- Molybdenum isotope behaviour in groundwaters and terrestrial hydrothermal systems,
 Iceland
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13 Key words groundwater, Hydrothermal, Mo isotopes, ocean mass balance

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15 Abstract

Molybdenum (Mo) isotopes have proved useful in the reconstruction of paleoredox 16 conditions. Their application generally relies upon a simplified model of ocean inputs in 17 which rivers dominate Mo fluxes to the oceans and hydrothermal fluids are considered to be a 18 minor contribution. To date, however, little attention has been paid to the extent of Mo 19 isotope variation of hydrothermal waters, or to the potential effect of direct groundwater 20 discharge to the oceans. Here we present Mo isotope data for two Icelandic groundwater 21 systems (Mývatn and Þeistareykir) that are both influenced by hydrothermal processes. 22 Relative to NIST 3134 = +0.25‰, the cold (<10°C) groundwaters ($\delta^{98/95}$ Mo_{GROUNDWATER} = -23 0.15% to +0.47%; n = 13) show little, if any, fractionation from the host basalt 24 $(\delta^{98/95}Mo_{BASALT} = +0.16\%$ to -0.12‰) and are, on average, lighter than both global and 25 Icelandic rivers. In contrast, waters that are hydrothermally influenced (>10 $^{\circ}$ C) possess 26 isotopically heavy $\delta^{98/95}$ Mo_{HYDROTHERMAL} values of +0.25‰ to +2.06‰ (n = 18) with the 27 possibility that the high temperature endmembers are even heavier. Although the mechanisms 28 29 driving this fractionation remain unresolved, the incongruent dissolution of the host basalt and both the dissolution and precipitation of sulfides are considered. Regardless of the 30 processes driving these variations, the δ^{98} Mo data presented in this study indicate that 31 32 groundwater and hydrothermal waters have the potential to modify ocean budget calculations.

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34 **1. Introduction**

Molybdenum (Mo) is an essential micronutrient and redox sensitive transition metal that provides key information in Earth and environmental studies. Molybdenum stable isotopes have been extensively used as a paleoredox proxy (e.g. Asael et al., 2013; Barling et al., 2001; Barling & Anbar 2004; Archer & Vance 2008; Pearce et al., 2008; Goldberg et al., 39 2009; Willie et al., 2008). Despite having generally low concentrations in the continental crust (~1-2 ppm; Taylor and McLennan, 1985), Mo is the most abundant transition metal in 40 the modern oceans (~10 ppb; e.g. Nakagawa et al., 2012, Table 1). This relatively high 41 concentration results from the efficient transport of Mo from the continents to the oceans, due 42 to the solubility of Mo phases under oxidative weathering and the subsequent transport of 43 dissolved Mo prior to its slow removal from the oceans in the presence of dissolved O_2 . The 44 resulting residence time of Mo in the oceans of 440 ka (Miller et al., 2011) is more than two 45 orders of magnitude greater than the ocean mixing time, so that the oceans have uniform Mo 46 elemental and isotope compositions (Nakagawa et al., 2012). 47

Under oxidising conditions Mo is present in solution as the stable molybdate ion, MoO_4^{2-} . 48 (Fig. 2). In this form Mo is slowly removed from the water column through uptake into 49 ferromanganese phases, which preferentially incorporate isotopically light Mo (e.g. Barling et 50 al., 2001; Barling & Andbar 2004; Goldberg et al., 2009; Miller et al., 2011; Wasylenki et al., 51 2011). As a result of this fractionation the modern oceans are the heaviest Mo reservoir on 52 Earth (Kendall et al., 2016). In contrast, Mo is readily removed from solution in anoxic-53 sulfidic waters with very little net isotopic fractionation. In the presence of reduced sulfur, 54 Mo forms oxothiomolybdate ions, $MoO_{4-x}S_x^{2-}$, which are highly particle-reactive and thus 55 rapidly removed from solution (e.g. Barling et al., 2001). This behaviour underpins the 56 application of Mo isotopes and abundances as a proxy for past ocean anoxia (e.g. Pearce et 57 al., 2008; Asael et al., 2013). 58

Early paleoredox studies assumed a comparatively straightforward ocean budget in which Mo input was dominated by the dissolved riverine phase that was assumed to be stable through time and to directly reflect the chemical signature of continental rocks. However, many studies have since demonstrated that the average riverine composition is typically heavier

than the catchment bedrock, both globally (e.g. $\delta^{98}Mo_{GLOBAL RIVERS} = +0.20\%$ to +2.30‰; 63 Archer & Vance 2008) and locally (e.g. δ^{98} Mo_{ICELAND RIVERS} = -0.25‰ to +1.65‰ in a 64 basaltic (<+0.25‰) catchment; Pearce et al., 2010). This enrichment in heavy isotopes in the 65 dissolved phase is attributed to a number of processes including: incongruent dissolution 66 during weathering (e.g. Archer & Vance 2008; Neubert et al., 2011; Voegelin et al., 2012); 67 adsorption of isotopically light Mo to organic phases in soils (e.g. Siebert et al., 2015; King et 68 al., 2016); and, although considered small in terms of mass balance, adsorption of light Mo to 69 riverine particles (e.g. Archer & Vance 2008; Pearce et al., 2010). 70

In contrast to the dissolved riverine Mo flux, little attention has been paid to the potential 71 72 contributions of groundwater to Mo in the oceans. Groundwaters may affect seawater chemistry both directly (through submarine groundwater discharge) and indirectly as a 73 significant source of river base flow. Indeed, Pearce et al. (2010) attributed some of the 74 progressive increase in riverine δ^{98} Mo to the addition of isotopically heavy groundwater. The 75 significance of groundwater contributions to riverine and seawater Mo signatures is poorly 76 77 constrained due to the paucity of data. To date King et al. (2016) have reported groundwater δ^{98} Mo data: characterised by isotopically heavy δ^{98} Mo compositions (+0.25‰ to +0.51‰) 78 relative to the catchment bedrock (δ^{98} Mo +0.06‰) in Hawaii, attributed to the retention of 79 light isotopes in soils and the preferential leaching of heavy Mo. 80

In terms of ocean budgets, groundwater contributions to base flow are accounted for in the global riverine discharge. However, the direct contribution of Mo to seawater from submarine groundwater discharge has rarely been taken into account in marine mass balance. Using ²²⁶Ra, Moore (1996) demonstrated that submarine groundwater discharge over 350 km of south-eastern coastline of the United States of America contributes up to 40% of the riverwater flux. Direct groundwater discharge may therefore contribute a significant proportion of the water flux to the oceans. 88 At the present day, rivers (potentially including substantial groundwater contributions) are thought to contribute some 90% of oceanic Mo inputs, with the remaining 10% accounted for 89 by chemical exchange in oceanic hydrothermal systems (McManus et al., 2002). For time 90 91 periods such as the Archean, hydrothermal heat losses were likely much greater than at present (Lowell & Keller 2003). During these time periods the hydrothermal input of Mo 92 may have been more important in the seawater mass balance. Through detailed study of fluid 93 inclusions from identified hydrothermal vents of mid-Archean age in the Barberton 94 formation, South Africa, De Ronde et al. (1997) found that the vent fluids likely had similar 95 96 chemical signatures to those of modern day vents. Therefore, the study and characterisation of modern hydrothermal systems will enable better constraints to be placed on inputs to the 97 oceans through geologic time. 98

