1 **A novel extraction chromatographic technique for Mo**

2 **separation from geological samples for MC–ICP–MS isotopic**

3 **measurement**

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15 We present a novel preconcentration method for the determination of Mo isotope

16 ratios by multicollector-inductively coupled plasma-mass spectrometry (MC–ICP–MS)

17 in geological samples. The method is based on the separation of Mo by extraction

18 chromatography using N-benzoyl-N-phenylhydroxylamine (BPHA) supported on a

19 microporous acrylic ester polymeric resin (Amberlite CG-71). By optimizing the

20 procedure, Mo can be simply and effectively separated from virtually all matrix

21 elements with a single pass through a small volume of BPHA resin (0.5mL). This

22 technique for separation and enrichment of Mo is characterized by high selectivity,

23 column efficiency, and recovery (~100%) and, low total procedural blank (~0.18 ng).

24 A ^{100}Mo–^{97}Mo double spike is mixed with samples before digestion and column

25 separation, which enables natural mass-dependent isotopic fractionation to be

26 determined with an external precision of < 0.09‰ ($\delta^{98/95}$Mo; 2 sd) by MC–ICP–MS.

27   The mean $\delta^{98/95}$Mo$_{SRM3134}$ (NIST SRM3134 Mo reference standard; Lot No. 891307)

28   composition of the IAPSO seawater reference material measured by this study is 2.00

29    $\pm$ 0.03‰ (2 sd, n = 3), which is consistent with previously published values. The

30   described procedure facilitates efficient and rapid Mo isotopic analysis of various

31   types of geological samples.

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33   **Keywords:** Molybdenum isotopes; N-benzoyl-N-phenylhydroxylamine; Extraction

34   chromatography; Preconcentration; Double spike; MC–ICP–MS

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36   The recent advent of multicollector-inductively coupled plasma-mass

37   spectrometry (MC–ICP–MS) has generated increasing interest in isotope fractionation

38   studies of "non-traditional" isotope systems (e.g., Arnold et al. 2004, Bermin et al.

39   2006, Asael et al. 2007, Ripperger and Rehkamper 2007). Of particular interest is the

40   highly redox-sensitive behavior of Mo that is accompanied by significant isotope

41   fractionation, which results in oxic, suboxic, anoxic and euxinic sediments possessing

42   isotopically distinct Mo isotope compositions (e.g., Barling et al. 2001,2004, Siebert

43   et al. 2003, 2006, Anbar 2004). Consequently variations in $\delta^{98/95}$Mo can be used as a

44   palaeo-redox proxy to trace the expansion of reducing marine conditions at a number

45   of times throughout Earth's history (e.g., Arnold et al. 2004, Siebert et al. 2005, Pearce

46   et al. 2008). The total range of $\delta^{98/95}$Mo compositions observed in terrestrial samples

47   is ~ 7‰. $\delta^{98/95}$Mo values can be as low as -3.4‰ (Pearce et al. 2010), as found in

48   hydrothermal waters from Iceland, and as high as $+3.5$‰ as measured in suboxic

49   sedimentary pore waters (McManus et al. 2002).

50   Given that Mo isotope variations are likely to be on the order of parts per thousand

51   or smaller in magnitude, high-precision analyses are required to quantify the degrees

52   of fractionations and evaluate their origins. However, this presents an analytical

53   challenge because of the difficulties in purifying Mo from potentially interfering ions

54   in geological samples. Moreover, incomplete recovery of Mo could lead to significant

55   isotope fractionation (Anbar et al. 2001, Siebert et al. 2001, Pietruszka et al. 2008). A

56   number of methods have been developed for the separation and purification of Mo

57   from geological samples (e.g., Qi and Masuda 1994, Anbar et al. 2001, Siebert et al.

58   2001, Dauphas et al. 2001, Malinovsky et al. 2005, Pietruszka et al. 2006, 2008,

59   Nakagawa et al. 2008, Pearce et al. 2009). Two-column ion-exchange processes have

60   generally been used for Mo separation from geological samples. This method involves

61   a two-stage separation using an anion-exchange column for separation of Zr and Mn

62   from Mo followed by a cation-exchange column for separation of Fe from Mo.

63   Malinovsky et al. (2005) proposed a single-stage column method using the chelating

64   resin Chelex 100. However, for some geological samples, this method is not

65   sufficiently effective in separating Mo from the Fe and Zr. Thus, a second pass

66   through the same column is necessary in order to remove traces of Zr and to reduce

67   the concentration of Fe to an acceptable level (Malinovsky et al. 2005). Recently,

68   Pearce et al. (2009) developed a single-pass anion-exchange separation method for

69   Mo and Re isotope and abundance determination by MC–ICP–MS from various types

70   of geological samples. Although all these separation and purification methods have

71 been successfully used for Mo isotope determinations, they require relatively large

72 elution volumes and numerous evaporation/transfer steps, which increases sample

73 preparation time and potential blank levels.

