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Molybdenum mobility and isotopic fractionation during subduction at the Mariana arc

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ABSTRACT

The fate of crustal material recycled into the convecting mantle by plate tectonics is important for understanding the chemical and physical evolution of the planet. Marked isotopic variability of Mo at the Earth's surface offers the promise of providing distinctive signatures of such recycled material. However, characterisation of the behaviour of Mo during subduction is needed to assess the potential of Mo isotope ratios as tracers for global geochemical cycles. Here we present Mo isotope data for input and output components of the archetypical Mariana arc: Mariana arc lavas, sediments from ODP Sites 800, 801 and 802 near the Mariana trench and the altered mafic, oceanic crust (AOC), from ODP Site 801, together with samples of the deeper oceanic crust from ODP Site 1256. We also report new high precision Pb isotope data for the Mariana arc lavas and a dataset of Pb isotope ratios from sediments from ODP Sites 800, 801 and 802. The Mariana arc lavas are enriched in Mo compared to elements of similar incompatibility during upper mantle melting, and have distinct, isotopically heavy Mo (high ^{98}Mo/^{95}Mo) relative to the upper mantle, by up to 0.3 parts per thousand. In contrast, the various subducting sediment lithologies dominantly host isotopically light Mo. Coupled Pb and Mo enrichment in the Mariana arc lavas suggests a common source for these elements and we further use Pb isotopes to identify the origin of the isotopically heavy Mo. We infer that an aqueous fluid component with elevated [Mo], [Pb], high ^{98}Mo/^{95}Mo and unradiogenic Pb is derived from the subducting, mafic oceanic crust. Although the top few hundred metres of the subducting, mafic crust have a high ^{98}Mo/^{95}Mo, as a result of seawater alteration, tightly defined Pb isotope arrays of the Mariana arc lavas extrapolate to a fluid component akin to fresh Pacific mid-ocean ridge basalts. This argues against a flux dominantly derived from the highly altered, uppermost mafic crust or indeed from an Indian-like mantle wedge. Thus we infer that the Pb and Mo budgets of the fluid component are dominated by contributions from the deeper, less altered (cooler) portion of the subducting Pacific crust. The high ^{98}Mo/^{95}Mo of this flux is likely caused by isotopic fractionation during dehydration and fluid flow in the slab. As a result, the residual mafic crust becomes isotopically lighter than the upper mantle from which it was derived. Our results suggest that the continental crust produced by arc magmatism should have an isotopically heavy Mo composition compared to the mantle, whilst a contribution of deep recycled oceanic crust to the sources of some ocean island basalts might be evident from an isotopically light Mo signature.

1. Introduction

The Mo stable isotope system has, in the past decade, emerged as an important tool to reconstruct paleo-redox conditions in the ocean (e.g. Siebert et al., 2003; Arnold et al., 2004). Fractionation of Mo isotopes has been shown to occur between seawater ($\delta^{98/95}$Mo = 2 ‰ relative to NIST SRM 3134, Siebert et al., 2003) and oxic sediments (e.g. $\delta^{98/95}$Mo ≈ −1 ‰ for Fe–Mn crusts, Barling et al., 2001; Siebert et al., 2003), whereas anoxic sediments (such as black shales) incorporate Mo from seawater quantitatively and therefore without isotopic fractionation (e.g. Arnold et al., 2004). Mo is also removed from seawater during hydrothermal circulation at mid-ocean ridges (Trefry et al., 1994), which could add an isotopically distinct Mo component to the mafic oceanic crust. Oceanic crust therefore likely comprises altered materials with isotopically highly variable Mo compositions, quite dis-similar to mantle values (−0.2 to 0 ‰, Burkhardt et al., 2014). This suggests

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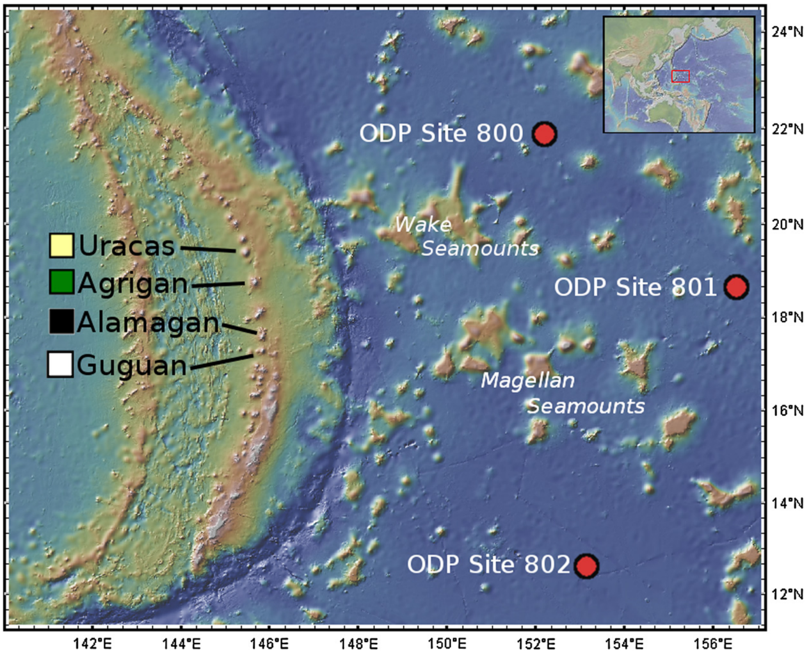

Fig. 1. Map of the Mariana arc showing the location of sampled islands and proximal ODP Sites 800, 801 and 802. The basemap is from geomapapp (http://www.geomapapp.org).