Data for mid-ocean ridge (MOR) hydrothermal waters are currently limited to a lowtemperature (sampling at 25°C, formation fluids ~63°C) flank system on Juan de Fuca. The end-member fluid was estimated to have a composition of δ^{98} Mo +0.8‰ (McManus et al., 2002). However, it is unclear if this signal represents basalt-seawater interaction or if it was inherited from the overlying sediments. Whilst high-temperature hydrothermal systems are not thought to be significant sources of Mo to the oceans (Miller et al., 2011) the only value currently available for a terrestrial hydrothermal system is δ^{98} Mo -3.7‰ (Pearce et al., 2010).

This study presents Mo isotope and elemental data for two groundwater systems, in northeast
Iceland, both of which have been influenced by hydrothermal activity along with limited
basalt and sulfide samples.

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110 2. Geological Setting and Methods

Hydrothermal activity in Iceland is widespread and associated with both active volcanic centres and off-axis fracture systems. The studied groundwater systems (Fig.1) are both meteoric in origin and located in the northern volcanic zone (NVZ), which extends from the centre of Iceland into the North Atlantic Ocean.

The first groundwater system is located in the Mývatn area of northeast Iceland (Fig. 1c). It is 116 associated with the volcanic centre of Krafla, an 8 km caldera with a fissure swarm extending 117 50 km to the north and 40 km to the south. The Krafla hydrothermal fields are located within 118 the caldera whilst the Námafjall field lies outside, within the southern fissure swarm 119 (Gudmundsson & Arnórsson 2005). The fluids are dilute (900 ppm to 1500 ppm total 120 dissolved solids; Gudmundsson & Arnórsson 2002, 2005; Kaasalainen & Stefánsson 2012) 121 and are of meteoric origin (based upon δD and $\delta^{18}O$ content; Darling & Ármannsson). 122 Groundwaters in this region have been divided into six distinct groups by Ármannsson et al. 123 (2000) based upon their geographic location, δD , $\delta^{18}O$, and Cl and B concentrations. These 124 125 classifications are shown in Fig. 1. The most important subset for this study is group V, thought to result from straightforward mixing between cold and geothermal groundwaters 126 (Darling & Ármannsson 1989) they were notably affected by the Krafla fires of 1977 to 1984 127 with their silica content one constituent yet to return to pre-fire values (Ólafsson et al., 2015). 128 In this region there is some debate as to whether the dominant hydrothermal source is from 129 Krafla or Námafjall (e.g. Armannsson et al., 2000; Ólafsson et al., 2015). Most recently 130 Ólafsson et al. (2015) used Cl/B ratios to demonstrate that the, warm, Mývatn groundwaters 131 may be dominated by fluids from the Krafla geothermal system. Due to the utilisation of 132 these fields for geothermal energy each is well characterised, and for this reason they are 133 ideal for investigating Mo behaviour in both cold groundwaters and hydrothermally 134 influenced systems. 135

The second groundwater system, Þeistareykir (Fig. 1b), is located in the westernmost fissure swarm in the NVZ, which is characterised by large normal faults and rift fissures (Sveinbjornsdottir et al., 2013). The high temperature geothermal activity is linked to magma intrusions associated with the most recent volcanic activity ~2500 years ago (Sveinbjornsdottir et al., 2013). Like the Mývatn groundwater system, the fluids are dilute meteoric waters (~750 ppm to 1100 ppm dissolved solids; Óskarsson et al., 2013) from the south of the area (Sveinbjornsdottir et al., 2013).

In addition to the water samples, four basalt and three sulfide samples were analysed (Table 143 2). The basalts are from drill core chippings at depth within the Reykjanes hydrothermal 144 145 system, Iceland (Fig. 1a). Sulfide minerals in Icelandic samples studied here were too finely disseminated to obtain sufficient material for Mo isotope analysis. The samples here are from 146 the main Outokumpu ore, Finland comprising a \sim 4 km long, >50 to 350 m wide and \sim 10 m 147 thick rectangular-shape sheet of semimassive-massive sulfides. These sulfides are thought to 148 have formed from hydrothermal fluids, perhaps in a mid-ocean ridge setting. Lead isotope 149 data for whole rock and galena samples from the Outokumpu ores define an age of 1943±85 150 Ma, which is indistinguishable from the 1.95–1.96 Ga U–Pb zircon ages for metagabbros and 151 plagiogranites that intrude the ultramafic rocks (Peltonen et al. 2008). Whilst not from the 152 153 same location as the groundwaters, combined with literature data, these samples allow some insight into the behaviour of Mo isotopes in these common mineral phases 154

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156 *2.2 Methods*

Groundwater samples (Mývatn: M01 – M20 and Þeistareykir: Þ01 – Þ11) were collected
during routine sampling carried out by the Icelandic GeoSurvey (ÍSOR) in conjunction with
Landsvirkjun (National Power Company of Iceland) (Kristinsson et al., 2014). Samples for

Mo isotope analysis were filtered $(0.2 \ \mu m)$ into 1 L, pre-cleaned, high density polyethylene bottles, acidified and stored in the dark before analysis. Physical properties, sampling conditions, and major- and trace-element concentrations, from Kristinsson et al. (2014), are reproduced in the electronic supplements (Table ES1). All Mo isotope data measured specifically for this study are reported in Table 1.

In situ pH and Eh (redox potential) values, at the measured sampling temperature of the 165 waters, were calculated by PHREEQC version 3.0.6 (Parkhurst & Appelo 2013) using the 166 minteq.v4 database. Redox potential was determined using the measured iron and sulfur 167 speciation and by assuming atmospheric oxygen saturation at the measured water 168 169 temperature. The results from these approaches were compared and although the absolute values vary depending on the defined redox couple, the relative trends do not. The best 170 approximation of redox shows that oxidised MoO_4^{2-} dominates the groundwaters (Fig. 2), as 171 is known to be the case for most Icelandic waters below 200°C (Arnórsson & Ívarsson 1985). 172

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174 2.3 Molybdenum isotope chemistry and analysis

Sample preparation and δ^{98} Mo measurements were undertaken in the Department of Earth 175 Sciences at Durham University. Preliminary Mo concentrations were determined by 176 inductively coupled plasma mass spectrometry (ICP-MS). A volume of each sample was then 177 weighed and spiked with a ⁹⁷Mo-¹⁰⁰Mo double-spike to yield a ~1:1 ratio of total 178 spike:natural Mo with 50-100 ng of natural Mo. Basalt samples were powdered in an agate 179 180 mill before total dissolution of ~50 mg in a concentrated HF:HNO3 mix (1:2). Basalts were spiked before digestion. After complete dissolution the basalts were dried down before re-181 dissolution in HCl and treated in the same manner as the groundwater samples. Chemical 182 separation of Mo was achieved using a single pass anion exchange procedure detailed in 183

Pearce et al. (2009), with an additional 12 ml 0.5 M HF matrix elution step to ensure
complete removal of Zn before final Mo elution in 3 M HNO₃.