74   Yang and Pin (2002) have described a method for preconcentration of Zr, Hf, Nb

75 and Ta in rock samples using N-benzoyl-N-phenylhydroxylamine (BPHA) supported

76 on a microporous acrylic ester polymeric resin (Amberlite CG-71). BPHA is relatively

77 small in size, has abundant π electrons, is stable in highly acidic solutions, and acts as

78 a superior ligand for solvent extraction of group 4, 5 and 6 elements in the Periodic

79 Table, such as Nb, Ta, Zr, Hf, Ti, Mo and W (Caletka and Krivan 1989, Goguel 1992,

80 Yang and Pin 2002, Shinotsuka and Suzuki 2007, Li et al. 2010). Amberlite CG-71

81 resin possesses excellent chemical and physical stability, and can absorb large

82 amounts of BPHA because it contains relatively large numbers of active aromatic sites

83 that allow π-π interactions. BPHA extraction chromatographic resin has high

84 selectivity for the adsorption of tetra-, penta- and hexavalent elements, whereas other

85 matrix elements have little affinity for the resin (Yang and Pin 2002).

86   This study reports the first utilization of BPHA extraction chromatographic resin

87 for the pre-concentration of Mo in geological samples and for the determination of

88 Mo isotopic ratios by MC–ICP–MS. The chemical separation parameters were

89 systematically investigated and optimized. It was found that Mo has very strong

90 affinity to this resin even in 0.1 mol L^{-1} HF, and 6 mol L^{-1} HF was necessary to

91 achieve quantitative recovery of Mo. The key objective of this study was to develop a

92 chemical separation procedure for subsequent accurate and precise determination of

93 $\delta^{98/95}$Mo and Mo concentrations by ^{100}Mo–^{97}Mo double-spike MC-ICP-MS analysis.

94 The efficiency and widespread applicability of our technique is demonstrated by

95 replicate analyses of geological reference materials and the IAPSO seawater standard.

96 **Experimental methods**

97 **Reagents and materials**

98 The Johnson Matthey Specpure Mo plasma standard solution (Lot No. 012773) and

99 NIST SRM3134 (Lot No. 891307) were used as the Mo isotopic standards. A

100 ^{97}Mo–^{100}Mo double spike was prepared as a mixture of individual concentrated spike

101 solutions of isotopically enriched ^{97}Mo (Batch 159791) and ^{100}Mo (Batch 159992)

102 which were purchased from the Oak Ridge National Laboratory, USA. The

103 compositions of the ^{97}Mo–^{100}Mo double spike and Mo reference solution were

104 calibrated by doping with Pd using the method detailed by Siebert et al. (2001) (for

105 double-spike and standard calibration results see Table 1). BPHA (Analytical grade,

106 Aladdin Reagent Inc. China) and Amberchrom CG-71 (50–100 μm particle size,

107 Supelco Inc., USA) were used without further purification. A synthetic multi-element

108 solution with a concentration of 1 μg mL^{-1} was prepared from AccuStandard fluoride

109 soluble elements (MISA 05-1), rare earth metals (MISA 01-1), transition metals

110 (MISA 06-1), alkaline earth elements (MISA 04-1), and precious metals (MISA 02-1)

111 for use in optimizing the column separation parameters. HCl, HF and HNO$_3$ were

112 purified by DST-1000 sub-boiling stills (Savillex Corporation, USA). Ultrapure water

113 prepared with a Milli-Q system (Millipore) was used to dilute all the acids, and is

114 referred to as Milli-Q water hereafter in this paper.

Preparation of BPHA resin

We prepared the BPHA resin column using procedures modified from those described by Yang and Pin (2002). Five grams of Amberchrom CG-71 resin was impregnated with 40 mL of 3% BPHA solution in ethanol rather than chloroform. The mixture was shaken at room temperature (25 ℃) for 2 h to ensure complete saturation and was then stored in a refrigerator without removing the ethanol prior to use. This material is hereafter referred to as the BPHA resin. Approximately 0.5 mL of BPHA resin (ca. 0.2 g of dry weight) was packed in a Bio-Spin chromatography column (Bio-Rad Laboratories Inc., USA).

Sample digestion and preparation

Sample preparation and all chemical separations and evaporations were carried out in a clean environment (Class 1000). Approximately 40–70 mg of samples powder was weighted accurately and combined with the ^{97}Mo–^{100}Mo double spike in 15 mL PFA beakers. The beakers were then placed on a hotplate at 120 ℃ along with ~ 6 mL of a 2:1 mixture of HF (22 mol L^{-1}) and HNO$_3$ (14 mol L^{-1}). To achieve total sample dissolution, the PFA beakers were placed in an ultrasonic bath for 5 min at various intervals during the dissolution period. After digestion and dryness at 120 ℃, the samples were dissolved in 1 mL of concentrated HCl, and again evaporated to dryness. The residue was re-dissolved in 2–4 mL of a mixture of 0.1 mol L^{-1} HF/1mol L^{-1} HCl, at which point it was ready for column separation. Approximately 10 mL of the seawater sample was acidified with 1 mL of concentrated HCl, and the ^{97}Mo–^{100}Mo double spike was then added. The spiked and acidified seawater solution was then

