to dryness 4 mL of *aqua regia* were added, again leaving the capped vials for 24 hours on a hotplate at 110°C, before dry down. The third step consisted of adding 1 mL of 14 M HNO_3, closing the vial, gently swirling it and then evaporating to dryness straight away, and was repeated once. The samples were finally taken up in 1.2 mL of 7 M HNO_3, transferred to a 1.5 mL centrifuge tube and centrifuged for 70 seconds at 6000 rotations per minute. As it was observed that the total amount of sample dissolved was too much to be taken up in the final 1.2 mL of 7 M HNO_3 and a significant deposit was left behind after centrifuging, only 1 mL was brought onto the separation columns. In a second series of analyses, the 0.2 mL residue of reference material AGV-2 was then taken through the last steps of the digestion procedure again and subsequently analysed to assess the impact of this incomplete uptake on data quality. The whole rock digestion procedure described above is only suitable for materials that do not contain refractory minerals such as zircon. However, for near zero-age samples of magmatic rocks the non-dissolution of zircons will only affect the Pb isotope ratio if they are much older xenocrysts.

Three series of separations and analyses were carried out. A first series aimed at determining the necessary level of resin purity and optimising the amount of resin and the volume and type of elution acids needed. In a second series, this method was validated through the analysis of 4 rock reference materials and finally applied to 25 volcanic rock samples from the South Aegean arc. The analysis of two duplicates of rock reference material JB-2 in this second series yielded one anomalous Pb isotopic composition, suggesting that this rock standard has an inhomogeneous Pb isotopic composition. Another 6 analyses of JB-2, and two more of BHVO-2, were therefore undertaken in a third series. For Sr isolation the protocol developed by De Muynck *et al.* [12] was largely followed. The procedure for Pb isolation was based on the method from Deniel and Pin [17], focusing on whether omitting and/or

reducing cleaning steps could reduce laboratory time and costs, without compromising accuracy and precision of the data. The separation scheme tested in the first series is described below and outlined in Table 1. Seven columns were filled with approximately 250 µL of Sr spec[TM] resin: four with 6 M HCl pre-cleaned resin and three with resin only rinsed with Milli-Q water. These columns were washed with 10 mL of 6 M HCl (instead of 20 mL [17]) before conversion to an aqueous environment with 3 mL of Milli-Q H_2O and conditioning with 1 mL of 7 M HNO_3. Then one set of columns, consisting of one column filled with HCl cleaned resin and one containing Milli-Q H_2O rinsed resin, was loaded with JB-2, one set was loaded with a 'full procedure blank' (an empty Teflon vial taken along during the full chemical procedure to quantify potential contamination from laboratory work and reagents), and one set was not loaded in order to get a 'column blank' to assess potential contamination from columns, resin and reagents. The additional column filled with HCl pre-cleaned resin was loaded with a solution of AGV-2. After loading, matrix elements were eluted with 5 mL of 7 M HNO_3 and the Sr fraction collected in 5 mL of Milli-Q H_2O. To obtain the hydrochloric environment in which Pb is stripped from the resin, 1 mL of 3 M HCl was brought onto the column. This 1 mL aliquot was collected to assess (i) the potential tailing of Sr into the Pb fraction and (ii) the amount of Pb that might be already eluted in this step. Finally, the Pb fraction was eluted with 4 mL of 8 M HCl, collected in 10 aliquots of 400 µL each to study the Pb elution profile. The collected fractions were evaporated to dryness, converted to nitrate with several drops of 14 M HNO_3, and evaporated to dryness again. The Pb and Sr fractions were finally taken up in 1 and 5 mL of 0.28 M HNO_3, respectively. In the second and third series of separations, this isolation procedure (Table 1) was completed in about 4-5 hours for 20 samples.