The sulfides: chalcopyrite (0.2 g), pyrrhotite (0.6 g) and pyrite (0.7 g) were dissolved using a combination of HNO₃ and HCl acids before being purified using a double pass through anion exchange columns following the protocol described in Willbold et al. (2017), where dilute ascorbic acid is used during sample loading for optimal Fe removal.

Molybdenum isotope compositions were measured using a multi-collector ICP-MS (Thermo-Finnigan Neptune, Durham University) equipped with an Aridus II desolvating nebuliser. Samples were aspirated at ~35 μ l min⁻¹ and the maximum sensitivity was ~400 V ppm⁻¹. Measurements were made in low resolution mode using X-cones and static collectors. Analyses consisted of 50 cycles of 4s integrations. Total procedural blanks were <1 ng Mo and data processing was conducted offline using a deconvolution routine (Pearce et al. 2009) based on the Newton-Raphson method.

All Mo isotope compositions are reported in conventional delta notation in parts-perthousand relative to a reference solution (Eq. 1), with errors given as 2 standard deviations offrom the mean. Given the inconsistent reporting of Mo isotope data in the literature it is important to note that all data, including literature data, are reported relative to SRM NIST 3134 = +0.25% (Nägler et al., 2014).

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$$\delta^{98/95} Mo = \left[\left(\frac{\frac{98}{95}Mo}{\frac{98}{95}Mo} \right) - 1 \right] \cdot 1000 + 0.25$$
 (1)

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205 Long-term machine reproducibility was determined by measurement of an in-house Romil standard, which gave δ^{98} Mo = +0.30 ± 0.05‰ (2SD, n = 183). The IAPSO seawater standard 206 gave a δ^{98} Mo composition of +2.34 ± 0.08‰ (2SD, n = 43(17) - where n is the number of 207 208 measurements and in brackets is the number of repeated chemical separations. This is indistinguishable from the mean of published values of $+2.33 \pm 0.10\%$ (given in Goldberg et 209 al., 2013). As this is the first Mo data from Durham University an additional Mo standard 210 (Ou-Mo from the Open University) was run; this gave a mean δ^{98} Mo value of $-0.10 \pm 0.03\%$ 211 (2SD, n = 11), comparable with values obtained from Imperial College London 212 $(-0.12 \pm 0.04\%)$ and the Open University $(-0.13 \pm 0.02\%)$ (Goldberg et al., 2013). Taken 213 together, these data suggest a long-term external reproducibility (2 s.d.) of $\pm 0.08\%$ or better. 214

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216 **3. Results**

Data from this study are presented in Tables 1 and 2. Additional data for the water samples are reproduced in Table ES1 (Kristinsson et al., 2014). Sampling temperatures range from 0°C to 93.2°C and in situ pH is generally alkaline with a mean of 8.4 (Fig. 2) and ranging from 6.9 to 10.0. Aqueous components such as total dissolved solids (TDS), SO_4^{2-} , and SiO_2 increase with temperature with marked increases at temperature over 10°C; therefore, for ease of discussion, samples >10°C are grouped together and considered as hydrothermally influenced groundwaters.

The overall range in Mo concentration in the groundwaters varies from 0.08 ppb to 4.85 ppb (Table 1; Fig. 3). In general, the cold groundwaters (sampling temperature <10°C) contain less Mo than the hydrothermally influenced waters. The Peistareykir waters (diamonds) have a narrow range of relatively low Mo concentrations (0.08 to 0.22 ppb) whilst the Mývatn waters (circles) range from 0.21 to 4.85 ppb. Curiously, although the group V waters are from the Mývatn groundwater system and are hydrothermally influenced, they have notably lower
Mo concentrations (0.21 to 0.37 ppb, Fig. 3) than the other hydrothermal samples.

The groundwaters possess a wide range of δ^{98} Mo isotope compositions, from -0.15‰ to 231 +2.06‰ (Table 1, Figs. 4 & 5). The cold Þeistareykir waters are isotopically light, with 232 δ^{98} Mo varying from -0.15% to +0.17%, whilst the more hydrothermally influenced waters 233 are isotopically heavier, up to +0.68‰. Similarly, the cold waters from the Mývatn area range 234 from δ^{98} Mo +0.18‰ to +0.47‰ whilst the hydrothermally influenced waters are heavier: 235 between +0.47 and +2.06‰. The exception to this is sample M03 (LUD-4), a cold water well 236 with a high Mo concentration (1.52 ppb), heavy Mo isotope composition of +1.12‰ (Table 237 1, Fig. 4), and distinctive chemistry including, for example, elevated TDS, SO_4^{2-} , and Al 238 (Table ES1). 239

The basalts contain between 0.14 ppm and 1.01 ppm Mo, with the hyaloclastite having the highest concentration of 4.67 ppm Mo (Table 2). In comparison, the chalcopyrite contains an order of magnitude more Mo, some 38 ppm, whilst the pyrite and pyrrhotite contain 0.074 ppm and 0.048 ppm, respectively. The basalts are isotopically light, ranging from +0.16‰ to -0.12%, whereas the sulfides are all isotopically heavy; the chalcopyrites are +1.16‰ and the pyrite and pyrrhotite +1.80‰ and +1.46‰, respectively.

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247 **4. Discussion**

248 4.1. Cold groundwaters

Generally, in the cold Icelandic groundwaters investigated here, as the Mo concentrations increase the isotopic composition becomes increasingly heavy (Fig. 4). However, with the exception of sample M03, the cold groundwaters show only a small degree of fractionation away from the average composition of Icelandic basalts (Fig. 4). Icelandic basalts, specifically, are isotopically light and in this study they have compositions that range from $\delta^{98}Mo_{BASALT} + 0.16\%$ to -0.12%, comparable with published data for Icelandic lavas of +0.1% (Yang et al., 2015). The cold Þeistareykir samples are also isotopically light (-0.15‰ to +0.17%), similar to the down-well Icelandic basalts measured in this study (Fig. 4).

