High-precision mass-dependent molybdenum isotope variations in magmatic rocks determined by double-spike MC-ICPMS

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Abstract
Small mass-dependent variations of molybdenum isotope ratios in oceanic and island arc rocks are expected as a result of recycling altered oceanic crust and sediments into the mantle at convergent plate margins over geological timescales. However, the determination of molybdenum isotope data precise and accurate enough to identify these subtle isotopic differences remains challenging. Large sample sizes – in excess of 200mg – need to be chemically processed to isolate enough molybdenum in order to allow sufficiently high-precision isotope analyses using double-spike MC-ICPMS techniques. Established methods are either unable to process such large amounts of silicate material or require several distinct chemical processing steps, making the analyses very time-consuming. Here, we present a new and efficient single-pass chromatographic exchange technique for the chemical isolation of Mo from silicate and metal matrices. To test our new method we analysed USGS reference materials BHVO-2 and BIR-1. Our new data are consistent with those derived from more involved and time-consuming methods for these two reference materials previously published. We also provide the first molybdenum isotope data for USGS reference materials AGV-2, the GSJ reference material JB-2 as well as metal NIST SRM 361.

Keywords: molybdenum, Mo, mass-dependent, stable isotopes, oceanic basalts, mantle recycling, anionic chromatographic exchange, double spike, MC-ICPMS

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Introduction

Mass-dependent variations of molybdenum (Mo) isotopes in marine sediments are a well-established geochemical tool to study redox conditions in the Earth’s water masses over the geological past (e.g. Barling et al. 2001, Siebert et al. 2003, Archer and Vance 2008). During surface processing, the speciation and thus solubility of Mo in aqueous systems strongly depends on the ambient redox conditions (e.g. Emerson and Hustedt 1991, Helz et al. 1996). This makes the Mo isotope system highly susceptible to natural mass-dependent isotope fractionation (McManus et al. 2002, Barling and Anbar 2004, Wasylenki et al. 2008). As a consequence, sedimentary rocks can show mass-dependent $^{98}$Mo/$^{95}$Mo isotope variations of up to 5‰ (e.g. Siebert et al. 2003, Anbar 2004, Pearce et al. 2008, Gordon et al. 2009, Scheiderich et al. 2010b). Similarly, exchange reactions between the seafloor and the hydrosphere are likely to impart Mo isotope variations on altered mafic and ultra-mafic oceanic rocks due to the rather large isotopic difference of ca. 2.5‰ between seawater and fresh oceanic crust (e.g. Anbar 2004). Thus, the $^{98}$Mo/$^{95}$Mo of mantle-derived rocks from subduction zones and ocean island basalts could be useful to trace crustal material recycled into the Earth’s mantle.

Although the $^{98}$Mo/$^{95}$Mo of the uppermost oceanic crust can be significantly perturbed, the bulk of recycled component, dominantly comprising mafic lithologies that have been little altered, is likely to carry a much less fractionated signal. Thus, only small isotopic perturbations are expected for oceanic mantle-derived rocks containing such a recycled component. In fact, the total variation in $^{98}$Mo/$^{95}$Mo of magmatic rocks from various tectonic settings analysed so far is less than 1‰ (Siebert et al. 2003, Pearce et al. 2009, Burkhardt et al. 2014, Greber et al. 2014, Voegelin et al. 2014, Freymuth et al. 2015, Greber et al. 2015, Yang et al. 2015). To resolve and understand such subtle isotopic variations, high-precision Mo isotope data for magmatic rocks are required. Highly precise and accurate Mo isotope data can be achieved by using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) combined with a double spike method (Siebert et al. 2001, Archer and Vance 2008, Pearce et al. 2009). This method allows robust correction of instrument-induced isotopic fractionation in natural samples (e.g. see Rudge et al. 2009).

Complications arise from the low concentration of Mo in mantle-derived melts when compared to chemical sediments on which most Mo isotope work to date has been conducted (see Anbar 2004). Even when using sensitive mass spectrometric techniques, such as MC-ICPMS, sufficient amounts of Mo in the order of ~100 ng of Mo per analysis are needed to obtain the levels of precision required for geologically relevant observations in mantle-derived samples. The low Mo concentrations in many mafic rocks, a few hundred ng g$^{-1}$ in mid-ocean ridge basalts (MORB) for example, means that large sample sizes (up to grams) have to be subjected to a chemical purification procedure. Previous single-column pass Mo separation techniques were designed to process small sample sizes (<0.1 g) and are perfectly suitable for the analyses of Mo-rich sediments (e.g. Archer and Vance 2008, Goldberg et al. 2012, Xu et al. 2012). However, these methods may struggle to cope with the large sample loads required when processing mafic magmatic rocks. One way of overcoming this obstacle is to simply scale up existing protocols by increasing the volumes of chromatographic exchange resins and mobile phases (i.e. mineral acids). However, anionic chromatographic exchange resins are a major source of Mo blank. Therefore, increasing the volume of resin is not ideal from considerations of blank contribution or processing time. Alternatively, several procedures employing solvent extraction as well as multiple passes on high-volume cationic and anionic resin columns have been developed (Dauphas et al. 2001, Yin et al. 2002, Becker and Walker 2003, Wille et al. 2007, Burkhardt et al. 2014, Nagai and Yokoyama 2014). These methods achieve isolation of Mo through step-wise reduction of matrix elements and may tolerate higher sample loads. They are, however, very time-consuming and still require large resin volumes. The lack of a more efficient and convenient
chemical separation technique therefore remains one of the main obstacles in undertaking a comprehensive study of Mo mantle isotope systematics. In fact, there are few Mo isotope data available for magmatic rocks (Siebert et al. 2003, Pearce et al. 2009, Burkhardt et al. 2014, Greber et al. 2014, Voegelin et al. 2014, Greber et al. 2015, Yang et al. 2015). This is also expressed in a lack of Mo isotope data for well-characterised magmatic geological reference materials.

This study reports on the development of a new, low-volume, single-pass anion exchange separation technique that allows quantitative isolation of Mo from a range of silicate and metal matrices. At the same time, it can cope with large sample amounts while maintaining low blank levels and processing times. We tested the efficiency and applicability of this new technique by analysing a range of silicate and metal reference materials. The method described will allow efficient processing of mantle-derived rocks and will therefore contribute to establishing mass-dependent Mo isotope variations in magmatic rocks as a geodynamic tracer for geochemical applications.