2.3. Instrumentation and measurement protocols

2.3.1 Quantitative analyses

Quantitative analyses were carried out using a quadrupole-based Perkin-Elmer SCIEX Elan 5000 ICP-MS instrument. The sample introduction system consisted of a multi-channel peristaltic pump (Minipuls-3, sample uptake rate of approximately 1 mL min^{-1}), a GemTip cross-flow nebulizer, a

Perkin-Elmer Type II spray chamber made of Ryton, and a Perkin-Elmer corrosion-resistant torch with alumina injector. Instrument settings and data acquisition parameters for this instrument are summarised in Table 2. All purified Sr and Pb fractions were analysed for Rb, Sr and Pb with ICP-Q-MS to (i) determine the Sr and Pb concentrations in each sample, (ii) assess whether Sr was adequately separated from Rb and (iii) find out how fast Pb was eluted from the column. For these measurements, calibration standard solutions with 100 µg L^{-1} Rb, Sr, Pb, Tl and Y were made, with the latter two elements acting as internal standards, correcting for signal drift and instrument instability. From each sample, an aliquot was diluted 10 times with 0.28 M HNO$_3$ and Y and Tl were added to obtain a final concentration of 100 µg L^{-1} for the latter two elements. The concentration data obtained were also used to make the dilutions for MC-ICP-MS measurements.

2.3.2 Isotope ratio determination

Sr and Pb isotope ratio measurements were carried out using a Thermo Scientific Neptune MC-ICP-MS instrument. This instrument provides double-focusing with a Nier-Johnson geometry and was operated in low resolution mode (m/Δm = 400). The sample introduction system consisted of an auto-aspirating low-flow (50 µL min^{-1}) PFA nebulizer (ESI Scientific, Omaha, NE, USA) mounted onto a combined cyclonic/double-pass spray chamber made of quartz glass. Instrument settings, data acquisition parameters and cup configurations used for Sr and Pb isotope ratio measurements are presented in Table 2.

2.3.2.1 Measurement of Sr isotope ratios

Sr concentrations of purified Sr fractions and a solution of NIST SRM 987 were adjusted to 300 µg L^{-1} by dilution with 0.28 M HNO$_3$ as it has been shown that the target element concentrations affect the extent of mass discrimination. [21] The MC-ICP-MS cup configuration chosen for Sr isotopic analysis is presented in Table 2. ^{83}Kr$^+$ was monitored to assess potential isobaric interferences from ^{84}Kr$^+$ and ^{86}Kr$^+$ on ^{84}Sr$^+$ and ^{86}Sr$^+$, respectively. Likewise, Rb was monitored at *m/z* 85 to allow correction for the isobaric interference of ^{87}Rb$^+$ on ^{87}Sr$^+$. The 300 µg L^{-1} Sr solutions of samples and standards resulted

in a $^{88}Sr^+$ ion current of 85 – 106 pA (8.5 – 10.6 V signal intensity). After every sample or standard measurement, the sample introduction system was rinsed with 0.28 M HNO_3 for 200 seconds in order to minimise memory effects. Instrument blanks (0.28 M HNO_3) were measured before and after each sample or standard and found to be negligible with a $^{88}Sr^+$ signal intensity <0.06% of the $^{88}Sr^+$ intensities for samples and standards. Procedure blanks (undiluted) were also negligible, as their $^{88}Sr^+$ ion current never exceeded 0.012 pA (corresponding to less than 300 pg), which is <0.13% of $^{88}Sr^+$ ion current of the samples which had been diluted 27 to 105 times (*i.e.* less than 0.005%).

2.3.2.2 Measurement of Pb isotope ratios

For Pb isotopic analysis, samples were diluted with 0.28 M HNO_3 to 200 µg L^{-1} Pb to match the 200 µg L^{-1} Pb NIST SRM 981 solution used for the sample-standard bracketing procedure. In order to also allow mass bias correction by external normalisation, NIST SRM 997 Tl was added to both samples and bracketing standards to obtain a concentration of 20 µg L^{-1}. Table 2 presents the MC-ICP-MS cup configuration used for Pb isotopic analysis. Potential isobaric interference of $^{204}Hg^+$ on $^{204}Pb^+$ was checked by monitoring the signal of $^{202}Hg^+$. Before and after every sample, a NIST SRM 981 standard solution was measured and a 0.28 M HNO_3 blank was measured every three samples. The $^{208}Pb^+$ ion current varied between 46 pA and 61 pA for 200 µg L^{-1} Pb (4.6 - 6.1 V signal intensity). After every sample or standard measurement the sample introduction system was rinsed with 0.28 M HNO_3 for up to 500 seconds until signal intensities for the different *m/z* ratios analysed returned to blank levels, which was between 0.0005 pA and 0.005 pA (0.5 – 5 mV) for $^{208}Pb^+$ (<0.09% of sample intensity). Procedure blanks for Pb (which were lower than 150 pg) were also negligible compared to Pb intensities for samples and standards (<0.07%).