The mean δ^{98} Mo value of the cold groundwaters at Peistareykir is -0.01‰ and at Mývatn, 257 258 +0.35‰. These values are comparable to the basalt-hosted Hawaiian groundwaters measured by King et al. (2016), which have a mean Mo isotope composition of +0.39‰ (range: 259 +0.25‰ to +0.51‰) (Fig. 4). Whilst the waters are isotopically similar, the Mo 260 261 concentrations in the Icelandic groundwaters are almost an order of magnitude lower than those in Hawaii. The Hawaiian groundwater Mo concentrations range from 1.83 ppb to 4.86 262 (mean: 3.0 ppb) whilst the maximum Mo in the cold Icelandic waters is 1.52 ppb with a mean 263 264 of 0.5 ppb (slightly higher than the 0.2 ppb mean of 150 cold groundwaters from an earlier study in north Iceland; Árnórsson & Óskarsson 2007). 265

The Icelandic groundwaters are within the range of Mo isotope values measured in rivers 266 both locally, in Iceland (δ^{98} Mo from -0.25‰ to +1.65‰ (Pearce et al., 2010), and globally 267 (-0.10% to +2.30%; summarised in Kendall et al. (2016)). However, on average they are 268 lighter than the global riverine mean of δ^{98} Mo +0.7‰ (Archer & Vance 2008) (Figs. 4 & 8) 269 and the Iceland riverine mean of +0.6‰ (Pearce et al., 2010). If the proportion of direct 270 groundwater discharge is anywhere close to the 40% of river discharge, as suggested by 271 Moore (1996), and the global groundwater mean is isotopically lighter than that of the global 272 273 river discharge, as indicated by these data and that of King et al. (2016), then the overall input to the oceans may need to be revaluated (see section 4.4). We recognise, however, that 274 current groundwater δ^{98} Mo data remain limited both in terms of their geological setting and 275 276 their host lithologies.

As with all groundwaters, the chemistry of the Peistareykir and Mývatn waters is determined by the composition of the source, precipitation, degree of water-rock interaction, mixing with other waters, and the introduction of volcanic gasses (Ármannsson et al., 2000). In the case of these two systems, the influence of hydrothermal waters is significant with mixing and, to a lesser extent, steam-heating known to be important controls on chemistry (Darling & Ármannsson 1989; Ólafsson et al., 2015).

For the Mývatn waters, the cold groundwater endmember is represented by M07, Garðslind 284 (Fig. 5; Table 1). It is one of the largest cold-water springs in the region and represents the 285 non-hydrothermally influenced endmember (Ólafsson et al., 2015). It is not possible to 286 287 account for all of the Mývatn groundwater data with one binary mixing model (Fig. 5), suggesting that either there are two distinct hydrothermal endmembers, or else that the 288 chemistry of these waters is not controlled by mixing alone. The most recent work on the 289 290 origin of these groundwaters (Ólafsson et al., 2015) concluded that the warm waters may be 291 related to the Krafla hydrothermal fluids as opposed to Námafjall. Sample M17 is therefore taken to represent a geothermal endmember; it is isotopically heavy, has a relatively high Mo 292 concentration (1.4 ppb), and negligible Mg, as is characteristic of hydrothermal waters. 293

Mixing between these two endmembers can account for the majority of the Mývatn groundwaters (solid line; Fig. 5). However, the group V waters do not fit this trend (dashed line; Fig. 5); instead they require an isotopically heavy but low Mo concentration endmember. The low Mo concentration is somewhat surprising as these waters are thought to result from straightforward mixing between cold and geothermal groundwaters (Darling & Ármannsson 1989) and Mo is known to be enriched in geothermal waters compared with cold groundwaters and surface waters (Arnórsson & Ívarsson., 1985). Therefore, there may have 301 been loss of light Mo to account for the low Mo concentrations seen in these three group V302 waters.

Ólafsson et al. (2015) argued that these warm waters are, in part, formed as a consequence of 303 steam-heating. Although the behaviour of Mo in the steam (vapour) phase remains poorly 304 understood and data on the isotope composition are limited, it has been suggested that lighter 305 Mo isotopes accumulate in the vapour whilst heavier isotopes remain in the brine (Kendall et 306 al., 2016). This is consistent with preliminary measurements of the vapour phase in 307 geothermal systems from Iceland. All show preferential partitioning of light Mo into the 308 vapour but the Mo concentrations in the vapour phase are relatively low, from 0.30 to 309 310 3.27 ppb (Neely et al., 2015).

As Mo can fractionate isotopically on partitioning into a vapour phase, it is possible that this 311 process has influenced the composition of the hydrothermally affected waters. Steam-heating 312 would add isotopically light Mo which cannot explain the isotopically heavy hydrothermal 313 314 waters. But the loss of steam could leave a residually heavy fluid phase (although this would 315 not explain the high Mo concentrations). Combined with the indication of relatively low Mo concentrations in the vapour (Neely et al., 2015) this suggests that steam-heating alone is not 316 a dominant control on the Mo composition of these waters, in agreement with the conclusions 317 of Ólafsson et al., 2015. 318

319 *4.3. Controls on hydrothermal endmember Mo composition*

Few minerals contain Mo as a major constituent. Of these sulfides such as molybdenite (MoS₂) and pyrite (FeS₂) dominate, with molybdenite containing approximately 60% Mo by weight and often dominating the mass balance in mineralising systems (Kendall et al., 2016). The association of Mo and S in sulfides and the high solubility of their oxidised species (MoO₄²⁻ and SO₄²⁻) indicates that they can be effectively mobilised during oxidative weathering. Indeed, based on a similar positive correlation to that shown in Fig. 3, Miller et al. (2011) concluded that pyrite weathering is the dominant source of Mo to modern day rivers. The observed agreement between the groundwater data presented in this study and global river data (Fig. 3) may therefore indicate that groundwater Mo in Iceland is similarly controlled by pyrite and sulfide dissolution.

However, the concentration of Mo in mid-ocean ridge basalt (MORB) sulfides appears to be 330 331 much lower than continental sulphides (~0.15 ppm; Patten et al., 2013). This suggests that igneous sulfides may not be a significant source of Mo in this setting, consistent with the low 332 Mo concentrations reported in this study for hydrothermal pyrite and pyrrhotite (see Table 2). 333 In contrast, chalcopyrite may be a significant Mo host, containing 38 ppm Mo (Table 2). 334 Molybdenum is also preferentially incorporated into minerals containing Ti⁴⁺ and Fe³⁺, so 335 that in basaltic and silicic igneous rocks Mo is often concentrated in ilmenite, titano-336 337 magnetite (~10 ppm), and sphene. Relatively high Mo concentrations are also found in olivine (~10 ppm), but are lower in pyroxenes (~0.4 ppm) and plagioclase (~0.2 ppm) (see 338 339 Arnórsson & Óskarsson, 2007). Arnórsson & Óskarsson (2007) found groundwaters to be more concentrated in Mo than comparable surface waters and, in general agreement with this 340 study, that Mo concentration tends to increase with increasing temperature. They concluded 341 342 that the main source of Mo to Icelandic groundwaters is the incongruent dissolution of basalt, dominated by plagioclase and to a lesser extent pyroxene and basaltic glass due to Mo 343 retention in titano-magnetite and olivine. 344

As the main source of Mo is likely to be from the dissolution of the isotopically light host basalts, some process is needed to explain the heavy hydrothermal endmember compositions (Fig. 5). There are several processes that could potentially drive the observed fractionation of Mo isotopes in the warm geothermal waters: (1) pedogenesis; (2) changes in redox state; (3) dissolution of primary minerals; (4) the formation of secondary minerals; and (5) the dissolution or precipitation of sulfides. To explain the dominant mixing trend in the Mývatn waters (solid line; Fig. 5) the geothermal end member requires an additional source of isotopically heavy Mo whilst the minor, group V endmember mixing (dashed line; Fig. 5) may require loss of isotopically light Mo.

