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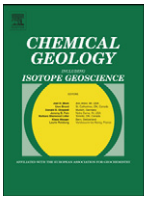

Comparative geochemistry of rhenium in oxidized arc magmas and MORB and rhenium partitioning during magmatic differentiation

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ABSTRACT

The geochemical behavior of Re in oxidized arc magmas (Eastern Manus basin) and MORB has been reexamined. In the early differentiation stage of oxidized arc magmas, Yb, Cu, Au, Ag, and Re have a bulk partition coefficient (D) between the crystallized mineral assemblage (olivine, clinopyroxene, and plagioclase) and the residual melt on the order of $0.33 = D_{Yb} \sim D_{Au} > D_{Re} > D_{Ag} > D_{Cu}$, while in the late stage they have a bulk D between the crystallized mineral assemblage (clinopyroxene, plagioclase, magnetite, and monosulfide solid solution — MSS) and the residual melt on the order $D_{Re} > D_{Cu} > D_{Au} \geq 1 > D_{Yb} = 0.29 > D_{Ag}$. In oxidized arc magmas, Cu, Au, and Ag are primarily controlled by crystalline MSS, whereas Re is primarily controlled by magnetite and it has a MSS/silicate melt partition coefficient significantly lower than 20. Unlike oxidized arc magmas, most MORB are saturated with sulfide liquid. Based on the positive correlation of $\log (D_{Cu} / D_{Re})$ and ΔFMQ regardless of fS_2, $\log (D_{Cu} / D_{Re}) = 0.997\Delta FMQ + 0.181$ ($R^2 = 0.99$) (D = partition coefficient between sulfide liquid and silicate melt; FMQ = fayalite–magnetite–quartz oxygen buffer), the partition coefficient of Re between sulfide liquid and silicate melt for MORB is estimated to be in the range of 600–10,000 at fO_2 of FMQ to FMQ − 1, increasing with decreasing fO_2. These partitioning data constrain that during MORB differentiation Re may be as compatible as Cu or Ag at relatively oxidized conditions ($FMQ - 0.5 < fO_2 < FMQ$) or as Au at relatively reduced conditions ($FMQ - 1 < fO_2 < FMQ - 0.5$), and its concentration in MORB maybe expected to decrease with decreasing MgO in a similar manner as Cu, Ag, or Au. Yb is an incompatible element during MORB differentiation. Consequently, during MORB differentiation Yb/Re ratio may be expected to increase with decreasing MgO. However, the previously observed nearly constant Yb/Re ratio in a suite of MORB indicates similar incompatibility of Yb and Re and thus a minor role of sulfide liquid in controlling the geochemical behavior of Re during MORB differentiation. More work is required to resolve this paradox.

1. Introduction

The Re–Os isotopic system is a useful tool for understanding the interaction and evolution of the Earth's crust and mantle (Shirey and Walker, 1998). This is mainly because Os behaves compatibly by being retained in sulfide and/or alloy during mantle melting, while Re is observed to be moderately incompatible (Brenan, 2008; Reisberg et al., 2005; Burnham et al., 1998; Fischer-Godde et al., 2011; Fonseca et al., 2011). However, the detailed interpretation of Re/Os fractionation, and a fuller application of this system is limited by the insufficient knowledge of the geochemical behavior of Re in high-temperature magmatic systems. Based on studying Re–Yb in some mid-ocean ridge basalts (MORB) (Hauri and Hart, 1997; Sun et al., 2003a), oceanic island basalts (OIB) (Schaefer et al., 2000), and some suites of peridotite (Burnham et al., 1998; Reisberg et al., 2005), a globally similar degree of incompatibility between Re and Yb during magmatic genesis and differentiation has been suggested, and a nearly constant Yb (ppm)/Re (ppb) ratio (2–5) has been observed in MORB. Furthermore, a nearly constant Yb/Re ratio has also been observed in oxidized arc magmas (Sun et al., 2003b). However, the reason for this similarity remains unresolved, as the geochemical behavior of these two elements is controlled by completely different phases. Re may be strongly compatible in sulfide liquid and possibly moderately compatible in garnet, but it is incompatible in the other silicate minerals (Righter and Hauri, 1998; Brenan et al., 2003; Mallmann and O'Neill, 2007; Brenan, 2008; Fonseca et al., 2011). The linear correlation between Re and sulfur in mantle peridotite (Reisberg and Lorand, 1995; Burnham et al., 1998; Reisberg et al., 2005) might suggest that the geochemical behavior of Re is controlled by sulfide during mantle melting. On the other hand, Yb is incompatible in sulfide but compatible in garnet (Righter and Hauri, 1998). The experimentally determined partition coefficients of Re between silicate minerals and silicate melt are in general lower than those of Yb (Brenan et al., 2003; Mallmann and O'Neill, 2007).

