



The effects of magmatic processes and crustal recycling on the molybdenum stable isotopic composition of Mid-Ocean Ridge Basalts



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ABSTRACT

Molybdenum (Mo) stable isotopes hold great potential to investigate the processes involved in planetary formation and differentiation. However their use is currently hampered by the lack of understanding of the dominant controls driving mass-dependent fractionations at high temperature. Here we investigate the role of magmatic processes and mantle source heterogeneities on the Mo isotope composition of Mid-Ocean Ridges Basalts (MORBs) using samples from two contrasting ridge segments: (1) the extremely fast spreading Pacific–Antarctic (66–41°S) section devoid of plume influence and; (2) the slow spreading Mohns–Knipovich segment (77–71°N) intercepted by the Jan Mayen Plume (71°N). We show that significant variations in Mo stable isotope composition exist in MORBs with $\delta^{98/95}\text{Mo}$ ranging from -0.24‰ to $+0.15\text{‰}$ (relative to NIST SRM3134). The absence of correlation between $\delta^{98/95}\text{Mo}$ and indices of magma differentiation or partial melting suggests a negligible impact of these processes on the isotopic variations observed. On the other hand, the $\delta^{98/95}\text{Mo}$ variations seem to be associated with changes in radiogenic isotope signatures and rare earth element ratios (e.g., (La/Sm)_N), suggesting mantle source heterogeneities as a dominant factor for the $\delta^{98/95}\text{Mo}$ variations amongst MORBs. The heaviest Mo isotope compositions correspond to the most enriched signatures, suggesting that recycled crustal components are isotopically heavy compared to the uncontaminated depleted mantle. The uncontaminated depleted mantle shows slightly sub-chondritic $\delta^{98/95}\text{Mo}$, which cannot be produced by core formation and, therefore, more likely result from extensive anterior partial melting of the mantle. Consequently, the primitive $\delta^{98/95}\text{Mo}$ composition of the depleted mantle appears overprinted by the effects of both partial melting and crustal recycling.

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1. Introduction

High-temperature stable isotope fractionations can provide important insights into the nature and conditions of the processes involved in planetary differentiation, such as core formation, crust production and crust–mantle interaction (e.g. Georg et al., 2007; Dauphas et al., 2009; Cabral et al., 2013). Based on experimental work showing that resolvable Mo isotopic fractionation exists between liquid silicate and liquid metal up to temperatures of $\sim 2500^\circ\text{C}$, Mo isotopes have much potential to investigate the conditions of core formation in the Earth and other planetary bodies (e.g., Hin et al., 2013; Burkhardt et al., 2014). However, the use of this experimental calibration to constrain core formation temperature requires the Mo isotopic composition of both the core and

the silicate portion of the Earth to be precisely known. While a $\delta^{98/95}\text{Mo}$ of $-0.16 \pm 0.02\text{‰}$ (relative to NIST SRM3134) can be assumed for the core (Burkhardt et al., 2014), a precise estimate of the Mo stable isotope composition for the bulk silicate Earth (BSE) is more difficult to obtain. This is because the current BSE comprises several reservoirs for which the production and/or evolution likely involved Mo isotopic fractionation. Indeed, the Mo stable isotope compositions of terrestrial igneous rocks vary by more than 1‰ (Burkhardt et al., 2014; Freymuth et al., 2015; Greber et al., 2014, 2015; Neubert et al., 2011; Siebert et al., 2003; Voegelin et al., 2012, 2014; Yang et al., 2015). These large isotopic variations either result from isotopic fractionation during magma production and differentiation, or reflect isotopic heterogeneities in the mantle source created by crustal recycling. One approach to constrain the Mo isotopic composition of the BSE is to analyse komatiites. This is because these volcanic rocks were formed by large-scale melting at very high temperatures, limiting poten-

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tial isotopic fractionation during partial melting. Using komatiites, Greber et al. (2015) argued that the Mo stable isotope composition of the BSE is indistinguishable from the composition of the bulk Earth as estimated from chondrites and iron meteorites (Burkhardt et al., 2014). However, the komatiites themselves showed rather large variations in $\delta^{98/95}\text{Mo}$ with a total spread of $\sim 0.8\%$ that was likely produced by crustal assimilation during magma ascent or post-emplacement isotopic fractionation (Greber et al., 2015). These variations, and the lack of a clear understanding of the processes controlling them, make the precise determination of the Mo stable isotopic composition of the BSE difficult. In the light of these complexities, and given the importance of precisely knowing the Mo stable isotope composition of the BSE for constraining core formation, it is important to further investigate this composition using another approach.

Another way to determine the Mo stable isotope composition of the BSE is to use recent oceanic basalts. The advantages of using recent oceanic basalts over komatiites include (1) the availability of fresh samples, limiting the chances of post-emplacement isotopic fractionation, as well as (2) a good knowledge of the conditions and geodynamical contexts of eruption and (3) the possibility to select representative samples covering the full range of mantle compositional variations defined by radiogenic isotopes and trace element concentrations. Nonetheless, whether the Mo stable isotope composition of oceanic basalts reflect those of their mantle sources, i.e., whether magmatic processes fractionate the mantle signature, remains to be further investigated. Indeed, Mo isotope fractionation during mantle partial melting has not yet been tested. Furthermore, isotopic fractionation during magma differentiation was not systematically observed. It was suggested to occur in hydrous arc rocks by Voegelin et al. (2014), based on correlations between Mo isotopes and indices of differentiation for a suite of igneous rocks from the Aegean arc (and heterogeneous $\delta^{98/95}\text{Mo}$ in mineral separates), but was neither recorded in the case of Mariana Arc lavas (Freymuth et al., 2015) or in Iceland lavas from the Hekla volcano (Yang et al., 2015).