137   evaporated to dryness before being re-dissolved in 4 mL of 0.1 mol L^{-1} HF/1mol L^{-1}

138   HCl.

Chemical separation

140   Prior to use, the BPHA resin column was washed with 6 mL of 6 mol L^{-1} HF/1 mol

141   L^{-1} HCl and 4 mL of Milli-Q water. Prior to sample loading, the column was

142   conditioned with 2 mL of 0.1 mol L^{-1} HF/1mol L^{-1} HCl. The chemical separation steps

143   and along with previously published methods were outlined in Table 2. A 2 mL aliquot

144   of the sample solution was loaded onto the column and the resin was washed with 8

145   mL of 0.1 mol L^{-1} HF/1mol L^{-1} HCl. This step effectively removes matrix and

146   interfering elements (Fe, Mn, Zr, Ru, Cu, Zn, Ni, etc.) from the sample. Finally, the

147   adsorbed Mo was eluted by passing in 8 mL of 6 mol L^{-1} HF/1mol L^{-1} HCl. The Mo

148   was collected in 15 mL PFA vials and evaporated on a hot plate at 120 ℃ to dryness.

149   Three drops of concentrated HNO_3 and H_2O_2 were added to the evaporated Mo to

150   decompose any organic residue. Following this, 1 mL of 3% HNO_3 was added to the

151   Mo residue, after which the solution was ready for Mo isotopic ratio measurement by

152   MC–ICP–MS.

Mass spectrometry measurements

154   During the method development stage of this work, a quadrupole ICP–MS

155   (Thermo-Scientific Xseries-2) was used in the conventional mode for

156   semi-quantitative and quantitative elemental measurements. Typical operating

157   conditions for this instrument have been reported elsewhere (Li et al., in press).

158   Mo isotopic ratios were determined on a Thermo-Fisher Scientific Neptune Plus

MC–ICP–MS at the State Key Laboratory of Isotope Geochemistry, Guangzhou

Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS), Guangzhou,

China. This instrument is equipped with eight moveable Faraday collectors and one

fixed central collectors, which are linked to amplifiers with 10^{11} Ω resistors. Samples

and standards were introduced into the plasma through an Aridus II® desolvating

sample introduction system (CETAC Technologies, Omaha, USA). This system

removes water from the sample solutions by passage through a desolvating membrane

at 160℃, providing a "dry" sample to the plasma, which increases sensitivity by a

factor of 5~10 over wet plasma sample-introduction systems. The typical Mo

sensitivity achieved was 180–200 V ppm^{-1}. The operating conditions and Faraday

collector configuration for the Neptune Plus are given in Table 3. Data for all samples

and standards were acquired in 6 blocks of 10 ratios. Subsequently, these 60 ratios

were filtered with a one-pass 2sd outlier removal test, and the mean value and

standard error (SE) were calculated. After each analysis, the sample was sequentially

washed from the system for ten min using solutions of 3% HNO_3, 0.2 mol L^{-1} HF/3%

HNO_3 and 3% HNO_3. The residual Mo signal was typically < 1 mv, which is

insignificant to the ion beams measured during sample analysis.

Prior to starting an analytical session, the reference solution (NIST SRM3134) was

typically analyzed five times to check the MC–ICP–MS performance. During an

analytical session, the reference solution was measured after each batch of three

samples. Correction for mass fractionation during chemical separation, as well as

during mass spectrometry followed the double–spike deconvolution methods

181　described by Siebert et al. (2001).

182　Mo isotopic ratios of all samples were normalized to those of the NIST SRM3134

183　Mo standard and expressed in conventional δ notation:

184　$\delta^{98/95}\text{Mo}(‰) = [(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}} / (^{98}\text{Mo}/^{95}\text{Mo})_{\text{SRM3134}} - 1] \times 1000$

185　**Results and discussion**

186　**Adsorption capacity of BPHA resin**

187　The adsorption capacity or maximum amount of Mo adsorbed per gram of freshly

188　synthesized BPHA resin was determined. The adsorption capacity of the BPHA resin

189　is defined as the amount of metal ions that can be extracted per unit mass under the

190　optimized chemical separation conditions. The method used here is based on that

191　recommended by Maquieira et al, (1994). Solutions containing 10 μg g^{-1} of Mo were

192　passed through the column continuously until detectable signal of Mo was observed in

193　the eluent. The maximum volume (V) of solution at concentration (c) and the amount

194　of metal adsorbed on the column were then calculated by the following equation:

195　$C = cV/W$

196　where C is the adsorption capacity and W is the weight of the BPHA resin. In this

197　study, the adsorption capacity for Mo was found to be 0.72 mg g^{-1}. The resin exchange

198　capacity was reduced by ~40 % after the resin had been used once. However, the

199　BPHA column could be refreshed by eluting a 3 % BPHA solution in ethanol through

200　it.