Re is generally thought to be a chalcophile element when sulfide is present. The partitioning of Re between sulfide liquid and silicate melt has been studied based on both natural and synthetic samples, however

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so far the partition coefficients of Re between sulfide phases (sulfide liquid and MSS) and silicate melt for MORB and oxidized arc magmas are either not available or inconsistent with each other. Based on coexisting sulfide globules and silicate glasses in MORB, a partition coefficient of 40 between sulfide liquid and silicate melt was measured by Roy-Barman et al. (1998), while Patten et al. (2013) determined values between 597 and 1218. Much higher partition coefficients (>30,000) between synthetic sulfide liquid and silicate melt were reported by Sattari et al. (2002). Fonseca et al. (2007) and Brenan (2008) found that the large variation of the partition coefficient of Re between sulfide liquid and silicate melt can be interpreted as a result of its high sensitivity to the variation of oxygen fugacity (fO_2) and sulfur fugacity (fS_2). Based on measured Re solubility in sulfide liquid, Fonseca et al. (2007) estimated sulfide liquid/silicate melt partition coefficients of 1–50 for MORB and 10^{-4} for oxidized arc magmas. However, considering the possible range of MORB fS_2, Brenan (2008) gave Re partition coefficients ranging from 370 to 1900. In a later study, Fonseca et al. (2011) chose a value of 1400. According to Brenan (2008), a precise determination of fS_2 is critical for a successful application of the experimental data to accurately estimate the partition coefficient of Re between sulfide liquid and silicate melt for MORB or oxidized arc magmas. The partitioning of Re between monosulfide solid solution (MSS) and silicate melt has never been investigated, but Brenan (2002, 2008) showed that Re moderately preferentially partitions into MSS relative to sulfide liquid. A direct measurement of the partition coefficients of Re between sulfide liquid, MSS, and silicate melt for oxidized arc magmas is still lacking.

Here, using the previous concentration data of Re, Cu, Au, Ag, and Yb in oxidized arc magmas and MORB and the previous partitioning data of these elements between sulfide liquid, MSS, oxides, silicate minerals, and silicate melt, I shall show that Re may have a fundamentally different geochemical behavior during the differentiation of oxidized arc magmas and MORB, which is a direct consequence of differences in Re partitioning behavior at conditions corresponding to these two suites of magmas.

2. Geochemical behavior of Re in oxidized arc magmas

In order to better understand the geochemical behavior of Re in oxidized arc magmas, I examined its compatibility relative to the other key chalcophile and lithophile elements, i.e., Cu, Au, Ag, and Yb. The data used for Cu, Au, Ag, Re, and Yb in oxidized arc magmas are mainly from a series of publications on volcanic glasses from Eastern Manus basin, Papua New Guinea (Sun et al., 2003b, 2004b, 2007; Jenner et al., 2010; Park et al., 2013a). The advantage of using such data is that these volcanic glasses ranging in composition from basalt to rhyolite represent a differentiation series with a homogeneous source region (Sinton et al., 2003; Sun et al., 2003b; Park et al., 2013a), thus providing unique insights into chalcophile element evolution with arc magmatic differentiation. The volcanic glasses from Eastern Manus basin can be subdivided into two groups; the mafic ones with MgO > ~3 wt.% and SiO_2 < ~60 wt.%, and the felsic ones with MgO < ~3 wt.% and SiO_2 > ~60 wt.% (Sun et al., 2003b; Jenner et al., 2010; Park et al., 2013a). The crystallized mineral assemblage in the high MgO group glasses consists mainly of olivine, clinopyroxene, and plagioclase in the proportion of 5:35:60; while in the low MgO group glasses, the assemblage consists mainly of clinopyroxene, plagioclase, and magnetite in the proportion of 40:50:10 (Kamenetsky et al., 2001; Sinton et al., 2003; Park et al., 2013a). The fO_2 of the high MgO group glasses has been suggested to be around FMQ + 2 (Sun et al., 2004b; Jenner et al., 2010), whereas the fO_2 of the low MgO group glasses is slightly lower due to magnetite crystallization, but it is still significantly higher than the fO_2 of MORB (see Fig. 11 in Jenner et al., 2010).

The variation of Yb, Cu, Au, Ag, and Re as a function of MgO in the glasses from Eastern Manus basin is illustrated in Fig. 1. The scattering of the data in particular for Au and Re may be caused by their inhomogeneous distribution in the glasses and the different analytical methods used (in situ LA-ICP-MS analyses by Jenner et al., 2010; Sun et al., 2003b, 2004b; whole-rock solution ICP-MS analyses by Park et al., 2013a). Fig. 1a shows that Yb increases with the decrease of MgO, indicating its incompatibility in the crystallized minerals. Fig. 1b shows that Cu increases with decreasing MgO until it reaches a peak value of ~280 ppm at =~3 wt.% MgO, and then an abrupt drop to 36 ppm occurs. After the drop, there is a continuous decrease with decreasing MgO. Au and Ag have a similar but less pronounced drop (Fig. 1c and d). After the drop Ag increases with decreasing MgO, but the behavior of Au is not very clear because of the data scattering (Fig. 1c). Re shows a similar behavior to Cu, Au, and Ag at >~3 wt.% MgO. However, there is no abrupt drop in Re at =~3 wt.% MgO; Re decreases continuously at ≤~3 wt.% MgO (Fig. 1e). The above observations indicate that Cu, Au, Ag, and Re are all incompatible in the crystallized mineral assemblage of olivine, clinopyroxene, and plagioclase at >~3 wt.% MgO, however they start to behave significantly differently at ≤~3 wt.% MgO.