3. Data handling and resulting isotopic composition of the rock reference materials

Microsoft Excel spreadsheets were used to calculate the $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of samples and reference materials from the raw intensity data of the different m/z ratios measured. We hereby assume that $^{87}Rb/^{85}Rb$, $^{204}Hg/^{202}Hg$, $^{205}Tl/^{203}Tl$ and $^{86}Sr/^{88}Sr$ ratios are

invariant, an assumption which is not necessarily correct but a simplification appropriate and permissible within the fit-for-purpose framework of this technical note.

3.1. Sr isotope ratios

For Sr isotope ratios, the average of the blanks measured before and after each sample was subtracted from the sample analysis on a scan-by-scan-basis. The remaining $^{83}Kr^+$ signal was negligible so that further correction for spectral overlap of $^{84}Kr^+$ and $^{86}Kr^+$ on $^{84}Sr^+$ and $^{86}Sr^+$ respectively, was unnecessary. Since there was a <0.2% contribution of Rb at m/z 87, interference of $^{87}Rb^+$ on $^{87}Sr^+$ was corrected for using a $^{87}Rb/^{85}Rb$ ratio of 0.3856 [22] and assuming that Rb and Sr display the same mass discrimination behaviour. Mass discrimination correction was carried out *via* internal normalisation to a $^{86}Sr/^{88}Sr$ ratio of 0.1194 [22], applying the mass dependent Russell equation [23] $R_{true}/R_{observed} = (m_1/m_2)^\beta$, in which β represents the mass discrimination factor, R_{true} the corrected isotopic ratio, $R_{observed}$ the experimentally measured isotopic ratio, and m_1 and m_2 the masses of the isotopes in the ratio R . Table 3 presents the $^{87}Sr/^{86}Sr$ ratios obtained for the 5 reference materials analysed, their experimental uncertainty expressed as 2 SD and their respective literature preferred values.

3.2. Pb isotope ratios

For the Pb isotope ratios (Table 3), a blank correction was carried out with the running average of the blanks measured before and after every three samples. $^{204}Pb^+$ ion current intensities were corrected for $^{204}Hg^+$ spectral overlap based on the intensity of $^{202}Hg^+$, which was generally negligible after blank correction, assuming a $^{204}Hg/^{202}Hg$ ratio of 0.230 [22]. Mass discrimination correction for Pb isotope ratios is commonly carried out by either sample-standard-bracketing (SSB) or thallium normalisation. Since the debate on the preference and suitability of these two methods is still ongoing[28,29], we carried out the mass discrimination correction via both methods and compared the results. For standard-sample-bracketing (SSB) the approach described by Elburg *et al.* [28] was followed, applying the NIST SRM 981 values reported by Baker *et al.* [24] of 36.7258, 15.499, and 16.9416 for $^{208}Pb/^{204}Pb$,

$^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$, respectively. All data were also corrected for mass discrimination with the thallium-normalisation method of White *et al.*[30] using the preferred NIST SRM 997 $^{205}Tl/^{203}Tl$ ratio of 2.3871 [31]. The isotope ratios resulting from these two different mass discrimination approaches were compared (see Table 3) and yielded isotopic compositions that are identical within analytical uncertainty.

4. Results and discussion

4.1. Sr spec™ resin cleaning

Comparison of the Pb concentrations found in the 10 mL of 6 M subboiled HCl used to wash the Sr spec™ resin on the columns showed that up to 20 times more Pb was present in the H_2O-rinsed resin than in the HCl pre-cleaned resin. However, blanks subsequently taken from both types of resins during Sr and Pb isolation are similar and contain only negligible amounts of Pb. Washing 250 µL of H_2O-cleaned resin with 10 mL of 6 M subboiled HCl prior to separation seemed sufficient to strip off all Pb. It was therefore concluded that in our case the expensive and time-consuming step of pre-cleaning 4-5 mL of Sr spec™ resin with 250 mL of 6 M ultrapure HCl can be omitted, as well as the procedure of washing and storing the separation columns in 1 M HBr. Procedure blanks for Pb isotope ratios from the second and third series of analyses, in which this shortened resin-cleaning protocol (rinsing and storing Sr spec™ in Milli-Q water) was adopted, were also negligible. It is however possible that the purity of Sr spec™ resin varies between different batches and that more thorough cleaning may be necessary in some cases. This could be tested for each batch by undertaking an experiment similar to the one described in this article, in which blanks derived from Sr spec™ resin cleaned in different ways are compared with one another to identify the optimal cleaning procedure for that specific batch of Sr spec™ resin.