201　**Optimization of the chemical separation procedure**

202　The presence of fluorides has a strong negative effect on the extraction of Zr, Hf,

203   Nb, Ta, Mo and W by BPHA (Caletka and Krivan, 1989, Goguel, 1992). We

204   examined the effect of HF concentration (0.1 to 8 mol L^{-1} HF) on the collection of Mo

205   by BPHA resin column and found that Ti, Zr, Hf, Nb and W were hardly retained on

206   BPHA resin at low concentrations of HF (0.1 mol L^{-1} HF), whereas the behaviors of

207   Ta and Mo on the resin were unaffected. This observation is consistent with those of

208   Goguel (1992), in that Mo and Ta have a greater affinity for BPHA. Mo and Ta are

209   gradually eluted from the column if the concentration of HF is above 1 mol L^{-1}, and

210   are quantitatively striped when the HF concentration is > 5 mol L^{-1}. The effect of HCl

211   concentration on the collection of Mo from the BPHA resin column was also

212   examined. In all the cases, from 0.5 to 4 mol L^{-1} HCl, Ti, Zr, Hf, Nb, Ta, W and Mo

213   are completely absorbed on the BPHA resin column, whereas other elements pass

214   straight through the column. In subsequent experiments, Mo collection was carried

215   out with 0.1 mol L^{-1} HF/1 mol L^{-1} HCl as matrix elements such as Ti, Nb, Zr, Hf and

216   W are not retained on the BPHA resin in this acid mix and Mo can be adsorbed by a

217   small resin volume. The Mo adsorbed on the column was removed in 8 mL of 6 mol

218   L^{-1} HF/1 mol L^{-1}HCl. Figure 1 shows a typical elution profile for Fe, Mn, Cr, Ti, Rb,

219   Sr, La, Zr, Hf, Nb, Ta, Ru and Mo. It is apparent that no Fe, Mn, Cr, Ru and rare earth

220   elements, as well as Ti, Zr, Hf, Nb and W, are extracted by the BPHA resin in a 0.1

221   mol L^{-1} HF/1 mol L^{-1} HCl acid mixture. Only Ta is quantitatively extracted with Mo.

222   **Isotopic fractionation during BPHA resin chemical separation**

223   It is widely recognized that Mo isotope fractionation can result from incomplete

224   Mo recovery during ion chromatographic separation (e.g., Anbar et al. 2001, Siebert

225   et al. 2001, Pietruszka and Reznik 2008). Isotopic fractionation during chemical

226   separation of Mo was examined using the BPHA resin column as described by Pearce

227   et al. (2009). Solution aliquots of 2 mL containing 0.5429 ppm Mo in 0.1 mol L^{-1}

228   HF/1 mol L^{-1} HCl were prepared from the NIST SRM3134 Mo standard solution and

229   passed through the BPHA column. Three of these solutions had an appropriate

230   amount of the ^{100}Mo–^{97}Mo double spike (the ^{97}Mo$_{spike}$/^{97}Mo$_{sample}$ = ~ 3) added prior to

231   separation ("spiked") whereas the other three solutions had the spike added afterwards

232   ("unspiked"). The "spiked" and the "unspiked" solutions gave mean $\delta^{98/95}$Mo values

233   of 0.01 ± 0.05‰ (2 sd, n = 3) and 0.03 ± 0.02‰ (2 sd, n = 3), respectively (Table 4).

234   These determinations are indistinguishable within analytical uncertainty, and are also

235   the same as the expected $\delta^{98/95}$Mo composition (0.00 ± 0.09‰; Fig. 2). Furthermore,

236   quantitative recovery of Mo from the column was confirmed by assessing the Mo

237   yields from each solution (Table 4). Measured Mo recoveries for the "unspiked" and

238   "spiked" solution are 98.9 ± 1.1% (2 sd; n = 3) and 99.4 ± 0.7% (2 sd; n = 3),

239   respectively. At this good recovery rate, an isotope fractionation of Mo by BPHA

240   column separation is unlikely.

241   **Matrix effect**

242   Coexisting elements in solutions can interfere with Mo isotopic ratio

243   measurements and produced inaccurate results. Although the BPHA resin column

244   pre-concentration method effectively separated the matrix and interfering elements

245   from Mo, Ta is collected along with Mo (Fig. 1). To test the matrix effect from Ta, we

246   measured Mo isotopic ratios on NIST SRM3134 Mo standard solutions doped with

247   various amounts of Ta. (Fig. 2). No significant change in measured $\delta^{98/95}$Mo was

248   found even at ratios of Ta/Mo = 100. Ta/Mo ratios in most geological samples are $\leq$

249   100 and, in particular, sedimentary rocks are highly depleted in Ta. Thus, we

250   concluded that potential matrix effects from the presence of Ta are insignificant.