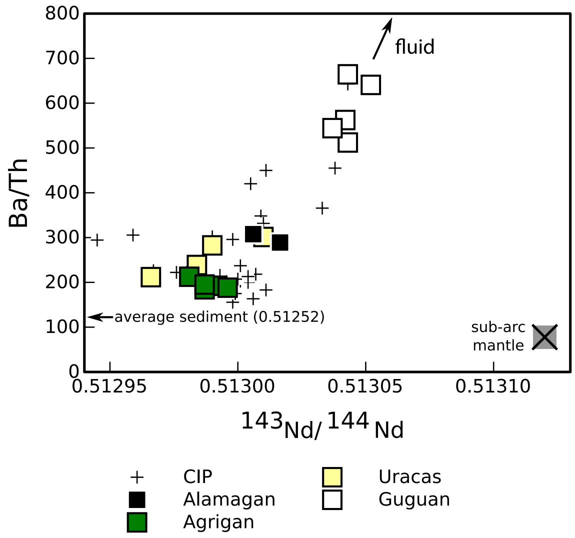

Fig. 2. Compositional variations of erupted magmas in the central island province (CIP) of the Mariana arc. Mariana arc lava samples used in this study are shown with large symbols. Other CIP data are from Woodhead (1989), Wade et al. (2005), Elliott et al. (1997) and Marske et al. (2011). Nd isotope composition of the average sediment subducted at the Mariana trench is from Plank and Langmuir (1998). The composition of the sub-arc mantle beneath the Mariana arc is based on the Mariana trough data from Woodhead et al. (2012) (average of their Nd isotope data, filtered by Woodhead et al. (2012) to exclude samples influenced by addition of subduction components) and Gale et al. (2013) (mean Ba/Th, weight ratio, of global MORB). The composition of slab-derived fluid from the mafic crust is inferred from the trend of the Mariana arc lavas and an arrow towards its approximate position is also indicated.

Mo isotope measurements might provide a diagnostic tracer of surface material returned to the Earth's interior, which can be used to track the remixing of subducted plates into the convecting mantle. Before such application, however, possibly modifications to the Mo isotope ratios of subducted material need to be assessed.

Volcanic arc magmas contain components derived from subducted sediments and elements carried in a fluid phase that is released from the mafic, altered oceanic crust (AOC) (Gill, 1981). The nature of this fluid phase, aqueous fluid, supercritical fluid, or melt is debated but empirically it is compositionally distinct from the sediment component (Kay, 1980). Although Noll et al. (1996) argued for minor fluid mobilisation of Mo during dehydration of subducting slabs, Green and Adam (2003) showed that Mo can be highly mobile in aqueous fluids at temperatures and pressures relevant for subduction zones. Mo transport in fluids derived from the subducted slab has further been suggested to be responsible for Mo enrichment in volcanic rocks from the Solomon arc (König et al., 2008). In addition, oxic oceanic sediments can be highly enriched in Mo and upon subduction potentially release Mo into the arc magma source. Volcanic arc magmas can therefore be expected to obtain a significant Mo contribution from subducted components.

As a consequence, Mo isotope measurements might act as a tracer for components derived from subducted slabs in arc magmas. Release of Mo from the subducted slabs in subduction zones also potentially alters the bulk isotopic composition of material that is being transported beyond subduction zones into deeper parts of the mantle. A comparison of the input material into subduction zones (AOC and sediments) with the volcanic output can provide information about the effect of these processes and the composition of the residual, deep subducted material.

The Mariana arc (Fig. 1) is an ideal location to address these questions because the islands of the Mariana arc are compositionally diverse, defining geochemical trends that implicate the variable influence of subducted sediments and slab-derived fluids (e.g. Woodhead, 1989; Elliott et al., 1997) (Fig. 2). In addition, samples of input material for the Mariana arc are available from ODP Sites 800, 801 and 802 (Fig. 1) which sampled the entire sediment columns at these locations. Furthermore, ODP Site 801 provides an unusually complete section through the upper AOC. Together, these samples allow us to constrain potential source components of the Mariana arc lavas in exceptional detail. We complement the data from the upper AOC with samples from ODP Site 1256, which is located further away from the Mariana arc on the younger Cocos plate in the Eastern Pacific ocean but is the stratigraphically deepest drill hole in the oceanic crust and thus allows us to constrain the Mo isotope composition of deeper parts of the AOC.