Soils: The retention of light Mo isotopes in soils has been recognised as an important process 354 in driving the preferential enrichment of heavy Mo isotopes in the dissolved phases of pore 355 water, rivers and groundwaters (e.g. Pearce et al., 2010; Siebert et al., 2015; King et al., 356 2016). Siebert et al. (2015) and King et al. (2016) used selective extraction techniques to 357 show that soil-bound Mo is associated with organic matter and a silicate and/or Ti-oxide 358 359 residue, as opposed to Mn-Fe oxyhydroxides. However, soils in the NVZ of Iceland are generally thin and sandy with much of the groundwater catchment described as a sand desert, 360 from Vatnajökull glacier in the south to the Atlantic Ocean in the north (see Fig. 5 in Arnalds 361 et al., 2001). Furthermore, as shown in Fig. 6, the *in situ* partial pressures of CO₂ in the cold 362 groundwaters (from 10^{-6} to $10^{-3.6}$ bars) are less than that of atmospheric pCO₂ ($10^{-3.4}$ bars). 363 This suggests that the dissolution and precipitation reactions in these waters take place in 364 isolation from the atmosphere and with little CO₂ contribution from soils (see Fig. 4 in 365 Gislason & Eugster 1987). Consequently it is unlikely that soils exert a significant control on 366 367 groundwater composition in this region due to their lack of development and coverage.

368 *Redox State*: The Eh is relatively difficult to constrain due to the challenges involved in 369 preserving speciation for later laboratory analysis (as demonstrated for Fe speciation in 370 thermal waters; Kaasalainen et al., 2016). For this reason, redox potential was calculated 371 using several approaches and redox pairs. While absolute values of Eh differ between these 372 approaches the speciation in all of the groundwaters is dominated by molybdate, MoO₄²⁻ (Fig. 373 2). A couple of the samples approach thiomolybdate speciation (MoO_{4-x}S_x²⁻) and removal of 374 thi isotopically light (e.g. Tossell 2005) species could leave the residual fluids isotopically heavy. However, despite spanning a wide range of Eh values, the redox conditions do not
appear to directly account for the isotope composition of dissolved Mo with no trend seen
between redox potential and the Mo composition of the groundwaters (Table 1).

Primary minerals: Redox potential can affect the stability and saturation state of mineral 378 phases and dissolution of basalt is thought to be incongruent with respect to Mo (e.g. 379 Arnórsson & Óskarsson 2007; Voegelin et al., 2012). Data on the Mo isotope composition for 380 381 individual minerals remains limited, but there may be significant isotope variation between phases. Initial data from Voegelin et al. (2014) indicate that hornblende and biotite are up to 382 0.6‰ lighter than bulk-rock. Maintenance of mass balance therefore requires other phases to 383 384 be isotopically heavier, and enhanced dissolution of these phases could be responsible for the heavier Mo isotope composition and increasing Mo concentration of the main geothermal 385 endmember (M17). Indeed, Voegelin et al. (2012) found, in both field (stream catchment) 386 387 and basalt leach experiments, that the preferential weathering of mineral phases, such as magmatic sulfides, resulted in the enrichment of isotopically heavy Mo in the aqueous phase 388 389 relative to the basaltic bedrock.

An assessment of the saturation state of primary basalt minerals in the groundwaters was 390 made using the PHREEQC database (Parkhurst & Appelo, 2013). Plagioclase, hydrated 391 basaltic glass, and olivine tend to be undersaturated - suggesting the potential to dissolve -392 whilst pyroxene and magnetite remain oversaturated - suggesting that these minerals are 393 stable and unlikely to dissolve (Fig. 7, Table ES2). As temperature increases, the tendency for 394 forsterite dissolution becomes dominant over plagioclase, coinciding with increasingly heavy 395 396 Mo isotope signatures. If olivine retains heavier Mo than plagioclase then incongruent dissolution of these phases may control the Mo isotope signatures of these waters. However, 397 additional Mo isotope data on mineral separates are required to assess this hypothesis and it 398

seems unlikely that any individual phase could be isotopically heavy enough and in sufficientabundance to generate 2‰ variations without other processes playing a role.

Secondary minerals: The formation of secondary phases provides a potential mechanism to 401 remove light Mo from solution (as may account for the group V waters). The formation of 402 secondary phases has been used to explain some of the Mo isotope variation in rivers, with 403 adsorption of light Mo onto Mn-Fe oxyhydroxides driving the waters to heavier values (e.g. 404 405 Archer & Vance, 2008; Miller et al., 2011). In this study, the most common Mn phases are significantly undersaturated in the groundwaters (Table ES2), whilst Fe phases only tend to 406 be oversaturated in the cold groundwaters. From the calculated saturation indices, there is no 407 408 indication that the formation of these secondary phases in the group V waters is any more likely than in the other hydrothermal waters (Table ES2). With the hydrothermally influenced 409 waters undersaturated for both Fe- and Mn- oxyhydroxides, their formation is considered to 410 411 exert little influence on Mo isotopes in these groundwaters.

412 Sulfides: Calculating the saturation state of sulfide minerals in the cold groundwaters is 413 difficult due to the absence of measureable reduced S in the system (Table 1; ES1). However, the oxidising nature of these fluids (Fig. 2) would suggest that they are undersaturated with 414 respect to sulfide minerals. It is known that the mixing of hydrothermal waters with cold 415 waters leads to molybdenite undersaturation and therefore favours dissolution of Mo sulfides 416 (Arnórsson & Ívarsson 1985). Consequently, the main mixing trend in Fig. 5 could, in part, 417 be explained by the dissolution of sulfide phases, increasing the Mo concentration in these 418 waters. Molybdenites show a large isotopic variation, ranging from δ^{98} Mo_{MOLYBDENITE} -1.4‰ 419 420 to +2.6‰ (Breillat et al., 2016) and the hydrothermally sourced chalcopyrite, pyrite, and pyrrhotite measured in this study are all isotopically heavy ($\delta^{98}Mo = +1.15$ to +1.8%; Table 421 2, Fig. 8). The dissolution of sulfide phases could be a source of heavy Mo to the 422 423 hydrothermal endmembers. However, saturation state calculations systematically show that the hydrothermally influenced waters are oversaturated for sulfide minerals (Table ES2),
indicating that they are stable and that dissolution is unlikely. Therefore, sulfides are unlikely
to be controlling the composition of the main hydrothermal endmember (M17).