**Chemical preparation procedure**

Molybdenum isotope measurements of this study were carried out using MC-ICPMS. This technique is highly susceptible to interfering elements and polyatomic ions. In particular, several elemental isobaric interferences exist for the seven stable isotopes of Mo (92Mo, 94Mo, 95Mo, 96Mo, 97Mo, 98Mo, 100Mo) namely those of 92Zr, 94Zr, 96Zr, 98Ru, 98Ru and 100Ru. Accordingly, the abundances of matrix elements and especially Zr and Ru need to be reduced to insignificant levels prior to mass spectrometric analysis. The double-spiking scheme we apply (see below) uses Mo isotopes that are not interfered by Zr. However, a procedure that separates both Zr and Ru from Mo is advantageous to allow flexibility in the range of double-spikes that can be used, to remove any negative impact of matrix elements on the sensitivity and to permit its use for mass-independent isotopic measurements.

**Reagents**

Ultra-pure grade (UpA) concentrated hydrofluoric acid (28 mol l⁻¹) and hydrogen peroxide (30% m/m), as well as super-pure grade (SpA) concentrated nitric acid (15 mol l⁻¹) were purchased from Romil Ltd. Concentrated HCl was purified twice in-house by sub-boiling distillation from analytical grade HCl (final molarity ~11 mol l⁻¹). For some samples, Romil Ltd. super-pure grade (SpA) concentrated hydrochloric acid (11 to 12 mol l⁻¹) was used. ACS-grade (99+%%) ascorbic acid was purchased from Alfa Aesar Ltd.

**Dissolution of silicate samples**

About 0.1 to 1.0g of rock powder and a combined 97Mo-100Mo tracer (in 0.4 mol l⁻¹ HNO₃ with traces of HF) were weighed into 15ml or 60ml PFA beakers (Savillex Corp.) depending on the sample size. Details concerning the preparation and composition of the combined 97Mo-100Mo tracer can be found in Archer and Vance (2008). For each 0.1 g of sample, about 0.1 ml of 15 mol l⁻¹ HNO₃ and 0.3 ml of 28 mol l⁻¹ HF were added and samples were digested for at least 24 hours in closed beakers at 150 °C. Samples were then dried down to incipient dryness. The residue was repeatedly dissolved in 6 mol l⁻¹ HCl until a clear solution was obtained. Normally less than two to three cycles of refluxing in HCl were required. We found that this step was necessary to ensure complete dissolution of the samples in low molarity HCl used for loading the samples on the columns.

**Dissolution of metal samples**

About 0.01 g of the steel reference material NIST SRM 361 was spiked with the 97Mo–100Mo tracer (see above) and dissolved in ca. 1 ml of 12 mol l⁻¹ HCl at 150°C over night. The solutions were
visually inspected to ensure complete dissolution. In some cases, dark sub-mm-sized flakes were observed. We assume that these particles represent graphite from the production process of the steel. After drying down the solution, the residue was re-dissolved in 1 ml of 15 mol l\textsuperscript{-1} HNO\textsubscript{3} and heated to 150 °C for several hours to ensure that any graphite flakes were fully oxidised and removed. The samples were then dried down at 150 °C. This step was repeated until a clear solution was obtained. The residues were then converted into chloride form by refluxing in 0.5 ml of 12 mol l\textsuperscript{-1} HCl.

**Chemical isolation of molybdenum**

Molybdenum was extracted from the silicate and metal matrices of the samples by ion exchange chromatography using the strongly anionic exchange resin AG1x8 (100-200 mesh; BioRad and Eichrom) with various acidic eluents. Before loading on the columns, the samples were brought into solution in a mixture of HCl and ascorbic acid. For ca. 200 mg of (basaltic) sample, the residue was dissolved in a mix of 4.50 ml 3 mol l\textsuperscript{-1} HCl and 0.25 ml 6 mol l\textsuperscript{-1} HCl at moderate temperatures (< 150 °C) on a hotplate. The solution was transferred into 10 ml centrifuge vials and centrifuged to remove any precipitates that may have formed during the dissolution of the sample in the dilute HCl loading solution, but which were not visible by the naked eye. Then, 0.25 ml of an aqueous 1 mol l\textsuperscript{-1} ascorbic acid (C\textsubscript{6}H\textsubscript{5}O\textsubscript{6}) solution was added. This step was normally accompanied by a change in colour from yellow (Fe\textsuperscript{3+} in HCl solution) to green/colourless (Fe\textsuperscript{2+}) depending on the total iron content of the sample. This yielded a final loading solution of 3 mol l\textsuperscript{-1} HCl – 0.05 mol l\textsuperscript{-1} ascorbic acid. If larger sample sizes or Fe-rich samples were processed (e.g. NIST SRM 361) the relative proportions of 3 mol l\textsuperscript{-1} HCl, 6 mol l\textsuperscript{-1} HCl, and 1 mol l\textsuperscript{-1} ascorbic acid solutions were adjusted accordingly. Separate addition of 6 mol l\textsuperscript{-1} and 3 mol l\textsuperscript{-1} HCl to the sample (see above) is not necessarily required but facilitates this adjustment.

This sample solution was loaded onto a resin bed of 1 ml of AG1x8 (100 to 200 mesh) in a column prepared from PTFE shrink tubing with 0.4 cm inner diameter (ca. 8 cm resin bed height), which was pre-cleaned and pre-conditioned (Table 1). The bulk of matrix elements (most major elements, rare earth elements) were eluted in 3 mol l\textsuperscript{-1} HCl, followed by rinsing with 0.5 mol l\textsuperscript{-1} HCl – 0.5% H\textsubscript{2}O\textsubscript{2} (m/m). The latter removed any remaining trace elements from the resin, most notably Ta, U, Pb and Zn, before Mo was quantitatively eluted in 2 mol l\textsuperscript{-1} HNO\textsubscript{3} (procedure 1). The solution containing Mo was dried down and the residue treated with 0.05 ml of 15 mol l\textsuperscript{-1} HNO\textsubscript{3} and 0.05 ml of 30% (m/m) H\textsubscript{2}O\textsubscript{2} to destroy any organic matter introduced during the anionic exchange chemistry (mainly material from disintegrating resin beads occasionally leaking through the polypropylene frit material). After drying down the HNO\textsubscript{3} – H\textsubscript{2}O\textsubscript{2} mixture, the samples were re-dissolved in 0.4 mol l\textsuperscript{-1} HNO\textsubscript{3} – 0.4 mol l\textsuperscript{-1} HF for mass spectrometric analysis.