251   Isobaric interferences from elemental and molecular ions in the solution may occur

252   during Mo isotopic ratio measurements. Zr interferes with ^{92}Mo, ^{94}Mo, and ^{96}Mo, and

253   Ru interferes with ^{96}Mo, ^{98}Mo, and ^{100}Mo. Polyatomic ions such as ^{52}Cr^{40}Ar$^+$,

254   ^{55}Mn^{40}Ar$^+$, ^{56}Fe^{40}Ar+, ^{60}Ni^{40}Ar$^+$, and ^{80}Se^{16}O$^+$ can also possibly interfere on Mo

255   isotopes. However, these interferences are completely removed from the separated

256   Mo by BPHA resin column, and concentrations of Zr, Cr, Mn, Fe, Ni, and Se in the

257   Mo solution are very low (a few ppb), and Ru was not detected in the analyte solution

258   by ICP–MS in the separated Mo solution. Moreover, the Aridus II® desolvating

259   sample-introduction system reduces these polyatomic ions to negligible level and,

260   coupled with the efficiency of our Mo separation procedures, means that our Mo

261   isotope data are unaffected by inference.

262   **Precision and accuracy**

263   The precision of our Mo isotope determination was assessed by analyzing spiked

264   aliquots of two Mo standard solutions: NIST SRM3134 and the Johnson Matthey

265   Specpure Mo plasma standard solution (JMC). It should be noted that the lack of a

266   commonly used Mo isotopic standard, means that the standards used by different

267   laboratories appear to be isotopically different at the level of ~0.2‰. Recently, Wen et

268   al. (2010) and Goldberg et al. (2013) recommend that NIST SRM3134 Mo standard

269 should be used as the universal reference material for reporting Mo isotopic

270 composition of natural samples. Here, we adopt NIST SRM3134 as the reference

271 standard and compare our $\delta^{98/95}Mo_{SRM3134}$ values with previously reported values (Fig.

272 3). The average $\delta^{98/95}Mo_{SRM3134}$ for NIST SRM3134 and JMC were 0.00 ± 0.09‰ (2

273 sd, n = 21) and -0.20 ± 0.06‰ (2 sd, n = 14), respectively. The accuracy of our Mo

274 isotope determination was also assessed by analyzing the IAPSO Atlantic seawater.

275 The measured $\delta^{98/95}Mo_{SRM3134}$ value of IAPSO was 2.00 ± 0.03‰ (Table 5), which is

276 comparable to the value reported by Greber et al. (2012).

277

278 **Application to geological materials**

279 The applicability of our technique for analysis of natural samples was assessed by

280 replicate analysis of three different types of reference samples: offshore marine

281 sediment GBW07316, the USGS basalt BHVO-2, and IAPSO Atlantic seawater

282 (Table 5).

283 The average $\delta^{98/95}Mo_{SRM3134}$ value determined for the BHVO-2 (n = 3) was $-0.05 \pm$

284 0.11‰ (2 sd) with individual analyses varying from -0.11‰ to $+0.01$‰. This mean

285 value for BHVO-2 is similar to values reported for this standard by Pearce et al.

286 (2009), and also falls within the range of other igneous rocks (Siebert et al. 2003). The

287 average Mo concentration determined for this basalt was 3.9 ± 2.3 μg g^{-1} (2 sd) with

288 individual analyses varying from 2.84 to 5.15 μg g^{-1}. Our average Mo abundance for

289 BHVO-2 is identical to the value reported by Hu et al. (2008). We note that the

290 measured $\delta^{98/95}Mo_{SRM3134}$ values for BHVO-2 were positively correlated with Mo

291 abundances, which suggests that the inhomogeneous distribution of minor magmatic

292 sulfides is responsible for these covariations (Voegelin et al. 2012). The mean

293 $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ composition of the analysed GBW07316 offshore marine sediment

294 reference material is $-0.60 \pm 0.10‰$, which falls within the range of Mo isotope

295 values obtained for pelagic clays and Fe–Mn crust (Siebert et al. 2003). However, it

296 should be noted that the $\delta^{98/95}\text{Mo}$ composition of such samples can vary considerably

297 depending on paleo-redox conditions (Siebert et al. 2003). The measured Mo

298 concentration for the GBW07316 is 5.32 ± 0.42 μg g^{-1} (2 sd), which is consistent with

299 the reference value for this standard when analytical uncertainties are considered. The

300 measured $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ value of seawater obtained by analysis of IAPSO was 2.00

301 $\pm 0.03‰$ which is similar to the value reported by Greber et al. (2012). The

302 concentration of Mo in IAPSO was 0.010 μg g^{-1} which is also indistinguishable from

303 previously studies (e.g., Siebert et al. 2003, Pearce et al. 2009, Nakagawa et al. 2008,

304 Grebert et al. 2012).

305   In summary, these results confirm that our analytical procedure is suitable for

306 precise and accurate determination of Mo isotopic composition and Mo abundances in

307 a wide range of geological materials.

308 **Total procedural blanks**

309   The procedural blank was determined using exactly the same methods applied to

310 the natural samples. Total procedural blanks varied from 0.14 ng to 0.21 ng (mean =

311 0.18 ± 0.06 ng; 2 sd; n = 3). Our total procedural blanks are considerably lower than

312 those of reported for other Mo chemical separation procedures (i.e., 0.5 to 47 ng; e.g.,

313   Siebert et al. 2001, Pearce et al. 2009, Nakagawa et al. 2012, Voegelin et al. 2012,

314   Goldberg et al. 2013), due to the relatively small volume of resin and acids used by

315   our method. The total Mo blank contribution never amounts > 0.3% of the sample Mo

316   and, as such, has no effect on the measured Mo isotope composition of the samples.

