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Tungsten geochemistry and implications for understanding the Earth's interior

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ABSTRACT

The concentration of tungsten (W) in basaltic melts provides a window into the behavior of this element during core–mantle separation, crust formation, silicate differentiation, and potentially core–mantle interaction. We have analyzed an extensive suite of modern basalts ($n=86$) for their trace element chemistry via laser ablation ICP-MS, with barium (Ba), thorium (Th), uranium (U), and W concentrations typically determined to ≤5% (2σ) uncertainty. We find that the partitioning behavior of U mirrors that of W during basalt genesis, whereas Ba and Th both behave more incompatibly. The W/U ratio of our complete sample suite (0.65 ± 0.45, 2σ) is representative of the mean modern mantle, and is indistinguishable from that of mid-ocean ridge basalts ($W/U_{MORB}=0.65\pm0.41$, $n=52$), ocean island basalts ($W/U_{OIB}=0.63\pm0.07$, $n=10$), and back-arc basin basalts ($W/U_{BABB}=0.62\pm0.09$, $n=12$). This ratio is also consistent with the W/U ratio of the continental crust, and thus represents the W/U ratio of the entire silicate portion of the Earth.

Assuming a concentration of 20 ± 8 (2σ) ng/g U in the bulk silicate Earth, the abundance of W in the silicate Earth is 13 ± 10 ng/g. Following mass balance, this implies a mean modern mantle and core composition of 8.3 ± 7.1 ng/g W and 500 ± 120 ng/g W, respectively. Additionally, the MORB source is modeled to contain approximately 3.0 ± 2.3 ng/g W, indicating a four-fold depletion of the highly incompatible elements in the MORB source relative to the silicate Earth.

Although both the isotopic composition of W and the constancy of the silicate Earth W/U ratio allow for potential insight into core–mantle exchange, both of these proxies are extremely dependent on the chemical composition of the source. A case study of three Hawaiian picrites with enrichments in ^{186}Os–^{187}Os but terrestrial ε_{182W} can be explained by: i) a lack of a core component in the Hawaiian "plume," ii) crustal contamination, or iii) a source composition enriched in incompatible trace elements relative to the bulk silicate Earth.

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1. Introduction

The metallic core separated from the silicate portion of the Earth some 10 to 70 million years after the formation of the solar system (e.g., Kleine et al., 2004a; Jacobsen, 2005), during which >90% of the planet's budget of tungsten (W) was sequestered into the core (Jagoutz et al., 1979; Sun, 1982; Newsom and Palme, 1984). The distribution of W, along with many other siderophile (iron-loving) elements, has been established by chemical differentiation processes that were controlled by a spectrum of pressure, temperature and oxygen fugacity conditions as the Earth has evolved (e.g., Righter, 2003 and references therein). Following core formation, however, the geochemical behavior of W in the silicate Earth has been dominantly lithophilic (silicate-loving) and highly incompatible during mantle melting and crust formation (Newsom et al., 1996 and references therein); therefore, W provides insights into both core–mantle segregation and the differentiation of the silicate Earth.

Recently, the isotopic composition of W has been used as a short-term geochronometer for dating planetary and asteroidal core formation (e.g., Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002; Kleine et al., 2004a, 2005a) and early silicate differentiation (e.g., Righter and Shearer, 2003; Kleine et al., 2004b, 2005b). Tungsten isotopic anomalies have also been implicated as a potentially robust geochemical tracer for core–mantle interactions (Scherstén et al., 2004; Brandon and Walker, 2005). However, the geochemical behavior of W in the silicate portion of the Earth is not well-constrained, largely due to its highly incompatible behavior during mantle melting and the depleted composition of mantle-derived basalts. Estimates of the abundance of W in the silicate Earth range from as low as 7 ng/g to as high as 29 ng/g (Jagoutz et al., 1979; Sun, 1982; Sims et al., 1990; McDonough and Sun, 1995; Newsom et al., 1996; Palme and O'Neill, 2003; Lyubetskaya and Korenaga, 2007). Defining the abundance and distribution of W within the Earth is imperative to: i) understand its geochemical behavior, ii) assess the usefulness of W as a tracer of geochemical processes, iii) quantitatively model the composition of the MORB (mid-ocean ridge basalt) source and any potential deep mantle reservoir, and iv) investigate putative core–mantle interactions through both W isotopes and concentration

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ratios. Here we report high-precision concentration data for Ba, Th, U, and W in an extensive suite of oceanic basalts in order to define the abundance of W in the modern mantle, bulk silicate Earth and core.

2. The abundance of W in the silicate Earth

2.1. The geochemical behavior of W

As a refractory element, the initial abundance of W in the bulk Earth can be calculated from chondritic relative abundances without a volatility correction. Estimates of W in the silicate portion of the Earth, however, are poorly constrained. Difficulties in determining the abundance of W in the silicate Earth stem from the binary behavior of the element; whereas W acts as a moderately siderophile element under reducing conditions (i.e., during core formation), it has behaved as an extremely incompatible lithophile element during the differentiation of the silicate Earth (Palme and Rammensee, 1981). Consequently, W is strongly enriched in the core and continental crust, respectively, leaving the modern mantle depleted.