4.2. Incomplete sample uptake and recovery

It was observed that the total amount of sample dissolved (0.1 g) was too much to be taken up in the final 1.2 mL of 7 M HNO_3 as a significant deposit was left behind after centrifuging. A comparison

between the Sr and Pb concentrations obtained after separation and the concentrations expected in the respective rocks, showed that up to 50% of the Sr and Pb was missing. It was therefore investigated in the second series of analyses whether the observed incomplete uptake could be responsible and whether or not this could introduce isotopic fractionation. The deposit of AGV-2 was hereby taken through the last steps of the digestion procedure again, this time resulting in complete uptake, and its Sr and Pb isolated and analysed. Table 3 shows that the Sr and Pb isotopic compositions of this deposit and its supernatant are identical within analytical uncertainty, indicating that the quality of the analyses is not compromised by incomplete sample uptake. Because of this incomplete uptake it is not possible to evaluate the recovery of Sr and Pb and therefore only an estimation of the achieved recovery could be made, based on the data from the two-step complete uptake of AGV-2. The calculated amount of Pb in the AGV-2 aliquot (1.36 µg) is higher than the total amount of Pb present in the two purified Pb fractions (1.0 µg) indicating a recovery of 78.6% for Pb in this case. The 'missing' Pb may have been lost from the column already during Sr elution and/or in the 1 mL of 3 M HCl step to convert to a hydrochloric environment. Another part may have been retained on the Sr spec[TM] resin. The difference for AGV-2 between the calculated amount of Sr present (68.3 µg) and the total amount retrieved after isolation (36.5 µg) reflects that the resin was overloaded for Sr. This is however unavoidable since most volcanic rocks have Pb concentrations up to 100 times lower than their Sr concentrations, so that approximately 0.1 g of whole rock powder needs to be digested to obtain Pb concentrations high enough for precise Pb isotopic analysis. The range of Sr and Pb concentrations in the rocks analysed for this study was 200-760 µg g^{-1} and 1.6-35 µg g^{-1}, respectively. The amounts of Sr and Pb retrieved in the isolated fractions of the digestion of approximately 0.1 g rock powder varied from 15.1 µg to 32.8 µg and from 0.13 µg to 2.0 µg, respectively.

4.3. Pb isotopic fractionation introduced by the isolation process

De Muynck et al. [12] already reported that no Sr isotopic fractionation occurs during the Sr isolation process using Sr spec[TM] resin. To assess potential isotopic fractionation of Pb during the isolation process and to obtain the elution profile of the Pb fraction, the 4 mL of 8 M HCl were collected in 10

aliquots of 400 μL each (see Table 1), that were afterwards analysed for their Pb concentration and Pb isotopic composition. Up to 2.1% of the total amount of Pb stripped off the resin was already eluted in the 1 mL of 3 M HCl brought onto the column to convert to hydrochloric acid medium (see Fig. 1). The first three elution fractions (1.2 mL of 8 M HCl) represented between 95.3% and 98.7% of the total amount of Pb eluted. Fig. 1 shows that the ^{207}Pb/^{204}Pb isotope ratio of the first three elution fractions of AGV-2 are in excellent agreement with the literature preferred isotopic value [24]. The ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios show similar patterns, as well as the Pb isotope ratios of the two JB-2 duplicates, indicating that no Pb isotopic fractionation was introduced by the Pb isolation process on the Sr spec^{TM} resin. This conclusion is in line with the previously reported absence of Pb isotopic fractionation during isolation of Pb on the chemically similar Pb spec^{TM} resin. [15] Gale [13], who obtained a recovery > 98%, also observed that Pb isotopic compositions obtained after separation with Sr spec^{TM} resin are indistinguishable from the ones resulting from other Pb separation methods. The increase of analytical uncertainty and aberrant isotopic ratios in the fourth and fifth fraction can be attributed to the very low Pb concentrations present in these elution fractions (< 8 μg L^{-1}).