Several months into the project, we replaced the high-aspect ratio PTFE shrink tube columns by BioRad ‘Poly-Prep’ low-aspect ratio PP columns with ca. 1 cm inner diameter (ca. 1.3 cm resin bed height) and filled with 1 ml of AG1x8 (100 to 200 mesh). While this new setup (procedure 2) resulted in a two-fold reduction in processing time we also found an insufficient extraction of Zn (see below). To quantitatively remove Zn while taking advantage of the reduced running time of the new column setup, a 1 mol l\textsuperscript{-1} HF solution was passed through the columns before Mo was collected in 1 mol l\textsuperscript{-1} HCl (Table 2). Again, after drying down, the Mo cut was treated with a mixture of 0.05 ml 15 mol l\textsuperscript{-1} HNO\textsubscript{3} and 0.05 ml 30% (m/m) H\textsubscript{2}O\textsubscript{2} before re-dissolution in 0.4 mol l\textsuperscript{-1} HNO\textsubscript{3} – 0.4 mol l\textsuperscript{-1} HF for mass spectrometric analysis.

For samples with Mo concentrations much lower than 100 ng g\textsuperscript{-1}, such as in the case of USGS BIR-1, ca. 1 g of sample material was processed through purification procedure 2. In this case, the
sample solution was passed over 2 ml of AG1x8 (100 to 200 mesh) resin bed volume and acid volumes were adjusted accordingly (see Table 2).

Mass spectrometric analysis
Instrument equipment and setup
Isotope ratios of Mo were determined on a ThermoFinnigan Neptune MC-ICPMS (serial number 1020) at the University of Bristol in ‘low-resolution’ mode. The instrument is equipped with nine faraday cups to feedback amplifiers with 10¹¹ Ω resistors and 50V digital voltmeters resulting in a maximum beam current of ca. 5 x 10⁻¹⁰ A. The operational settings of mass spectrometric source are given in Table 3. A dry plasma set-up was used with the sample solution being introduced into the mass spectrometer via a Cetac Aridus desolvating system (Table 3) equipped with a 50 μl min⁻¹ micro-concentric PFA nebuliser (Elemental Scientific Ltd.). We found that bleeding small amounts of N₂ into the sample gas flow resulted in an up to two-fold increase of sensitivity and a suppression of oxide formation. All gas flow settings (Table 3) were adjusted on a daily basis to yield maximum sensitivity and signal stability.

Standard nickel sampler and skimmer ‘h’ cones were used. This setup gave an average (total) sensitivity of ca. 2.5 x 10⁻⁹ A for a 1 μg ml⁻¹ Mo solution. The use of high-performance-type cones (i.e. ‘x-type’ skimmer cones) resulted in an up to five-fold increase of sensitivity but also in unacceptable levels of interferences on masses 96, 94 and 98 of up to several 10⁻¹² A. Detailed scans using the high-resolution mode of the ThermoFinnigan Neptune instrument when equipped with x-type skimmer cones revealed that these interferences were caused by polyatomic ions ⁴⁰Ar₂¹⁶O, ⁴⁰Ar₂¹⁴N and ⁴⁰Ar₂¹⁸O (Table 4). The formation of polyatomic ions appears to be linked to the intrinsic geometry of the high-sensitivity cones. The highest contribution from these interferences was observed when the system was fully optimised to maximum signal intensity. Similar observations have been made for the Nd isotope system when using MC-ICPMS instruments equipped with high-sensitivity cones (e.g. Newman et al. 2009, Newman 2012). Therefore, we refrained from using high-sensitivity cones for the analyses carried out as part of this study.

Pre-sequence checks
After the set-up of the cup configuration (Table 4) and optimisation of the instrument settings (Table 3) for maximum Mo sensitivity, the signals of ⁴⁰Ar₂¹⁶O and ⁴⁰Ar₂¹⁴N were monitored by measuring a 0.4 mol l⁻¹ HNO₃ – 0.4 mol l⁻¹ HF blank solution and checked to be less than 10⁻¹⁵ A. The ⁴⁰Ar₂¹⁶O and ⁴⁰Ar₂¹⁴N interferences have the highest abundance of all Ar₂O and Ar₂N polyatomic ions and this procedure ensured that all di-argon-oxides and -nitrides were well below detection limits. This was followed by an amplifier gain calibration as well as a six-minute measurement of an electronic baseline with a deflected beam. These factors were used to correct all subsequent measurements (acid blanks, sample-spike mixtures and reference solutions) performed on each day. Before each analytical session, the concentration of sample solutions was adjusted to match the ⁹⁸Mo signal of the 400 ng ml⁻¹ bracketing ‘CPI Mo reference solution’ (prepared from a 1000 μg ml⁻¹ mono-elemental Mo reference solution purchased from CPI International) to within 10% peak height. Only for samples with very low Mo content (i.e. USGS BIR-1), the concentration in the bracketing reference solution was slightly adjusted accordingly. To ensure that the instrument set-up was operating according to our specifications, all sessions were preceded by the measurement of three aliquots of our in-house CPI Mo reference solution mixed with the ⁹⁷Mo–¹⁰⁰Mo double spike. The reference solution/spike ratios ranged from 2:1 to 1:2 by mass and enabled us to assess the effect of variable sample/spike ratio on
the accuracy of the determined Mo isotope ratios (see below). For a spiked sample, ion currents for

$^{100}$Mo and $^{95}$Mo typically were ca. $3 \times 10^{-10}$ A and $1.2 \times 10^{-10}$ A, respectively.

**Analytical protocol**

Samples were analysed in a sequential and fully automated mode using a Cetac ASX-100 micro
autosampler. The start of each measurement was delayed by 90 seconds to allow the sample to be fully
aspirated and ion signals to stabilise. Usually, ca. 0.25 ml of sample solution was consumed during
one measurement corresponding to ca. 100 ng of Mo. The CPI Mo reference solution (400 ng ml$^{-1}$, see
Archer and Vance 2008) was measured as a bracketing reference solution before and after each sample
using the identical measurement conditions (sample take-up time, integration time, number of scans)
as a sample/spike mixture (Table 4). Each measurement of a bracketing reference or a sample solution
was preceded by a four minute washout period (0.4 mol l$^{-1}$ HNO$_3$ – 0.4 mol l$^{-1}$ HF solution contained
in a ‘wash’ autosampler vial) followed by a measurement of an 0.4 mol l$^{-1}$ HNO$_3$ – 0.4 mol l$^{-1}$ HF
solution from a separate ‘blank’ autosampler vial (15 scans, 4 seconds each). The same HNO$_3$ – HF
solution mix was used to prepare the reference and sample solutions (see above). This procedure
allows the determination of the acid blank and also ensures that cross-contamination between samples
and bracketing reference solutions due to protracted wash-out can, if at all present, be identified.
Generally, the ion intensities of $^{96}$Mo measured in the acid blanks were of the order of $10^{-15}$ A
resulting in a conservative estimate of signal/background ratio of better ca. 150,000.