Alternatively, it is possible that the precipitation of sulfides from reducing, sulfide-bearing 427 waters may instead remove Mo from solution as indicated by the minor group V mixing trend 428 (Fig. 5). When redox is defined using sulfur speciation and trace levels of H_2S are assumed to 429 430 be present in the hydrothermally influenced waters (at levels of 0.01 ppm to 0.01 ppb) then the hydrothermal samples tend towards sulfide (molybdenite, pyrite, and chalcopyrite) 431 saturation (Table ES2). Whilst molybdenite has not been found in active geothermal systems 432 433 in Iceland, it is known to occur in some New Zealand geothermal systems and has been identified in hydrothermally altered Tertiary basalt formations at Reydarártindur in southeast 434 Iceland (Árnorsson & Ívarsson 1985). Although the sulfides measured in this study are all 435 436 isotopically heavy and the compiled molybdenite data show a range from -1.4‰ to +2.6‰ (Breillat et al., 2016), Tossell (2005) calculated that aqueous Mo-sulfide complexes are some 437 2‰ lighter than oxidised complexes. Greber et al. (2014) also suggested that light Mo is 438 preferentially incorporated in molybdenite during crystallization leaving behind a residually 439 heavier hydrothermal fluid. If isotopically light, sulfide formation could generate the M14 440 441 endmember and the group V waters, but cannot be responsible for the main groundwater trend. 442

In the absence of isotope data for sulfides local to the study sites, it is not clear what role, if any, sulfide plays in controlling the Mo chemistry of the waters. Sulfides span a large isotope range and are only sometimes significant hosts of Mo. Although sulfide dissolution and precipitation are potentially contributing factors to the Mo chemistry of these waters, due to the saturation state calculations it is considered more likely that sulfides are stable or forming in these waters, thereby unlikely to be contributing Mo to solution. 449 The mechanisms controlling the compositions of these waters appear to be complex. There are potentially two distinct hydrothermal endmembers as shown on the mixing diagrams (Fig. 450 5): both are isotopically heavy but one possesses high Mo concentrations and the other low 451 452 concentrations. We suggest that an important control on Mo in the groundwaters is the incongruent dissolution of basalt. The hydrothermal waters are increasingly influenced by the 453 dissolution of olivine over plagioclase, with correspondingly heavier Mo isotope 454 compositions as temperature increases. However, it is unlikely that primary mineral 455 dissolution alone could control the composition of the hydrothermal endmember as it would 456 457 require extraordinary fractionation between these minerals at high temperatures when forming the basalts. The group V waters are likely to be more strongly influenced by Mo 458 removal mechanisms involving the precipitation of isotopically light phases, such as 459 460 molybdenite or other sulfide minerals.

461 *4.4. Ocean mass balance*

462 Although the mechanisms responsible for the observed Mo isotope composition in groundwater remain complex, the new data allow a more detailed assessment of the Mo 463 budget of the oceans. Typically, the source of Mo to the ocean is considered to be dominated 464 by rivers, with a minor (~10%) hydrothermal component contributing the remaining flux 465 (McManus et al., 2002), and the sinks of Mo comprise euxininc, suboxic, and oxic 466 sedimentary deposition (e.g. Kendall et al., 2016). There are currently two approaches to 467 evaluating the Mo input composition: (1) the assumption that over long time scales the 468 riverine flux will represent the average crustal value (e.g. Asael et al., 2013); and (2) the 469 470 direct measurement of the riverine compositions (e.g. Archer & Vance 2008). These two approaches result in slightly different estimates of the Mo isotope input to the oceans. The 471 continental crust has a bulk composition of between δ^{98} Mo +0.35‰ and +0.6‰ and a 472 473 maximum of +0.4‰ for the upper continental crust alone (Willbold et al., 2017). The riverine 474 average has a higher δ^{98} Mo value of +0.7‰ (Archer & Vance 2008) and when combined in 475 mass balance with a poorly constrained hydrothermal input of δ^{98} Mo +0.8‰ (McManus et 476 al., 2002) results in a Mo input of ca. +0.7‰ (Eq. 2).

477

478
$$\delta^{98} \text{Mo}_{input} = f_{river} \times \delta^{98} \text{Mo}_{river} + f_{hydrothermal} \times \delta^{98} \text{Mo}_{hydrothermal}$$
(2)

479

If, as the data from these Icelandic cold groundwaters suggest (see section 4.1), the 480 481 concentration of Mo in groundwaters is similar to that of rivers, and groundwater discharge is the equivalent of 40% of the riverine water flux as suggested by Moore (1996), then 482 groundwaters may account for nearly 30% of the total Mo flux to the oceans (e.g. Rivers: 483 65%; Groundwater: 27%; Hydrothermal: 8%). The available Mo isotope data for 484 groundwaters indicate that they are isotopically lighter (δ^{98} Mo +0.2‰ for the data in this 485 486 study and King et al. (2016)) than river compositions, thus necessitating a re-evaluation of the 487 Mo ocean input (Eq. 3).

488

 $489 \qquad \delta^{98} Mo_{input} = f_{river} \times \delta^{98} Mo_{river} + f_{hydrothermal} \times \delta^{98} Mo_{hydrothermal} + f_{groundwater} \times \delta^{98} Mo_{groundwater}$ (3)

490

The result is a Mo input to the oceans of δ^{98} Mo +0.55‰ which, if correct, brings this combined Mo input closer to that of the estimate based upon crustal values. Furthermore, the data from King et al. (2016) indicate that groundwaters can contain around four times more Mo than the riverine average, in which case their contribution ($f_{groundwater}$) would increase, potentially even becoming the dominant source, and the total Mo input would be lighter still, 496 more closely matching that of the crustal values. However, while groundwater data remain 497 limited both in terms of potential flux to the oceans and the isotope composition it is not 498 possible to accurately constrain these values.