317   **Conclusions**

318   We have developed a new method using BPHA extraction chromatography and

319   MC–ICP–MS for the determination of Mo isotopic compositions in geological

320   materials. The method has excellent selectivity and efficiency. This single-pass

321   technique is relatively straightforward and has ~100% Mo recovery, which ensures

322   that Mo isotope fractionation does not occur during chemical separation of Mo. The

323   small volume of the resin (0.5 mL) and eluates (<20 mL) required results in very low

324   total procedural blanks (~0.18 ng). The BPHA method thus offers significant

325   analytical advantages over some of the other chemical procedures that are currently

326   used for Mo separation and isotope determination. However, a disadvantage of our

327   method is the relatively large volumes of HF used, and the highly toxic and corrosive

328   nature of even dilute HF acid. Multiple analyses of marine sediment reference

329   material GBW07316, basalt reference material BHVO-2, and IAPSO seawater salinity

330   reference materials demonstrate that this new analytical procedure can be reliably

331   applied to a wide range of geological materials.

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Table captions

532 Table 1. Compositions of the [100]Mo–[97]Mo double spike and NIST SRM3134 Mo

533 standard.

	^{100}Mo/^{97}Mo	^{98}Mo/^{97}Mo	^{96}Mo/^{97}Mo	^{95}Mo/^{97}Mo	^{94}Mo/^{97}Mo	^{92}Mo/^{97}Mo
Double spike	0.979966	0.061740	0.027146	0.018081	0.009581	0.016851
2s (n=10)	0.000075	0.000074	0.000057	0.000056	0.000031	0.000055
Standard solution	1.003817	2.523671	1.747802	1.671446	0.972042	1.564659
2s (n=10)	0.000060	0.000171	0.000132	0.000127	0.000095	0.000113

534

535 Table 2. The BPHA extraction chromatographic column procedure for Mo purification

536 chemistry, and along with other purification methods for comparison.

Mehods	Resin	Volume (mL)	Step	Volume(mL)	Purpose
This study	BPHA resin	0.5	0.1 M HF/1 M HCl	2.0	Condition
			0.1 M HF/1 M HCl	2−4	Load
			0.1 M HF/1 M HCl	8	Matrix removal
			6 M HF/1 M HCl	8	Collection of Mo
Two column ion-exchange (Pietruszka et al. 2006)	AG1X8	10	6M HCl	30	Condition
			6M HCl	5	Loading
			6M HCl	40	Matrix removal
			0.1 M HF/0.01 M HCl	40	Matrix removal
			1 M HCl	120	Collection of Mo
			5 M HNO$_3$	50	Collection of Mo
	AG 50WX8	3.5	1.4 M HCl	20	Condition
			1.4 M HCl	10	Load and Collection of Mo
Single column chelating resin (Malinovsky et al. 2005)	Chelex 100	3	0.3 M HNO$_3$	10	Condition
			0.3 M HNO$_3$	12	Load
			0.07 M HCl	10	Matrix removal
			0.1 M HF	50	Matrix removal
			6 M NH$_3$	12	Collection of Mo
Single column ion-exchange (Pearce et al. 2009)	AG1X8	2	1 M HF/0.5 M HCl	4	Condition
			1 M HF/0.5 M HCl	6−10	Load
			1 M HF/0.5 M HCl	10	Matrix removal
			4 M HCl	8	Matrix removal
			3 M HNO$_3$	12	Collection of Mo

537

538

539 Table 3. MC–ICP–MS operating conditions and Faraday collector configurations.

	Neptune								
RF power	1165 W								
Ar cooling gas flow rate	16.00 L min-1								
Ar auxiliary gas flow rate	0.93 L min-1								
Ar sample gas flow rate	0.91 L min-1								
Sample cone	Ni sampler cone								
Skimmer cone	Ni X-skimmer cone								
Instrument resolution	400 (low)								
Integration time	4.194 s								
Idle time	3 s								
Cup configuration	L4	L3	L2	L1	C	H1	H2	H3	H4
	^{91}Zr	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{99}Ru	^{100}Mo
	Aridus II								
Sweep gas flow rate	3.45 L min-1								
Nitrogen gas	0.05 L min-1								
Spray chamber temperature	110 ℃								
Desolvator temperature	160 ℃								

540

541 Table 4. $\delta^{98/95}$Mo values and Mo concentrations obtained for the BPHA column

542 fractionation and Mo yield tests.

|		Unspiked solution	Spiked solution
$\delta^{98/95}$Mo$_{SRM\ 3134}$ (‰)	solution 1	0.00 ± 0.07	0.04 ±0.08
	solution 2	0.03 ±0.08	-0.01 ±0.06
	solution 3	0.02 ±0.07	-0.01 ±0.05
	Mean (2s)	0.02 ±0.03	0.01 ±0.06
Mo concentration (ug g-1)	solution 1	0.5402	0.5419
	solution 1	0.5342	0.5389
	solution 1	0.5365	0.5385
	Mean	0.5369	0.5398
	Stock solution	0.5429	0.5429

543

544 Table 5. $\delta^{98/95}$Mo$_{SRM3134}$ and Mo concentration data determined for different

545 geological materials.