**Data reduction and results**

The raw intensity data for sample/spike mixtures, reference solutions and acid blank measurements
were exported from the ThermoFinnigan Neptune software and further reduced off-line using a $^{95}$Mo–
$^{97}$Mo–$^{98}$Mo–$^{100}$Mo double spike inversion implemented into a MATLAB script. Firstly, the average
intensities of the solution blank measured before and after each reference solution and sample
measurement were subtracted. From these corrected ion intensities, raw isotope ratios $^{97}$Mo/$^{95}$Mo,
$^{98}$Mo/$^{95}$Mo and $^{100}$Mo/$^{95}$Mo were calculated. Mass $^{99}$Ru was continuously monitored during mass
spectrometric analyses (Table 4) and, although no significant levels of Ru were identified in the
analyses of this study, a Ru interference correction on Mo masses $^{96}$Mo, $^{98}$Mo and $^{100}$Mo was included
to account for any potential minor residual interferences. However, monitored Ru/Mo and Zr/Mo
ratios throughout this study were generally below $3 \times 10^{-5}$ and were found to be negligible (see below).

To account for small differences in instrumental conditions, and hence drift in absolute ratios
between the time when the double $^{97}$Mo–$^{100}$Mo spike was calibrated relative to the in-house CPI Mo
reference solution (Archer and Vance 2008) and the time of the sample/spike mixture measurements
of this study, the measured ratios were first re-normalised to the averages of the bracketing CPI Mo
reference solutions. The time interval between two measurements of bracketing reference solution,
including the measured sample, is short (about 15 minutes) and thus a linear interpolation between the
two bracketing standards was assumed. Our final deconvolution calculations of the sample/spike
mixtures were based on the equations described in Rudge et al. (2009). The inversion itself involves
the simultaneous solution of three non-linear equations for three unknowns, i.e. the relative proportion
of the double spike in the spike-sample mixture, the mass fractionation occurring in the instrument
during measurement of the spike-sample mixture and the natural fractionation factor relative to the
normalising reference solution. The sample-spike mixing ratios from the inversion were then used to
calculate the Mo concentrations of the samples, using sample and tracer weights measured at the
beginning of the procedure (see above).
The mass-dependent isotope variations here are reported in the delta notation as parts-per-thousand relative to a reference solution \( \delta^{98}\text{Mo} = \left[ \left( \frac{^{98}\text{Mo}^{95}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{sample}} - 1 \right] \times 1,000 \). To make our results comparable with those from other laboratories, we cross-calibrated our in-house CPI Mo reference solution (Archer and Vance 2008) with NIST SRM 3134 by repeated measurements over the course of the study. NIST SRM 3134 is a Mo concentration standard and widely used as a commonly available isotopic reference solution (Greber et al. 2012, Goldberg et al. 2013). However, we do not follow the procedure suggested by Nägler et al. (2014) of off-setting the NIST SRM 3134 reference scale to maintain compatibility with earlier \( \delta^{98}\text{Mo} \) values referenced to various reference solutions with slight isotopic differences, such as our CPI Mo reference solution (Archer and Vance 2008). Relative to NIST SRM 3134 we obtained \( \delta^{98}\text{Mo} = 0.23 \pm 0.01 \) (2se) for our whole CPI Mo reference solution dataset (see below). All \( \delta^{98}\text{Mo} \) values for geological and steel reference materials are reported relative to NIST 3134 in Table 5 using this conversion factor.

**Discussion**

*Matrix separation using a single-step anionic exchange column chemistry*

When isolating Mo from silicate matrices, two elements – Fe and Ti – are of particular interest. Both elements occur at wt.%-levels in the samples of interest and potentially behave similarly to Mo during most chromatographic separation procedures. Previous studies used a cationic exchange column step to separate Mo from major matrix elements (Barling et al. 2001, Burkhardt et al. 2014). In this case, Fe weakly partitions on the cationic resin, whereas Mo is not retained. However, an additional column step is then required to further separate Mo from other elements with a preference for forming anionic species in acidic solutions, such as Zr, Ti, Nb. Alternatively, a mixture of 0.5 mol l\(^{-1}\) HCl – 1 mol l\(^{-1}\) HF may be used as the main eluent on strongly anionic resin (Pearce et al. 2009). When loading in a mixture of low-molarity HCl and HF, Fe is not retained on the resin owing to the low partition coefficient of trivalent Fe at low molarity of HCl (Kraus and Nelson 1956). At the same time Ti is strongly retained on the resin in the presence of HF (Münker et al. 2001, Leya et al. 2007) leading to a possible saturation of the resin when Ti-rich and Mo-depleted samples are processed.

Several previous studies described a method, in which the samples are loaded in a 7 mol l\(^{-1}\) HCl solution with traces of H\(_2\)O\(_2\) (Maréchal et al. 1999, Archer and Vance 2004, Archer and Vance 2008). In such a medium, Ti is not retained on the resin, but Fe is quantitatively oxidised to the trivalent state in the presence of H\(_2\)O\(_2\) and thus strongly retained on the anionic exchange resin (Kraus and Nelson 1956). As such, this method can only be used for Mo-rich samples with a high Mo/Fe ratio such as sediments (Archer and Vance 2008). It also requires a second clean-up column to eliminate traces of Fe (Archer and Vance 2004).

In this study, silicate samples were processed with Mo concentrations ranging between tens and hundreds of ng g\(^{-1}\) and low Mo/Fe, Mo/Ti ratios. At the same time we aimed to maximise sample throughput as well as to minimise the operator workload and the volume of anionic exchange resin required to process a sample. We therefore chose to design a single column chemistry that circumvents the above complications. Loading is carried out in 3 mol l\(^{-1}\) HCl – 0.05 mol l\(^{-1}\) L-ascorbic acid. Under these conditions, Fe\(^{3+}\) is reduced to Fe\(^{2+}\) by the presence of ascorbic acid (e.g. Pin et al. 2014) and thus not retained on the anionic resin (Kraus and Nelson 1956). At the same time, the loading solution does not contain HF and thus Ti is efficiently eluted during the loading step. Figure 1 shows a typical elution curve for selected major and trace element using our in-house reference material LP-32b. This sample is an alkaline oceanic basalt from La Palma comprising relatively elevated concentrations of incompatible elements such as Mo. Notably, most elements are either not retained on the AG1x8 resin when loading in 3 mol l\(^{-1}\) HCl – 0.05 mol l\(^{-1}\) ascorbic acid or are
quantitatively washed off the resin in the following 3 mol l⁻¹ HCl washing step. Some elements, like Nb, Ta, Pb, U and Zn, are still present on the resin after rinsing it with 3 mol l⁻¹ HCl (Fig. 1). We found that Nb, Ta, Pb and U can be quantitatively removed in 0.5 mol l⁻¹ HCl – 0.5 % H₂O₂ whilst retaining Mo on the resin. In this case, H₂O₂ acts as a complexing agent that prevents Mo from hydrolysing on the column, comparable to the function of HF in HCl – HF mixtures (Kraus et al. 1955, Pearce et al. 2009). A similar observation was made when using H₂O₂ as a complexing agent of Ti in a HNO₃ – acetic acid mixture (Münker et al. 2001). Figure 1 shows that elimination of remaining matrix elements is achieved when washing the resin with a few column volume equivalents of 0.5 mol l⁻¹ HCl – 0.5 % H₂O₂ (step 4.2 in Table 1).