Up to now, only a limited Mo stable isotope data set exists for oceanic basalt and it remains unconstrained as to whether parts of the current mantle could have preserved the BSE composition. Overall, little is known about the impact of the main differentiation processes, i.e., partial melting and crustal recycling, on the mantle $\delta^{98/95}\text{Mo}$. Nevertheless, mantle heterogeneities related to crustal recycling are predicted based on arc studies (Freymuth et al., 2015; König et al., 2016). These investigations suggest that Mo stable isotopes fractionation in oceanic crust and sediments occurs during subduction, resulting in a lighter signature for the slab after dehydration. Thus, the incorporation of residual slabs to the mantle likely results in Mo isotope variations in the mantle. On the other hand, the Mo signature of arc rocks does not provide information about the impact of partial melting on the Mo isotope composition of the mantle because the Mo of arc lavas dominantly originates from the subducting slab, not the mantle wedge (Freymuth et al., 2015). In other words, partial melting alone may not produce Mo isotopic fractionation and mantle zones devoid of recycled oceanic crust may, therefore, have preserved their primitive composition.

Here we address the role of magmatic processes and mantle source heterogeneities on the Mo stable isotopic composition of Mid-Ocean Ridge Basalts (MORBs) using volcanic glasses from two contrasting ridges: Pacific–Antarctic (66–41°S) and Mohns–Knipovich (77–71°N) including a sample from the intercepting Jan Mayen plume (Elkins et al., 2016). In addition to providing the first extensive dataset for Mo stable isotopes in MORBs, our results provide critical information for the appraisal of the Mo stable isotope composition of the BSE.

2. Samples and analytical method

2.1. Samples

We selected twenty MORB glasses from the Pacific–Antarctic ridge (66–41°S; Fig. 1a) as well as seven glasses from the Mohns–Knipovich ridges (77–71°N) and one Oceanic Island Basalt (OIB) from Jan Mayen Island (71°N), which is located on the southern extremity of the Mohns ridge (Fig. 1b). The Pacific–Antarctic MORBs were sampled during the oceanographic cruises PACANTARCTIC (PAC1; 66–56°S) and PACANTARCTIC 2 (PAC2; 53–41°S). Amongst these samples, fourteen represent magmas erupted through the ridge axis while six were erupted off-axis. For all the on-axis glasses, major and trace elements (including Cl and S) as well as Sr, Nd, Pb, Hf and S isotope data are available (and He and Ne isotopes for some samples; Hamelin et al., 2010, 2011; Labidi et al., 2014; Moreira et al., 2008; Vlastélic et al., 1999, 2000). The off axis samples are characterised in terms of major elements, Cl and S concentrations and Pb and S isotopes. All on-axis Pacific–Antarctic samples are N-MORBs ('normal' MORBs, defined by $\text{La}/\text{Sm}_\text{N} < 1$) except for one sample displaying a T-MORB composition ('transitional' MORBs, defined by $1 < \text{La}/\text{Sm}_\text{N} < 1.7$). Based on their location and radiogenic isotope signatures, Pacific–Antarctic magmas were suggested to be devoid of mantle plume influence (e.g. Dosso et al., 2005). Mohns–Knipovich MORBs (77–71°N) and Jan Mayen (71°N) Oceanic Island Basalt (OIB) were sampled during the Norwegian sampling program, SUBMAR (four different cruises between 2000 and 2003 onboard the R.V. Håkon Mosby). Major and trace elements as well as Sr, Nd, Hf and Pb isotopic compositions are available for two of the seven samples selected (Elkins et al., 2016).

The Pacific–Antarctic samples are well suited to constrain how the Mo stable isotopic composition of magmas changes with the dominant magma differentiation processes occurring at mid-ocean ridges: mineral fractionation and crustal/hydrothermal fluid assimilation. Although the samples are not cogenetic, they evolved under similar magmatic conditions and cover the range of MgO typically observed at mid-ocean ridges (MgO = 4–10 wt.%). Diagrams in which various major elements are plotted versus MgO (wt.%) illustrate this common liquid line of descent for samples that are spread over 1000 km of a ridge section (supplementary figure in Hamelin et al., 2010). Furthermore, the selected samples have previously been shown to be variably affected by crustal and hydrothermal fluid assimilation (Labidi et al., 2014), allowing the impact of such processes on Mo isotopes to be constrained.

Pacific–Antarctic and Mohns–Knipovich MORBs together are pertinent to investigate the effect of mantle partial melting since they allow comparison between magmas typically formed by high, moderate and low degrees of partial melting occurring at fast (northern Pacific–Antarctic segment investigated; PAC2 samples; up to 110 mm/yr; DeMets et al., 1990), intermediate (southern Pacific–Antarctic segment; PAC1 ~ 55 mm/yr; DeMets et al., 1990) and slow ridge segments (Mohns–Knipovich; ~ 15 mm/yr; Dick et al., 2003), respectively. In addition, the comparison of the Mohns–Knipovich MORBs with the Jan Mayen OIB could provide further insights into the impact of partial melting on Mo isotopic compositions, given the very distinct degrees of melting for MORBs and OIBs.

Finally, the selected Pacific–Antarctic and Mohns–Knipovich samples are also relevant to explore the role of mantle heterogeneities. Based on radiogenic isotope compositions (e.g., Fig. 2), the source of Pacific–Antarctic MORBs comprises dominantly depleted Mantle (DMM) as well as small amounts of recycled oceanic crust, with both components thought to be intrinsic to the asthenospheric mantle (i.e., no plume from the deeper mantle involved; e.g. Hamelin et al., 2011). The source of Mohns–Knipovich

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