Sample	$\delta^{98/95}Mo_{SRM3134}$ (‰)	Mo concentration (ug g^{-1})
BHVO-2	-0.11 ±0.08	2.84
BHVO-2	-0.05 ±0.08	3.79
BHVO-2	0.01 ±0.06	5.15
Average (2 sd)	-0.05 ±0.11	3.9 ±2.3
Pearce et al.(2009)	0.08±0.10	4.48
GBW07316	-0.56 ±0.05	5.55
GBW07316	-0.58 ±0.10	5.14
GBW07316	-0.66 ±0.05	5.27
Average (2 sd)	-0.60 ±0.10	5.32 ±0.42
Previously reported [8,10]	-1.0 to 1.6	3.4 to 132
Reference value		5.70
IAPSO	2.01 ±0.09	0.010
IAPSO	2.01 ±0.10	0.010
IAPSO	1.98 ±0.11	0.010
Average (2 sd)	2.00 ±0.03	0.010
Greber et al.(2012)	2.08±0.09	0.010

546

Figure captions

547

Fig.1 Elution profile for a synthetic multi-element solution from a BPHA resin
column packed with 0.5 mL resin. f(SL) = 2 mL of 0.1 mol L^{-1} HF/1 mol L^{-1} HCl for
sample loading, f(mx) = 2 mL of 0.1 mol L^{-1} HF/1 mol L^{-1} HCl for matrix elution,
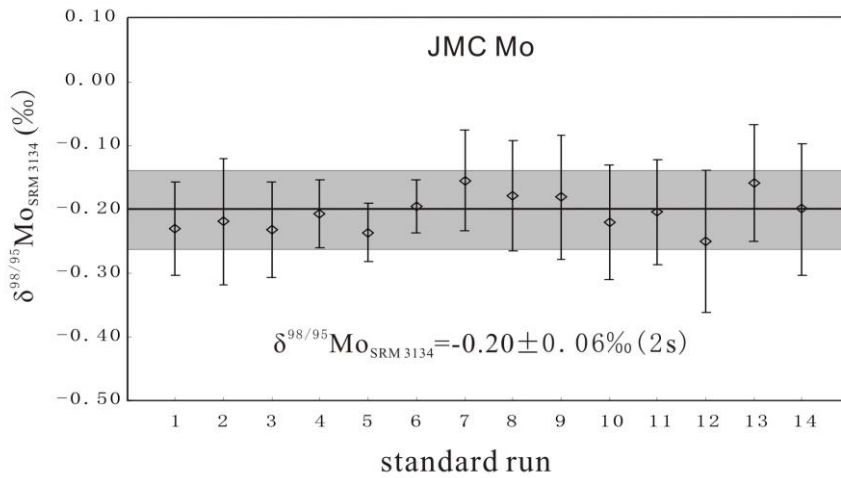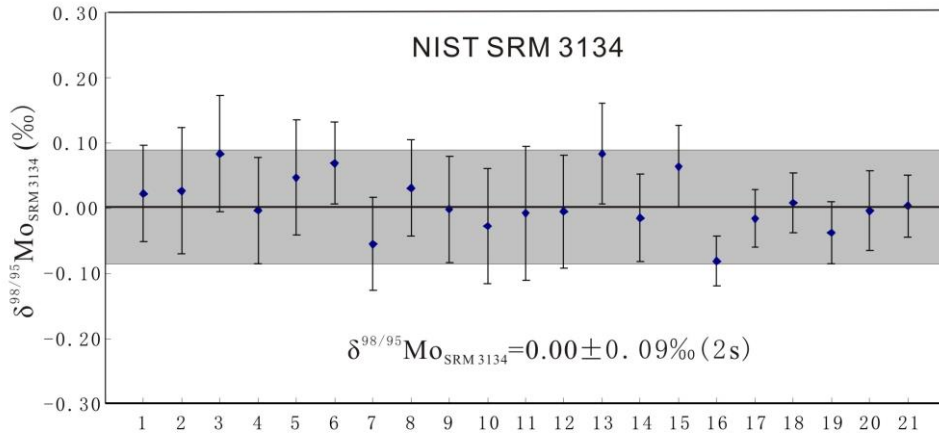and f(Mox) = 2 mL of 6 mol L^{-1} HF/1 mol L^{-1} HCl for Mo elution.