Using the high-aspect ratio columns of protocol 1, matrix elements are quantitatively separated from Mo. However, after switching to the low-aspect ratio BioRad ‘Poly-Prep’ columns (see above), we observed an incomplete separation of Zn from Mo when applying the elution scheme shown in Table 1. We concluded that this protracted elution of Zn was due to the inherent low-aspect column geometry causing a pronounce tailing of the elution peak of Zn. The latter lead to the occasional spurious formation of a ⁶⁴Zn⁹²Cl interference on mass 99, which was measured to monitor ⁹⁹Ru during mass spectrometric analyses (see below). To efficiently eliminate Zn from the Mo fraction, we included an additional short washing step in protocol 2 using a 1 mol l⁻¹ HF solution followed by a H₂O step to wash out any remaining HF from the resin (steps 4.3 and 4.4 in Table 2). Under these conditions, Mo is strongly retained on the anionic exchange resin (Kraus et al. 1955) while any remaining traces of Zn are quantitatively removed.

Cleaning procedure of resin and procedural blank

As detailed in Tables 1 and 2, the resin is cleaned before loading the samples using a combination of alkaline and acid reagents (step 1). We found that, as an oxy-anionic complex, Mo is strongly retained on anionic exchange resins in acid media. At the same time, MoO₃ precipitates at room temperature at pH <1 (Greenwood and Earshaw 1997) but is highly soluble in alkaline media. To avoid cross-contamination of Mo still retained on the resin from previous usage of the columns (either as oxy-anionic complex or as precipitates), we rinsed the resin with a mixture of 2 mol l⁻¹ NH₄NO₃ – 2 mol l⁻¹ NH₄OH in an aqueous solution. Under these alkaline conditions, AG1x8 has a high retention factor of NO₃ (BioRad), which efficiently displaces traces of Mo oxy-anionic complexes and dissolves any MoO₃ precipitates still present. After washing out the alkaline solution with H₂O, the cleaning procedure further included a conventional cleaning step using 2 mol l⁻¹ HNO₃ – 1 mol l⁻¹ HF. Again, Mo and ‘high-field strength elements’ are not retained on the resin in a HNO₃ – HF medium.

The procedural blank of our method was assessed by processing the same quantities of acids through our procedure as would be used for a regular sample. Several tests were performed using resin previously used to process rock samples and yielded blank contributions ranging between 40 and 600 pg for 1 ml of AG1x8 (100-200) of resin bed volume. We found that acid mixtures comprising HF are prone to contain elevated levels of blank Mo. For this reason, we chose to use a dilute HCl – H₂O₂ mixture to wash out the majority of remaining matrix elements from the resin (see above and step 4.2 in Tables 1 and 2) and only use small amounts of dilute HF and H₂O to remove Zn before collecting Mo using procedure 2 (steps 4.3 and 4.4 in Table 2). Note that the molarity of HCl in the HCl–H₂O₂ mixture is very low and, although the total volume of acid used in this cleaning step is large, its effect on the total procedural blank of the method setup is negligible. Using this setup, the contribution of reagents used for sample dissolution and chemical purification to the blank is minor – ca. 2 pg – with the majority of blank contributed by the resin. We have tested different batches of AG1x8 (100-200) resins (BioRad and Eichrom) and found variable procedural Mo blanks from 40 to up to 800 pg Mo.
While the above blank contamination has no effect on the $\delta^{98}$Mo of Mo-rich samples, minor corrections were necessary for the Mo-depleted sample USGS BIR-1 (Table 5). Nevertheless, the blank-corrected value of USGS BIR-1 is well within the uncertainty of the measured value (Table 5) and consistent with previous findings (Burkhardt et al. 2014).

Recovery of Mo after chemical separation and time consumption

The double-spike approach adopted here allows the simultaneous assessment of a sample’s Mo concentration and the amount of Mo recovered after chemical separation. The latter is determined by comparing the measured $^{95}$Mo signal in the sample solution and the bracketing reference solutions taking into account the dilution factors as well as the sample weight. Throughout the study, a yield of $\sim 95\%$ for both column procedures was observed for a range of silicate and metal reference materials analysed as part of this study. Analyses of a wider range of previously uncharacterised oceanic basalts yielded a similar result. We speculate that a recovery of less than 100% is due to the formation of small amounts of insoluble MoO$_3$ precipitates following the dry-down of the Mo fraction after column chemistry. A similar observation was made during the chemical isolation of W (Willbold et al. 2011) and Mo (Burkhardt et al. 2014). Nevertheless, we note that a near-quantitative recovery of Mo can be achieved using the anionic exchange method described here.

Methods previously described for the chemical isolation of Mo from geological matrices (Maréchal et al. 1999, Barling et al. 2001, Archer and Vance 2004, Archer and Vance 2008, Pearce et al. 2009, Burkhardt et al. 2014, Voegelin et al. 2014, Greber et al. 2015) involve significant amounts of effort and durations in excess of 24 hours. The present method significantly reduces the time required for the isolation of Mo from matrix elements. From our experience, the purification procedure 2 described here can be completed in less than 6 hours – from sample dissolution in 3 mol l$^{-1}$ HCl – 0.05 mol l$^{-1}$ ascorbic acid to the collection of the pure Mo cut – and therefore provides a significant reduction in sample preparation time.

Imperfect sample-spike ratio and instrument reproducibility

While we aimed for a 1:1 sample/spike ratio for measuring samples (Archer and Vance 2008), imperfect sample/spike mixtures inevitably occurred when measuring unknown samples with unknown Mo concentrations. To assess the robustness of imperfect mixtures on the accuracy of determined $\delta^{98}$Mo values we measured mixtures of our in-house CPI Mo reference solution and the $^{97}$Mo – $^{100}$Mo spike that ranged between 2:1 and 1:2. Note that sample/spike ratios for samples processed as part of this study (geological reference materials as well as geological samples) all ranged well within these set limits. The results of these measurements ($N = 42$) are shown in Fig. 2 and their average is given in Table 5. The data agree to within $0.04\%$ $\delta^{98}$Mo (2$s$). The latter value also serves as an estimate of the instrumental reproducibility of $\delta^{98}$Mo data using the setup described here. Our average value for the CPI Mo reference solution is $\delta^{98}$Mo = -0.23 and in very good agreement with recent results (‘BIG-Mo’, $\delta^{98}$Mo = -0.26 ± 0.05; 2$s$) of an inter-laboratory study (Goldberg et al. 2013).

