



# Molybdenum isotope behaviour in groundwaters and terrestrial hydrothermal systems, Iceland

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## ABSTRACT

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

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## 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 and Anbar, 2004; Archer and Vance, 2008; Pearce et al., 2008; Goldberg et al., 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 the modern oceans (~10 ppb; e.g. Nakagawa et al., 2012, Table 1). This relatively high concentration results from the efficient transport of Mo from the continents to the oceans, due to the solubility of Mo phases under oxidative weathering and the subsequent transport of dissolved Mo prior to its slow removal from the oceans in the presence of dissolved O<sub>2</sub>. The resulting residence time of Mo in the oceans of 440 ka

(Miller et al., 2011) is more than two orders of magnitude greater than the ocean mixing time, so that the oceans have uniform Mo elemental and isotope compositions (Nakagawa et al., 2012).

Under oxidising conditions Mo is present in solution as the stable molybdate ion, MoO<sub>4</sub><sup>2-</sup>, (Fig. 2). In this form Mo is slowly removed from the water column through uptake into ferromanganese phases, which preferentially incorporate isotopically light Mo (e.g. Barling et al., 2001; Barling and Anbar, 2004; Goldberg et al., 2009; Miller et al., 2011; Wasylenko et al., 2011). As a result of this fractionation the modern oceans are the heaviest Mo reservoir on Earth (Kendall et al., 2016). In contrast, Mo is readily removed from solution in anoxic–sulfidic waters with very little net isotopic fractionation. In the presence of reduced sulfur, Mo forms oxo-oxiomolybdate ions, MoO<sub>4-x</sub>S<sub>x</sub><sup>2-</sup>, which are highly particle-reactive and thus rapidly removed from solution (e.g. Barling et al., 2001). This behaviour underpins the application of Mo isotopes and abundances as a proxy for past ocean anoxia (e.g. Pearce et al., 2008; Asael et al., 2013).

Early paleoredox studies assumed a comparatively straightforward ocean budget in which Mo input was dominated by

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**Table 1**  
Selected data for Mývatn and Þeistareykir groundwaters ( $\delta^{98}\text{Mo}$  relative to NIST = +0.25‰).

	Temp (°C)	pH <i>in situ</i>	Eh <sup>a</sup> (V)	Na (ppm)	Mg (ppm)	Cl (ppm)	H <sub>2</sub> S (ppm)	SO <sub>4</sub> (ppm)	Mo (ppb)	$\delta^{98}\text{Mo}$ (‰)	2 SD	n
Mývatn 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	1.968	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	Vogaffló	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)
Þeistareykir groundwaters												
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
IAPSO seawater									10.8	2.34 ± 0.08	43(17)	

<sup>a</sup> Calculated using PHREEQC and the minteq.v4 database (Parkhurst and Appelo, 2013) at *in situ* temperature conditions b.d.l. – below detection limit (0.01 ppm for H<sub>2</sub>S). Errors are reported as 2 SD of the mean when  $n \geq 3$  and as the 2 SD of repeat IAPSO analyses when  $n < 3$ .

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

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

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 <sup>226</sup>Ra, 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 river-water flux. Direct groundwater discharge may therefore contribute a significant proportion of the water flux to the oceans.

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 by chemical exchange in oceanic hydrothermal systems (McManus et al., 2002). For time periods such as the Archean, hydrothermal heat losses were likely much greater than at present (Lowell and Keller, 2003). During these time periods the hydrothermal input of Mo may have been more important in the seawater mass balance. Through detailed study of fluid inclusions from identified hydrothermal vents of mid-Archean age in the Barberton formation, South Africa, De Ronde et al. (1997) found that the vent fluids likely had similar 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 oceans through geologic time.

Data for mid-ocean ridge (MOR) hydrothermal waters are currently limited to a low-temperature (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  $\delta^{98}\text{Mo} +0.8\text{‰}$  (McManus et al., 2002). However, it is unclear if this signal represents basalt-seawater interaction or if it was inherited from the overly-

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