Despite high temperature hydrothermal systems generally not being considered a significant 499 source of Mo to the oceans these terrestrial hydrothermal systems maintain relatively high 500 Mo concentrations (up to 4.8 ppb). Without exception, in this study there is preferential 501 enrichment of heavy δ^{98} Mo in the hydrothermal fluid, with minimum δ^{98} Mo in endmember 502 fluids of more than +2%. If this is indicative of the processes contributing to the evolution of 503 MOR hydrothermal fluids then the hydrothermal portion of the Mo input to the oceans may 504 505 be heavier than previously estimated. Within the modern ocean budget hydrothermal contributions of Mo are minor; increasing the hydrothermal Mo isotope composition to an 506 extreme of δ^{98} Mo +2.0‰ only increases the combined input (δ^{98} Mo_{input}) by some 0.1‰. 507 508 However, during early periods of Earth's history, when hydrothermal fluids may have comprised a greater proportion of total inputs to the ocean, the accurate characterisation of 509 510 these fluids is of greater importance for the interpretation of ocean chemistry. With only one other direct study of hydrothermal fluids, the significance of these systems and reactions at 511 both low and high temperatures remains, at best, uncertain (cf. McManus et al., 2002). 512

513

514 **5.** Conclusions

We present a comprehensive study of the Mo isotopic composition of waters from two hydrothermally influenced groundwater systems in northeast Iceland with variations in δ^{98} Mo from -0.15‰ to +2.06‰. Although data are currently limited to the basaltic terrains of Hawaii and Iceland, this study represents an important increase in the available data for both cold and hydrothermally influenced groundwaters, with the main findings being: 520 1) Cold groundwaters in Iceland are isotopically light, ranging from δ^{98} Mo -0.15‰ to 521 +0.47‰ (mean: δ^{98} Mo_{*GROUNDWATER* +0.18‰), and are comparable with the Mo composition 522 of groundwaters from Hawaii (mean δ^{98} Mo +0.39‰) reported in King et al. (2016). On 523 average the groundwaters are isotopically lighter than rivers and have Mo isotope signatures 524 that are similar to their basaltic host-rocks (δ^{98} Mo_{*BASALT*} -0.12‰ to +0.16‰).}

2) The majority of hydrothermally influenced groundwaters in this study have higher dissolved Mo concentrations (up to 4.81 ppb) and heavier Mo isotope compositions than the regional cold groundwaters ($\delta^{98}Mo_{HYDROTHERMAL}$ +0.25‰ to +2.06‰). Mixing between the cold groundwaters and hydrothermal endmembers (+2.06‰ and +1.08‰) is the main control on the Mo composition of the groundwater samples. The incongruent dissolution of basalt and dissolution and precipitation of sulfide minerals are both processes capable of controlling hydrothermal endmember Mo compositions.

532 3) With the inclusion of a direct groundwater contribution to the Mo flux to the oceans the 533 combined groundwater and river input is re-evaluated to δ^{98} Mo +0.55‰, in closer agreement 534 with estimates based upon the crustal composition alone. However, whilst groundwater data 535 remain limited these estimates should be considered with caution.

536

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Figure Captions:

Figure 1: Map showing the location and sampling temperatures of the Mývatn (M) and Þeistareykir (Þ) groundwater samples in the northern volcanic zone (NVZ) of Iceland. Inset A shows the two groundwater systems in relation to the major geographical features of Iceland; the main volcanic and fracture zones are shown in red and major icecaps and glaciers in white; and the black star is the Reykjanes hydrothermal system, location of the basalt samples. Inset B depicts the Þesitaryekir sampling locations (diamonds) and inset C the Mývatn groundwater samples (circles). The Mývatn samples overly a simple base map including the Krafla caldera features (Gudmundsson & Arnorsson 2002) and the groundwater types (I-VI) defined on the basis of their chemistry by Ármannsson et al. (2000). The cold growdwaters for both systems are sourced from as far south as Vatnajöjull (VJ) glacier.

Figure 2: pH-Eh diagram at 25°C and 105 Pa for the S-O-H system with available, oxidised, Mo data superimposed. Mo speciation below the SO_4^{2-} - H₂S transition is not well characterised although it is thought to be dominated by oxythiomolybdate species (MoO_{4-x}S_x²⁻). Calculated in situ pH and Eh for the groundwater samples are plotted: filled circles are Mývatn groundwaters whilst the diamonds are from Þeistareykir; blue denotes a sampling temperature of less than 10°C and red, hydrothermally influenced waters. Despite a range in Eh values, all samples are dominated by MoO₄²⁻. Calculations are based on the minteq.v4 database within PHREEQC (Parkhurst & Appelo 2013). The stability field for water lies between the two dashed lines.

Figure 3: Molybdenum versus SO_4^{2-} in precipitation, surface waters, groundwaters, and geothermal systems after Miller et al. (2011). The grey data are from the literature: river and precipitation data from Miller et al. (2011) and Neubert et al. (2011), geothermal from Kaasalainen & Stefánsson (2012) and Arnórsson & Ívarsson (1985), and groundwaters from Leybourne & Cameron (2008). The coloured data are from this study: filled circles are Mývatn groundwaters whilst the diamonds are from Peistareykir, blue denotes a sampling temperature of less than 10°C and red, hydrothermally influenced waters. After Miller et al. (2011), a best-fit regression line, forced through the origin, is plotted through the groundwaters from this study (excluding the group V waters as described in the text) and the resulting slope and coefficient of determination (R^2) are shown and are in agreement with those reported in Miller et al. (2011) for rivers (y = 0.01x, $R^2 = 0.69$).

Figure 4: Mo concentration and isotope data for terrestrial groundwaters including those that are geothermally affected (red). All data are from this study save for the four Hawaiian groundwaters (blue crosses) from King et al. (2016). For reference, values for a range of Icelandic basalts (Table 2 & Yang et al., 2015) and the mean global river composition (Archer & Vance 2008) are plotted.

Figure 5: Relationship between Mo isotopes and Mo and SO_4^{2-} concentrations in the Mývatn groundwater system. Cold groundwaters (sampling temperature <10°C) are depicted in blue whilst those that are geothermally influenced are shown in red. The distinct group V waters (as discussed in the main text) are open red circles. For reference, the Mo isotopic range of Icelandic basalts ($\delta^{98}Mo_{BASALT} = -0.1$ to -0.4%) is shown as the shaded band (Table 2). There are two mixing lines, both have a common cold groundwater endmember (M07) but two distinct geothermal endmembers: one low [Mo], mid-range SO_4^{2-} , and isotopically heavy (M14, dashed line) and one high [Mo], high SO_4^{2-} , and heavy Mo isotopes (M17solid line).

Figure 6: Log pCO_2 for all of the groundwaters. The pH and pCO_2 are calculated for the sampling conditions using PHREEQC (Parkhurst & Appelo 2013) and the minteq.v4 database. The reference line is the pCO_2 of the modern atmosphere.

Figure 7: Basalt primary mineral saturation indices (SI) in the Mývatn and Þeistareykir groundwaters plotted against both the Mo isotope composition and sampling temperature of the waters. Saturation indices are calculated using the PHREEQC database and SI >0 suggests that the mineral phase is stable whilst SI <0 indicates the possibility of dissolution. The grey arrows highlight the potential increase in olivine dissolution over plagioclase dissolution with increasing temperature.

Figure 8: Molybdenum isotope compositions for sources of Mo to the modern oceans. The grey bars denote the range whilst the black diamonds show mean values and the stars are minimum estimates of the hydrothermal endmembers. The grey outline for the high temperature fluids shows the range of values measured for the mixed fluids in this study. River data is summarised in Kendall et al. (2016), Hawaii groundwater data from King et al. (2016), and the low temperature hydrothermal fluids from McManus et al. (2002). In addition, the individual sulfide values from this study are plotted (black squares) with the entire molybdenite range (from Breillat et al., 2016) for comparison. * denotes data from this study.