Comparison between separation procedures 1 and 2 and data for reference material

Our instrumental reproducibility of $\delta^{98}$Mo $0.04\%$ (2$s$; $N=42$) based on repeated measurements of the CPI Mo reference solution (Table 5) is comparable to the overall reproducibility of a natural sample such as our basaltic in-house reference material LP-32b (2$s$ = 0.04$\%$ $\delta^{98}$Mo; $N=12$; Table 5). Our average $\delta^{98}$Mo value obtained for USGS basaltic reference material BHVO-2 (-0.07± 0.04$\%$; 2$s$; $N=48$) is consistent with that recently published by Burkhardt et al. (2014) and is about two times
more precise than the value published by Pearce et al. (2009), although detailed comparison for this reference material may be compromised by its intrinsic sample heterogeneity, as we discuss below. Aliquots of BHVO-2 were processed through both types of separation procedures (Tables 1, 2 and 5) and data for individual analyses are shown in Fig. 3. Average δ²⁸Mo for BHVO-2 using both procedures yielded near identical results (Procedure 1: -0.07 ± 0.04‰; 2σ; Procedure 2: δ²⁸Mo = -0.06 ± 0.05‰; 2σ) demonstrating that no systematic error was introduced when changing the analytical setup.

We have deconvolved our BHVO-2 data with and without applying a Ru correction using the raw data as outlined above. Both approaches yielded identical δ²⁸Mo values and reproducibility. We are therefore satisfied that interferences of ⁶⁹Ru, ⁹⁵Ru and ¹⁰⁰Ru on Mo or interferences on mass 99 (see above) that would lead to spurious Ru interference corrections are insignificant for the purpose of this study. The Mo concentrations measured in several aliquots of BHVO-2 ranges considerably between ca. 2.4 and 6.0 µg g⁻¹ with an average of ~ 4.2 µg g⁻¹ (Table 5). This is in line with previous findings (Burkhardt et al. 2014, Li et al. 2014, Yang et al. 2015). A plot of δ²⁸Mo values in BHVO-2 versus the inverse of Mo concentrations (Fig. 4) shows weak negative trend suggesting that BHVO-2 powder is heterogeneous on a sampling scale of ca. 50 to 100 mg of rock powder in terms of concentration and isotopic composition. However, the contaminant must have a similar δ²⁸Mo to the natural sample to generate such a shallow slope in Figure 4. Preliminary data for Hawaiian basalts (Willbold, unpublished data; sample powders prepared using metal-free tools) suggest an average concentration of ca. 0.3 to 0.5 µg g⁻¹. Assuming a similar concentration range for the starting material of BHVO-2 (i.e. before industrial scale milling by the USGS) we suggest that the Mo isotopic composition and concentration of BHVO-2 is dominated by a high-Mo component most likely introduced during the bulk preparation of the rock powder. This contamination must be fairly well mixed with the original basaltic rock material although significant heterogeneities persist at the sampling scale and Mo concentration precision levels of this study. Given the siderophile character of Mo and the high Mo concentrations in some industrial steel tools, abraded material from the equipment used to homogenise large amounts of original rock material could represent the source of Mo contamination. Contamination during preparation of the BHVO-2 powder has been suggested previously to explain the highly variable Pb concentration in BHVO-2 (Willbold and Jochum 2005) as well as the significantly distinct Pb isotopic composition between both generations of reference materials, BHVO-1 and BHVO-2 (Woodhead and Hergt 2000, Baker et al. 2004, Jochum et al. 2005, Weis et al. 2005). A similar case was made by comparing Mo concentrations of 0.986 and 0.912 µg/g in BHVO-1 obtained by isotope dilution ICPMS methods (Makishima and Nakamura 1999, Lu et al. 2006) with much higher values in the range of ca. 4 µg g⁻¹ obtained by double-spark MC-ICPMS for BHVO-2 (Pearce et al. 2009, Babechuk et al. 2010, Burkhardt et al. 2014)

We note that the reproducibility as well as absolute value of δ²⁸Mo in the basaltic USGS reference material BIR-1 (-0.12 ± 0.03‰; Table 5) is nearly identical to the values obtained by Burkhardt et al (2014). Despite of the very low concentration of Mo in BIR-1 (0.032 ± 0.005 µg g⁻¹; 2σ), the reproducibility of δ²⁸Mo is comparable to that of other Mo-rich reference materials. This demonstrates that our new chemical preparation method and the one employed by Burkhardt et al. (2014) are capable of processing large amounts of rock material necessary to achieve such a good reproducibility. At the same time we stress that our procedure only requires a single chromatographic pass. It shows that, while maintaining a high level of data quality, our method significantly reduces time and effort required to produce highly reproducible and accurate results. Our concentration for BIR-1 is significantly lower than the value of 0.07 ± 0.02 µg g⁻¹ obtained by Wieser and DeLaeter (2000). However, we note that the method employed by Wieser and DeLaeter (2000) required
correction for procedural blanks in the order of 10 ng Mo, which may compromise the accuracy of Mo concentrations for low-Mo samples. In contrast, our value for BIR-1 is consistent with that of Burkhardt et al. (2014) obtained by double-spike MC-ICPMS (0.032 μg g⁻¹).

We also provide the first Mo isotope data for the andesitic USGS geological reference material AGV-2 and the basaltic Geological Survey of Japan reference material JB-2. Both samples contain intermediate levels of Mo (1.96 ± 0.05 and 0.92 ± 0.03 μg g⁻¹; 2s, respectively; Table 5). The δ⁸⁸⁹Mo value of AGV-2, -0.15 ± 0.01‰ (2s), is similar to that of BIR-1 and BHVO-2. In contrast, JB-2 is the only sample of our set of reference materials that displays a small positive δ⁸⁹⁹Mo offset of +0.05 ± 0.03‰ (2s). Over the course of this study, we have routinely measured basalt LP-32b as an in-house reference material (Fig. 5). This sample is a historic basanite that erupted in 1712 on La Palma, Canary Islands (Elliott 1991). It displays a significant offset to lower δ⁸⁹⁹Mo (-0.36 ± 0.04‰; 2s; Table 5) and a high, but uniform Mo concentration of 4.30 ± 0.05 μg g⁻¹ (2s), in keeping with it being an alkali basalt formed by low-degree mantle melting. Overall, the magmatic silicate materials analysed in this study display a narrow range in δ⁸⁹⁹Mo from -0.36 to +0.05‰. We tentatively assume this range to be representative of rocks originating from subduction zone and mantle recycling processes that is well-resolved at the level of reproducibility achieved (2s of better than 0.04‰ δ⁸⁹⁹Mo).