The variation of element ratio as a function of MgO is illustrated in Fig. 2. Fig. 2a shows that Cu/Yb ratio increases with decreasing MgO at >~3 wt.% MgO, indicating a greater incompatibility of Cu relative to Yb, i.e., $D_{Yb} > D_{Cu}$ (D = bulk partition coefficient between crystallized solids and residual melt) in the early differentiation stage of oxidized arc magmas. Based on similar reasoning, at >~3 wt.% MgO, D_{Yb} may be higher than D_{Re} ($D_{Yb} > D_{Re}$) (Fig. 2b), and D_{Ag} higher than D_{Cu} ($D_{Ag} > D_{Cu}$) (Fig. 2c). The decrease of Au/Ag ratio with decreasing MgO at >~3 wt.% MgO indicates a lesser incompatibility of Au relative to Ag, i.e., $D_{Au} > D_{Ag}$ (Fig. 2d). Yb/Au ratio is nearly constant at >~3 wt.% MgO, indicating a very close similarity in degree of incompatibility between Au and Yb (Fig. 2e). Re/Ag ratio decreases with decreasing MgO at >~3 wt.% MgO, hence $D_{Re} > D_{Ag}$ (Fig. 2f). Determining the relative compatibility between Cu and Re is hindered by the appearance of two Cu/Re trends (Fig. 2g). The first trend defined by the data taken from Park et al. (2013a) indicates $D_{Cu} > D_{Re}$, whereas the second trend defined by the data taken from Sun et al. (2003b, 2004b) and Jenner et al. (2010) indicates $D_{Cu} < D_{Re}$. The difference may be mainly caused by the inhomogeneous distribution of Re in the glasses and the different analytical methods used, as mentioned above (see also below for a more detailed discussion). As D_{Ag} is higher than D_{Cu} and D_{Re} is higher than D_{Ag} (Fig. 2c and f), based on the data taken from Jenner et al. (2010), here $D_{Cu} < D_{Re}$ is preferred. At >~3 wt.% MgO, D_{Yb} was constrained to be 0.33 by Park et al. (2013a). Therefore, in the early differentiation stage (at >~3 wt.% MgO), Yb, Cu, Au, Ag, and Re may have a bulk partition coefficient between the crystallized mineral assemblage and the residual silicate melt on the order of $0.33 = D_{Yb} \sim D_{Au} > D_{Re} > D_{Ag} > D_{Cu}$. At = ~3 wt.% MgO, there is an abrupt drop for Cu/Yb (Fig. 2a), Cu/Re (Fig. 2g), and Au/Re (not shown), and an abrupt rise for Yb/Ag (Fig. 2h) and Re/Ag (Fig. 2f), but which is lacking for Yb/Re (Fig. 2b), indicating a very different geochemical behavior of Re as compared to Cu, Au, and Ag. At <~3 wt.% MgO, the ratios of Yb/Re and Cu/Re increase with decreasing MgO (Fig. 2b and g), whereas the ratio of Cu/Yb decreases (Fig. 2a). These together with the decrease of Cu and Re with decreasing MgO at <~3 wt.% MgO (Fig. 1b and e) indicate that $D_{Re} > D_{Cu} > 1 > D_{Yb}$. At <~3 wt.% MgO, Yb/Ag ratio remains decreasing with decreasing MgO (Fig. 2h), indicating $D_{Yb} > D_{Ag}$. Furthermore, Au/Ag ratio also remains decreasing with decreasing MgO (Fig. 2d), indicating that $D_{Au} > D_{Ag}$. According to Figs. 1c and 2e, a relative compatibility of $D_{Au} \geq 1 > D_{Yb}$ is highly possible. At <3 wt.% MgO, D_{Yb} was constrained to be 0.29 by Park et al. (2013a). Therefore, at <~3 wt.% MgO, Yb, Cu, Au, Ag, and Re may have a bulk partition coefficient between the crystallized mineral assemblage and residual silicate melt on the order of $D_{Re} > D_{Cu} > D_{Au} \geq 1 > D_{Yb} = 0.29 > D_{Ag}$.

3. Geochemical behavior of Re in MORB

For a better understanding of the geochemical behavior of Re in MORB, I also tried examining its compatibility relative to Cu, Au, Ag, and Yb. The data used for Cu, Au, Ag, Yb, and Re in MORB were taken