4.4 Note on rock powder reference materials as Pb isotopic standards

The suitability of rock powder reference materials as isotopically homogeneous, matrix-matched standards for Pb isotope ratio analysis of real geological samples has been a 'hot topic' in the geochemical community for about a decade. Pb isotopic analyses of the same rock reference materials have been carried out by different researchers and according to a range of analytical procedures and mass discrimination correction methods. This resulted in the discovery of varying degrees of Pb isotopic heterogeneity between different rock reference materials, and sometimes also between different splits from the same standard. [24,28,32,33] The Pb isotopic analyses carried out by Baker et al.[24] using a ^{207}Pb-^{204}Pb double spike and Tl to correct for mass bias show the best external reproducibilities and are therefore chosen as the literature preferred values to compare our results with. The external precision of the data obtained via the method presented in this paper is somewhat lower, but the fact that they match the data of Baker et al. [24] within analytical uncertainty reflects their accuracy (see

Table 3). Out of the 8 analyses of JB-2 carried out for this research, 7 rendered isotopic compositions in agreement with the preferred value of Baker *et al.* [24], who suggested JB-2 to be the most homogenous and therefore the most suitable rock reference material for Pb isotopic measurements. However, an 8th duplicate of our split of JB-2 yielded an anomalous isotopic composition outside the analytical uncertainty of previously published high-precision Pb isotopic data, regardless of its lower precision (see Fig. 2). After thorough checking of the data reduction process and ruling out potential contamination, this is thought to be no analytical outlier but a true reflection of the Pb isotopic value for this replicate. So far, only one anomalous Pb isotopic measurement of JB-2 has been reported in literature. [28] This was ascribed by Elburg *et al.* [28] to the presence of nugget contamination, causing good reproducibility of most analyses with only incidental dissolutions suffering from contamination introduced during production of the reference material. The aberrant value found in the present study therefore represents growing evidence that JB-2 is less homogeneous in its Pb isotopic composition than previously reported. The one anomalous BHVO-2 analysis in our study (see Table 3) confirms the earlier observations of Baker *et al.* [24] that BHVO-2 is one of the most heterogeneous rock reference materials for Pb isotope data. This is indeed shown by the low external precision of the average value we obtained for this standard, calculated from three different aliquots that individually agreed within 2 SD with the literature preferred value.

5. Conclusions

We adapted and optimised the single-stage isolation procedure for Sr and Pb of Deniel and Pin [17] into a more straightforward procedure for routine application to Sr and Pb isotope ratio analyses of volcanic rocks with MC-ICP-MS. Simplifying the pre-cleaning procedure of the Sr spec^{TM} resin and cutting out the use of HBr were major cost- and time-saving adaptations, which we could introduce for our batch of Sr spec^{TM} resin without compromising the quality of the isotope ratio data. It may be possible, however, that different batches of Sr spec^{TM} resin vary in purity and that it therefore needs to be assessed for each batch individually to what extent the resin should be cleaned.

Our analytical procedure does not always allow for complete uptake of the 0.1 g of rock powder in the final volume in which it is taken up before separation chemistry. But analysis of AGV-2's dissolved fraction on the one hand and its deposit on the other hand, yielded Sr and Pb isotopic compositions identical within analytical uncertainty. This indicates that incomplete uptake of the sample does not compromise the resulting Sr and Pb isotopic data.

The isotopic homogeneity of the first three Pb elution fractions, representing up to 98.7% of the total amount of Pb stripped from the resin, indicates that no Pb isotopic fractionation is introduced during the isolation procedure.

Out of eight analyses of JB-2, one gave a distinct Pb isotopic composition outside analytical uncertainty. Together with the one other published anomalous JB-2 analysis [28] this now strongly suggests that this rock reference material, like many others, is isotopically heterogeneous for lead and therefore not as suitable as a Pb isotopic standard as previously thought. Suitable rock reference materials however need to be run within batches of unknowns to be able to demonstrate data accuracy, and JB-2 still seems to be the most suitable Pb isotopic rock reference material. The growing evidence of its nugget contamination, resulting in a varying percentage of 'wrong' aliquots for different splits, can be taken into account by analysing at least two JB-2 duplicates with each batch of samples. Additionally, an internal lab standard with known isotopic composition gathered *via* different high-precision isotopic analyses could be used to monitor long-term reproducibility.

Acknowledgements

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Table captions

Table 1 Separation scheme for the single-stage separation of Sr and Pb using Sr spec^{TM} chromatographic resin, as carried out in the first series (test phase) and the second and third series (optimised protocol).

Table 2 Instrument settings and data acquisition parameters for the ICP-MS instruments used in this work, and Sr and Pb cup configurations applied on the multi-collector ICP-MS.