NIST SRM 361 has a δ⁸⁹⁹Mo of -0.13 ± 0.03‰ (2s; Fig. 6) and high levels of Mo (2008 ± 167 μg g⁻¹; 2s). Note that SRM 361 also displays a rather large range in measured Mo concentrations. Nevertheless, our average Mo concentration for SRM 361 is within the range of the certified value (1900 ± 100 μg g⁻¹, May and Trahey 2001). However, we speculate that the range in Mo concentration is due to a variable distribution of Mo within the steel. Although we did not analyse other element concentrations in SRM 361 we note that some, like Cu, Co or Mn, also have large uncertainties at the 10% (2s) level (May and Trahey 2001). We therefore suggest that SRM may not be homogeneous at the sampling scale of this study.

Our sample set also includes an aliquot of the Kyoto JMC Mo reference solution, for which we obtained a δ⁸⁹⁹Mo value of -0.37 ± 0.01; 2s (Table 5). This value is in excellent agreement with the δ⁸⁹⁹Mo value of -0.37 ± 0.06 (2s) obtained in a recent inter-laboratory study (Goldberg et al. 2013) and confirms the notion that different batches of in-house JMC Mo reference solutions display significant variations and off-sets to NIST SRM 3134 standards (see Goldberg et al. 2013).

Conclusions

The chemical purification method presented here allows quantitative isolation of Mo from matrix elements for a wide range of sample materials including low-concentration silicate samples and Fe-rich metal samples. In particular, the combination of a strongly anionic exchange resin with a loading solution comprising a mixture of HCl and ascorbic acids allows sample sizes in excess of 200 mg to be processed. This makes the method ideally suited to the handling of silicate samples with low Mo concentrations such as basalts and andesites. The data quality of our method is comparable to more complex procedures (Burkhardt et al. 2014) even when low-Mo samples are processed. When compared with recent standard techniques for silicate matrices, the reproducibility of δ⁸⁹⁹Mo data is improved by at least a factor of two (Siebert et al. 2003, Wille et al. 2007, Pearce et al. 2009, Scheiderich et al. 2010a, Voegelin et al. 2012, Burkhardt et al. 2014, Li et al. 2014, Voegelin et al. 2014, Greber et al. 2015) likely largely due to the capability of our method to process larger sample sizes, which allows the samples to be analysed at larger ion intensities. Processing larger sample sizes may also mitigate against problems related to the potentially heterogeneous distribution of Mo within the rock sample although this critically depends on the length-scale of sample heterogeneity. Our δ⁸⁹⁹Mo value for the CPI Mo reference solution and Kyoto JMC Mo compares favourably with values
determined in a recent inter-laboratory study (Goldberg et al. 2013) and confirm that our analytical setup is able to accurately determine Mo isotope ratios.

Overall, the purification technique described here is more efficient and less time-consuming when compared with previous methods allowing a higher sample throughput while maintaining a high level of data quality. We therefore suggest that our method is fit-for-purpose to identify small but systematic differences in the mass-dependent Mo isotope variation of mantle-derived rocks.

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Figures

Figure 1. Schematic elution curves for selected major and trace elements using basaltic sample LP-32b and employing separation procedure 1. HAsc: ascorbic acid. See Table 1 and text for discussion.
Figure 2. Average value and variations of $\delta^{98}\text{Mo}$ in our in-house CPI Mo reference solution. Grey bar represents 2s variation of the dataset. Note that data for different reference solution (CPI) – double spike (DS) mixtures agree within 0.04‰ $\delta^{98}\text{Mo}$ (2s). We use this value as an estimate of the instrumental reproducibility of our analytical setup.
Figure 3. Average value and variations of $\delta^{98}$Mo in basaltic reference material USGS BHVO-2. Line represents average value ($\delta^{98}$Mo -0.07‰) and grey bar the 2σ (0.04‰) variation of the dataset. Note that Mo was isolated from the sample matrix using two different procedures. See text for further explanation and discussion.
**Figure 4.** $\delta^{98}$Mo values in BHVO-2 plotted against the inverse of Mo concentration (in $\mu$g g$^{-1}$). Straight line is a simple linear regression through the dataset. Error bars represent $2\sigma$ uncertainties of individual measurements. See text for discussion.
Figure 5. Average value and variations of $\delta^{98}$Mo in La Palma basalt LP-32b used as an in-house reference material. Line represents average value ($\delta^{98}$Mo -0.36‰) and grey bar the 2s (0.04‰) variation of the dataset.
Figure 6. Average value and variations of $\delta^{98}\text{Mo}$ in NIST SRM 361 (steel). Line represents average value ($\delta^{98}\text{Mo} -0.13‰$) and grey bar the $2s$ (0.03‰) variation of the dataset.
# Tables

**Table 1.**
Separation procedure 1 on strongly anionic exchange resin (BioRad AG 1x8, 100-200 mesh, 1ml). High-aspect ratio PTFE shrink-tube columns

| Step        | Resin bed volume equivalent | Reagent                          |
|-------------|-----------------------------|----------------------------------|
| 1) Cleaning |                             |                                  |
| 1.1)        | 4 x 2.5                     | 1 mol l⁻¹ NH₄NO₃ - 1 mol l⁻¹ NH₄OH |
| 1.2)        | 2 x 1.5                     | H₂O                              |
| 1.3)        | 4 x 2.5                     | 2 mol l⁻¹ HNO₃ - 1 mol l⁻¹ HF     |
| 1.4)        | 2 x 1.5                     | H₂O                              |
| 2) Condition|                             |                                  |
| 3) Load sample|                             |                                  |
| 5) Collect Mo |                             |                                  |

1 mol l⁻¹ NH₄NO₃ - 1 mol l⁻¹ NH₄OH

|                  |                  |                                 |
|------------------|------------------|---------------------------------|
|                  |                  | 3 mol l⁻¹ HCl                   |
|                  |                  | 3 mol l⁻¹ HCl - 0.05 mol l⁻¹ HAAsc⁻¹ |
|                  |                  | 3 mol l⁻¹ HCl - 0.05 mol l⁻¹ HAAsc⁻¹ |
|                  |                  | 0.5 mol l⁻¹ HCl - 0.5% H₂O₂      |
|                  |                  | 2 x 5                           |
|                  |                  | 0.5 mol l⁻¹ HCl - 0.5% H₂O₂      |
|                  |                  | 2 x 5                           |
|                  |                  | 2 x 5                           |
|                  |                  | 2 x 5                           |