Fig. 1







Fig. 4



Fig. 5



Fig. 6





Fig. 8



Table 1. Selected data for Myvall and Perstarcykii gloundwaters (o Wolfelative to Mist +0.25700).														
		Temp	pH*	Eh*	Na	Mg	CI	H₂S	SO₄	Мо	δ ⁹⁸ Μο		2 SD	n
		°C	situ	V	ppm	ppm	ppm	ppm	ppm	ppb	‰			
MÝVA	ATN GROUNDWATERS													
M01	Hliðardalslækur	15.9	8.23	0.08	91.3	12.50	26.00	b.d.l	199.00	4.81	1.05	±	0.04	4(2)
M02	AB-2	3.3	8.16	0.60	11.2	5.15	4.36	b.d.l	13.80	0.331	0.29	±	0.08	2
M03	LUD-4	5.4	8.29	0.58	53.6	9.20	12.30	b.d.l	96.20	1.52	1.12	±	0.08	2
M04	LUD-2	5.6	8.55	0.15	18.6	7.60	5.74	b.d.l	16.10	0.565	0.39	±	0.08	2
M05	LUD-3	4.5	8.64	0.51	15.3	7.07	5.29	b.d.l	15.30	0.594	0.39	±	0.08	2
M06	Svelgur	19.2	6.94	0.22	119.0	1.21	54.00	0.05	181.00	4.85	1.55	±	0.08	2
M07	Garðslind	6.5	8.96	0.10	17.4	4.64	2.11	b.d.l	7.33	0.654	0.47	±	0.08	2
M08	Bjarg	19.0	8.11	0.56	44.3	4.02	9.71	b.d.l	47.10	0.988	0.47	±	0.01	3
M09	Helgavogur	23.3	8.24	0.19	52.3	5.56	8.04	b.d.l	66.20	0.832	0.72	±	0.08	3
M10	Hverfjallsgjá	6.5	8.75	0.48	21.5	6.84	5.08	b.d.l	22.10	0.713	0.38	±	0.08	2
M11	Vogaflói	5.0	8.79	0.56	21.1	6.26	4.75	b.d.l	21.20	0.812	0.33	±	0.08	2
M12	Langivogur	21.5	8.51	0.47	76.9	3.64	15.10	b.d.l	108.00	0.371	1.06	±	0.08	2
M13	LUD-10	25.3	8.20	0.21	37.3	8.57	4.54	b.d.l	40.50	1.43	0.62	±	0.03	3
M14	Grjótagjá	46.1	8.27	0.17	86.3	3.09	17.70	0.08	109.00	0.206	2.06	±	0.03	5(2)
M15	Stóragjá	26.5	8.23	0.20	61.8	5.58	9.57	b.d.l	81.90	1.04	0.93	±	0.06	3
M16	Vogagjá	40.0	8.21	0.51	88.0	2.49	17.50	b.d.l	128.00	0.219	1.37	±	0.06	3
M17	Skiljustöð	93.2	8.52	0.16	250.0	0.01	81.30	22.4	232.00	1.4	1.08	±	0.08	2
M18	AE-10	40.6	8.05	0.27	42.0	0.99	4.09	0.03	66.80	0.954	0.59	±	0.01	3
M19	LUD-5	4.3	8.68	0.48	13.6	6.55	4.88	b.d.l	10.60	0.579	0.18	±	0.06	3
M20	LUD-6	33.0	8.22	0.51	51.7	7.11	5.67	b.d.l	57.00	0.888	0.81	±	0.08	5(2)
ÞEIS	TAREYKIR GROUNDWATI	ERS												
Þ01	Þeistareykir-vatnsból	15.7	7.15	0.70	15.2	5.68	5.81	b.d.l	14.20	0.176	0.68	±	0.13	3
Þ02	Þeistareykir-Sæluhús	11.6	8.14	0.57	20.8	3.69	7.41	b.d.l	26.10	0.235	0.50	±	0.08	2
Þ03	ÞR-5	26.6	8.09	0.58	20.8	3.68	7.45	b.d.l	26.20	0.283	0.47	±	0.06	3
Þ04	Krossdalur	3.4	8.68	0.52	9.3	2.67	8.73	b.d.l	3.50	0.181	0.00	±	0.08	2
Þ05	Fjöll - lind	2.6	10.00	0.27	16.3	0.05	7.84	b.d.l	4.26	0.209	-0.08	±	0.08	2
Þ06	Fjöll - vatnsból	2.8	9.18	0.42	11.9	0.42	10.40	b.d.l	2.76	0.103	0.17	±	0.08	2
Þ07	Lón	4.4	7.97	0.62	8.7	2.59	7.68	b.d.l	2.91	0.255	0.06	±	0.10	3
Þ08	Rifós - Tangabrunnur	10.2	8.24	0.59	14.8	3.41	10.00	b.d.l	8.73	0.269	0.25	±	0.03	3
Þ09	ÞR-15	15.3	8.03	0.54 -	13.0	3.91	7.50	b.d.l	14.00	0.171	0.55	±	0.12	3
Þ10	ÞR-8	2.5	8.40	0.28	6.9	1.95	6.95	0.03	1.71	0.097	-0.15	±	0.08	2
Þ11	ÞR-16	5.2	8.95	0.42	8.6	3.37	5.45	b.d.l	1.84	0.189	-0.04	±	0.07	3

Table 1: Selected data for Mývatn and Þeistareykir groundwaters (δ^{98} Mo relative to NIST= +0.25‰).

IAPSO seawater

10.8 2.34 ± 0.08 43(17)

*Calculated using PHREEQC and the minteq.v4 database (Pankhurst and Apello, 2013) at *in situ* temperature conditions

b.d.l. - below detection limit (0.01 ppm fpr H_2S)

Errors are reported as 2 SD of the mean when $n\geq 3$ and as the 2 SD of repeat IAPSO analyses when n<3

Table 2:	Selected	data	for	basalt	and	sulphide	samr	oles

		Мо	δ ⁹⁸ Mo		2 SD	n		
		ppm	‰					
ICELANDIC B								
						4		
RN09-642		1.007	-0.06	±	0.06	(2)		
RN09-900		0.242	-0.12	±	0.08	2		
RN09-1102		0.135	0.00	±	0.08	2		
						3		
RN09-1200	(Hyaloclastite)	4.665	0.16	±	0.03	(2)		
SULPHIDES, Outokumu Finland								
279-1	Chalcopyrite	38.11	1.17	±	0.03	4		
279-8	Chalcopyrite	37.97	1.15	±	0.03	3		
279-9	Pyrite	0.074	1.80	±	0.08	1		
279-10	Pyrrhotite	0.048	1.46	±	0.08	1		

 $\delta^{98}Mo$ relative to NIST= +0.25‰ Errors are reported as 2 SD of the mean when n≥3 and as the 2 SD of repeat IAPSO analyses when n<3 *Bulk rock measurements