Table 3 Experimental and preferred $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios obtained for the four rock and two isotopic reference materials analysed in this work. Pb isotope ratios have been calculated with both the sample-standard-bracketing procedure (SSB) and Tl normalisation method (Tl-norm) (see text). Analytical uncertainty represents 2SD of one measurement run of 50 scans, unless multiple duplicates of the rock reference material have been measured on different occasions, in which case it is indicated how many duplicates were measured (n=x) and the uncertainty then represents 2SD on the average value obtained for the different duplicates. The Sr and Pb isotopic compositions obtained in this study for NIST SRM 987 and NIST SRM 981, respectively, are also presented, giving the best estimate for the external reproducibility. The preferred Pb isotopic compositions of AGV-2, BHVO-2, JB-2 and NIST SRM 981 are taken from Baker et al. [24], the value for LB43 from Elburg et al. [18].

Figure captions

Fig. 1. Pb elution profile for rock reference material AGV-2 with Pb concentrations (bars) expressed in µg L^{-1}, determined quantitatively with ICP-Q-MS. The profile shows that Pb elution already starts during the conversion from nitric to hydrochloric acid medium in 1 mL 3 M HCl and that most of the Pb is subsequently released in the first three 400 µL 8 M HCl elution fractions. The evolution of the ^{207}Pb/^{204}Pb ratio over the first 5 elution steps (2 mL 8 M HCl) is also shown (filled circles), with error bars representing 2SD uncertainty intervals. Black solid line and grey dotted lines respectively represent the literature preferred ^{207}Pb/^{204}Pb ratio of AGV-2 and corresponding 2SD uncertainty interval. [24]

Fig. 2. ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plot for rock powder reference material JB-2 in which the eight measurements from this study are compared to JB-2 Pb isotopic compositions previously reported in literature [24, 28, 34]. The one anomalous analysis from this study is presented with its 2SD error bars.

Table 1 – Smet *et al.*

Test phase							Action	Optimised protocol
250 µL HCl pre-cleaned Sr spec™ resin				250 µL H$_2$O rinsed Sr spec™ resin			bringing resin onto the column	250 µL H$_2$O rinsed Sr spec™ resin
10 mL 6 M HCl							cleaning resin	10 mL 6 M HCl
3 mL Milli-Q H$_2$O							removal of HCl	3 mL Milli-Q H$_2$O
1 mL 7 M HNO$_3$							resin conditioning	1 mL 7 M HNO$_3$
JB-2 A	AGV-2	procedural blank A	/	JB-2 B	procedural blank B	/	sample loading	1 mL sample (in 7 M HNO$_3$)
5 mL 7 M HNO$_3$							matrix removal	4 mL 7 M HNO$_3$
5 mL Milli-Q H$_2$O							Sr fraction elution	4 mL Milli-Q H$_2$O
1 mL 3 M HCl							conversion to hydrochloric acid medium	1 mL 3 M HCl
4 mL 8 M HCl in 10 steps of 400 µL							Pb fraction elution	3 mL 8 M HCl

Table 2 -Smet *et al.*

Instrument settings

	ELAN 5000 ICP-Q-MS	Neptune MC-ICP-MS
RF power	1000 W	1200 W
Plasma gas flow rate	15 L min^{-1}	13 L min^{-1}
Auxiliary gas flow rate	0.8 L min^{-1}	0.7 L min^{-1}
Nebulizer gas flow rate	0.8-0.85 L min^{-1} *	1.0 L min^{-1} **
Sampling cone	Ni, aperture diameter 1.1 mm	Ni, aperture diameter 1.1 mm
Skimmer	Ni, aperture diameter 0.9 mm	Ni, aperture diameter 0.7 mm

* optimised daily for (i) maximum sensitivity for ^{9}Be^{+}, ^{59}Co^{+}, ^{103}Rh^{+}, ^{115}In^{+}, ^{208}Pb^{+} and (ii) minimal oxide formation (^{232}Th^{16}O^{+}/^{232}Th^{+} < 5%)
** optimised daily for maximum ^{88}Sr^{+} or ^{208}Pb^{+} intensity

Data acquisition parameters for the ELAN 5000 ICP-Q-MS

Scanning mode	Peak hopping
Dwell time	50 ms
Settling time	5 ms
Number of acquisition points per spectral peak	1
Number of sweeps	20
Number of readings	3
Number of replicates	5
Replicate time	~ 17 s per isotope
Detector dead time	69 ns