5) Collect Mo

|                  |                  |                                 |
|------------------|------------------|---------------------------------|
|                  |                  | 2 mol l⁻¹ HNO₃                  |

¹ HAAsc: ascorbic acid
Table 2. Separation procedure 2 on strongly anionic exchange resin (BioRad and Eichrom AG 1x8, 100-200 mesh, 1ml). Low-aspect ratio BioRad ‘Poly-Prep’ columns

| Step       | Resin bed volume equivalent | Reagent                              |
|------------|-----------------------------|--------------------------------------|
| 1) Cleaning|                             |                                      |
| 1.1)       | 4 x 2.5                     | 1 mol l⁻¹ NH₄NO₃ - 1 mol l⁻¹ NH₄OH   |
| 1.2)       | 2 x 1.5                     | H₂O                                  |
| 1.3)       | 4 x 2.5                     | 2 mol l⁻¹ HNO₃ - 1 mol l⁻¹ HF        |
| 1.4)       | 2 x 1.5                     | H₂O                                  |
| 2) Condition|                             |                                      |
|            | 3 x 1                       | 3 mol l⁻¹ HCl                        |
| 3) Load sample|                             |                                      |
|            | 5 x 1                       | 3 mol l⁻¹ HCl - 0.05 mol l⁻¹ HAsc¹   |
| 4) Rinse matrix|                             |                                      |
| 4.1)       | 3 x 1                       | 3 mol l⁻¹ HCl                        |
| 4.2)       | 3 x 1                       | 0.5 mol l⁻¹ HCl - 0.5 % H₂O₂         |
|            | 2 x 5                       | 0.5 mol l⁻¹ HCl - 0.5 % H₂O₂         |
| 4.3)       | 1 x 10                      | 1 mol l⁻¹ HF                         |
| 4.4)       | 1 x 3                       | H₂O                                  |
| 5) Collect Mo|                             |                                      |
|            | 1 x 12                      | 1 mol l⁻¹ HCl                        |

¹ HAsc: ascorbic acid
Table 3.
Typical instrument settings of ThermoFinnigan Neptune MC-ICPMS during analysis

| Parameter          | Setting          | Parameter          | Setting          |
|--------------------|------------------|--------------------|------------------|
| RF power           | 1,300 W          | Sample cone        | Ni standard      |
| Reflected power    | < 5 W            | Skimmer cone       | Ni 'h-type'      |
| Cool gas           | 15 l min⁻¹       | Nebuliser          | PFA, concentric  |
| Auxilliary gas     | 0.8 l min⁻¹      | Aridus             | Ar sweep gas     |
| Sample gas         | 1.0 l min⁻¹      | N₂                 | 5.5 l min⁻¹      |
| Extraction Voltage | 2,000 V          |                    |                  |
| High Voltage       | 10,000 V         |                    |                  |
Table 4.
Cup configuration of ThermoFinnigan Neptune MC-ICPMS, possible interferences and measurement conditions. Each measurement consists of 30 scans, each with an integration time of 4 seconds.

| Faraday cup | L4 | L3 | L2 | L1 | C | H1 | H2 | H3 | H4 |
|-------------|----|----|----|----|---|----|----|----|----|
| Monitored mass | $^{90}\text{Zr}$ | $^{91}\text{Zr}$ | $^{94}\text{Mo}$ | $^{95}\text{Mo}$ | $^{97}\text{Mo}$ | $^{99}\text{Mo}$ | $^{99}\text{Ru}$ | $^{99}\text{Ru}$ | $^{100}\text{Mo}$ |
| Interfering isotopes | $^{94}\text{Zr}$ | $^{96}\text{Zr}$ | $^{96}\text{Ru}$ | $^{98}\text{Ru}$ | $^{100}\text{Ru}$ | | | |
| Major interfering species | $^{40}\text{Ar}^{16}\text{O}$ | $^{40}\text{Ar}^{17}\text{O}$ | $^{40}\text{Ar}^{18}\text{O}$ | | | | |
| Integration time (in s) | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| No. of scans | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
### Table 5.
Molybdenum isotope compositions and concentrations of geological and isotopic reference materials

| Sample          | Type    | Distributor       | N | Mo (µg g⁻¹) | 2σ  | δ⁹⁸/⁹⁵ Mo measured | 2σ  | δ⁹⁸/⁹⁵ Mo blank corrected | 2σ  | Separation procedure |
|-----------------|---------|-------------------|---|-------------|-----|-------------------|-----|-------------------------|-----|-----------------------|
| **Geological reference materials** |         |                   |   |             |     |                   |     |                         |     |                       |
| BHVO-2          | basalt  | USGS⁵             | 48| 4.2         | 1.8 | -0.07             | 0.04| -0.07                 | 0.04| 1 and 2               |
| AGV-2           | andesite| USGS              | 3 | 1.96        | 0.05| -0.15             | 0.01| -0.15                 | 0.01| 2                     |
| BIR-1           | basalt  | USGS              | 3 | 0.032       | 0.005| -0.11             | 0.03| -0.12                 | 0.03| 2                     |
| JB-2            | basalt  | GSf⁶              | 4 | 0.92        | 0.03| 0.05              | 0.03| 0.05                  | 0.05| 2                     |
| LP-32b⁴         | basalt  | University of Bristol  | 12| 4.30       | 0.05| -0.36             | 0.04| -0.36                 | 0.04| 2                     |
| **Steel and isotopic reference materials** |         |                   |   |             |     |                   |     |                         |     |                       |
| SRM 361         | steel   | NIST              | 21| 2008        | 167 | -0.13             | 0.03| -0.13                 | 0.03| 1                     |
| Kyoto JMC       | solution| Johnson-Matthey   | 5 | 1019        | 0.3 | -0.37             | 0.01| -³                    | -³ | -⁹                   |
| CPI Mo reference solution⁷ | solution| CPI International | 42| -⁸         | -⁸ | -0.23             | 0.04| -³                    | -³ | -⁹                   |

1 Number of analyses
2 Relative to NIST SRM 3134
3 Using average procedural blanks processed with respective samples. Uncertainties propagated through the corrections.
4 In-house reference material
5 US Geological Survey
6 Geological Survey of Japan
7 Prepared from 1000 µg ml⁻¹ CPI International Mo concentration standard
8 Not determined
9 Not processed through column chemistry
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