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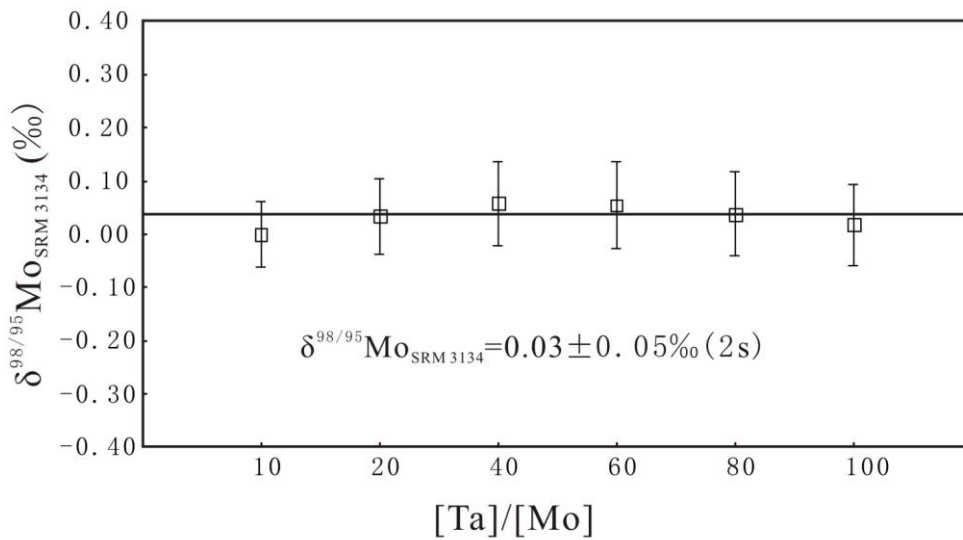
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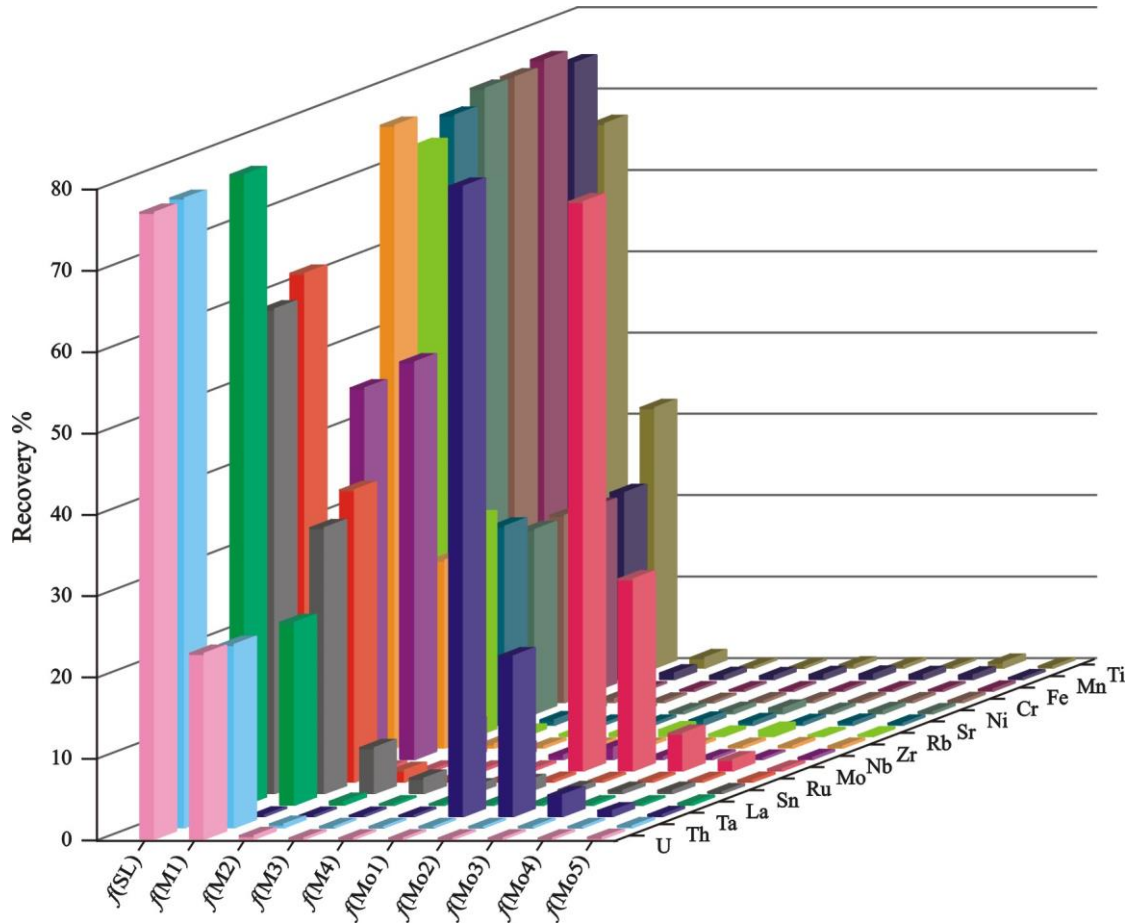
Fig.2 Plot of $\delta^{98/95}$Mo standard measurements for one session. The $\delta^{98/95}$Mo values were normalized to the mean standard value of the session. Error bars are the internal uncertainty (2 se; standard error) and the external precision is represented by the gray band (2 sd; standard deviation).

559

Fig.3 Effect of Ta doping on measured $\delta^{98/95}$Mo values.

561