Data acquisition parameters for the Neptune MC-ICP-MS

Integration time	4.2 s
Number of cycles	10 per block
Number of blocks	5
Measurement time per sample	~ 210 s

Sr cup configuration on Neptune MC-ICP-MS

L3	L2	L1	C	H1	H2
^{83}Kr^{+}	^{84}Sr^{+}	^{85}Rb^{+}	^{86}Sr^{+}	^{87}Sr^{+}	^{88}Sr^{+}
	^{84}Kr^{+}		^{86}Kr^{+}	^{87}Rb^{+}	

Pb cup configuration on Neptune MC-ICP-MS

L3	L2	L1	C	H1	H2	H3
^{202}Hg^{+}	^{203}Tl^{+}	^{204}Pb^{+}	^{205}Tl^{+}	^{206}Pb^{+}	^{207}Pb^{+}	^{208}Pb^{+}
		^{204}Hg^{+}				

Table 3 – Smet *et al.*

	$^{87}Sr/^{86}Sr$	2SD	$^{206}Pb/^{204}Pb$	2 SD	$^{207}Pb/^{204}Pb$	2SD	$^{208}Pb/^{204}Pb$	2 SD
AGV-2 -1st solution - Sr	0.703971	0.000130						
AGV-2 - redissolved precipitate - Sr	0.704023	0.000104						
AGV-2 - 1st solution - Pb – SSB			18.8740	0.0074	15.6149	0.0070	38.5438	0.0152
AGV-2 - redissolved precipitate -Pb – SSB			18.8722	0.0096	15.6211	0.0084	38.5479	0.0242
AGV-2 Preferred	*0.703995* [25]	*0.000012*	*18.8730*	*0.0050*	*15.6210*	*0.0030*	*38.5520*	*0.0100*
BHVO-2 - Sr (n=4)	0.703480	0.000052						
BHVO-2 - Pb – SSB (n=3)			18.6626	0.0474	15.5398	0.0222	38.2353	0.0602
BHVO-2 - Pb – Tl-norm (n=3)			18.6613	0.0476	15.5377	0.0220	38.2295	0.0560
BHVO-2 Preferred	*0.703469* [26]	*0.000034*	*18.6490*	*0.0190*	*15.5400*	*0.0150*	*38.2490*	*0.0220*
BHVO-2 aberrant - SSB			18.4746	0.0118	15.5433	0.0100	38.1010	0.0260
BHVO-2 aberrant – Tl-norm			18.4730	0.0118	15.5421	0.0100	38.0941	0.0238
JB-2 - Sr (n=10)	0.703697	0.000028						
JB-2 - Pb – SSB (n=9)			18.3440	0.0062	15.5636	0.0046	38.2808	0.0124
JB-2 - Pb – Tl-norm (n=9)			18.3434	0.0046	15.5642	0.0054	38.2825	0.0126
JB-2 Preferred	*0.703709* [27]	*0.000058*	*18.3435*	*0.0017*	*15.5619*	*0.0016*	*38.2784*	*0.0050*
JB-2 aberrant - SSB			18.3252	0.0086	15.5596	0.0084	38.2575	0.0200
JB-2 aberrant – Tl-norm			18.3215	0.0088	15.5557	0.0082	38.2453	0.0224
LB43 - Sr (n=1)	0.703914	0.000098						
LB43 - Pb – SSB (n=1)			18.7121	0.0086	15.5947	0.0080	38.8174	0.0200
LB43 - Pb – Tl-norm (n=1)			18.7120	0.0066	15.5936	0.0062	38.8132	0.0168
LB43 Preferred	*0.703897* [18]	*0.000035*	*18.7250*	*0.0080*	*15.5900*	*0.0060*	*38.8200*	*0.0160*
NIST SRM 987- Sr (n=35)	0.710266	0.000048						
NIST SRM 987 Preferred	*0.710244* [28]	*0.000014*						
NIST SRM 981- Pb – Tl-norm (n=86)			16.9419	0.0042	15.4997	0.0036	36.7243	0.0094
NIST SRM 981 Preferred			*16.9416*	*0.0011*	*15.4999*	*0.0011*	*36.7258*	*0.0031*

Fig. 1 – Smet *et al.*

Fig. 2 – Smet *et al.*