In the silicate Earth, the abundances of siderophile elements that are compatible during mantle melting ($D^{\text{sil-crystal/sil-liq}}>1$; e.g., Ni and Co) are established from studies of massif peridotites and mantle xenoliths because these elements are largely retained in olivine during partial melting. However, in order to determine the silicate Earth abundances of siderophile elements that behave incompatibly during mantle melting, it is necessary to determine the abundances of these elements in both the modern mantle and continental crust. Knowledge of the composition and relative mass contributions of the mantle and crustal reservoirs allows a reconstruction of the concentration of these elements in the silicate Earth to be calculated (Newsom, 1990; Sims et al., 1990).

2.2. Incompatible element concentration ratios

The concentration of incompatible elements in basaltic melts is controlled by the concentration of these elements in the source mantle as well as a variety of fractionation processes, including partial melting, fractional crystallization and crustal contamination. Concentration ratios of similarly incompatible trace elements provide a reliable estimate of the trace element composition of the source and can complement information derived from radiogenic isotopes (Hofmann, 2003 and references therein). Concentration ratios must be used with care, however, because unlike isotope ratios they may be fractionated during processes of magma genesis. A concentration ratio that is uniform in all types of oceanic basalts (e.g., mid-ocean ridge basalts, MORB, oceanic island basalts, OIB, and back-arc basin basalts, BABB) and is independent of the absolute concentrations of the elements involved represents a mantle value that has been unfractionated by silicate differentiation. Such constant ratios (e.g., Zr/Hf, Sm/Hf, Rb/Ba, Nb/Ta, etc.) reflect element pairs with nearly identical bulk partition coefficients during the genesis of basaltic partial melts and may be inferred to be representative of their source ratios (Hofmann et al., 1986; Newsom et al., 1986; Sun and McDonough, 1989). Constant concentration ratios of highly incompatible elements are particularly likely to represent the trace element ratios of their source regions, as these elements are quantitatively removed from their source after only a few percent of partial melting (Salters and Stracke 2004).

Because W is one of the most incompatible elements during mantle melting, a concentration ratio involving W and another similarly incompatible element (e.g., W/Ba, W/Th or W/U) likely characterizes the ratio of the modern mantle if the ratio remains constant throughout a range of MORB, OIB and BABB samples. Although no other element behaves exactly like W in all geologic processes, previous work suggests that the geochemical behavior of W in silicate systems is most comparable to that of Ba, Th and U (Newsom and Palme, 1984; Newsom et al., 1986, Sims et al., 1990; Newsom et al., 1996; Noll et al., 1996).

2.3. Tungsten in the bulk continental crust

Newsom et al. (1996) estimated the abundance of W in the silicate Earth by measuring relatively constant W/Th ratios in representative samples of both the continental crust and modern mantle. In order to characterize the abundance of W in the bulk crust, they examined a comprehensive collection of samples representative of the lower, middle and upper crustal reservoirs; over 145 crustal samples were analyzed, including 18 lower crustal xenoliths, 20 rocks from high-grade metamorphic terrains, 45 samples of continental sediments, 13 rocks from oceanic volcanic arcs, 35 rocks from continental volcanic arcs, 8 continental basalts, and 7 komatiites. Their study, which established the concentration of W in the continental crust as ~1000 ng/g, still serves as the standard for examining the abundance of W in the bulk continental crust (Rudnick and Gao, 2003).

2.4. Tungsten in the modern mantle

Newsom et al. (1996) also estimated the abundance of W in the modern mantle, but they analyzed only a limited sample set of mantle-derived oceanic basalts ($n=20$) and altered mantle nodules ($n=7$) with measured reproducibilities between 10 and 30% (2σ). As opposed to mantle xenoliths, examining a broad spectrum of MORB, OIB and BABB is instrumental to constraining the abundance of W in different mantle reservoirs because oceanic basalts represent the most significant volume of terrestrial magmatism (an average rate of ~30 km^3/yr of basalt has been produced over the past 180 Myr; Crisp, 1984) and carry the smallest risk of being contaminated during magma transport (Jochum et al., 1989; Hofmann, 1997). In this study, 86 mantle-derived samples are analyzed, including 52 MORB, 16 intraplate basalts and 18 convergent margin samples. The reproducibility of our measurements (typically ≤5%, 2σ) are improved over previous studies, and the extensive compilation of mantle-derived materials considered here characterizes source regions from various depths of the mantle, a wide spatial distribution across the globe and every major tectonic setting.

3. Materials and methods

3.1. Sample descriptions

The mantle rocks analyzed in this study include both normal-type MORB (N-MORB, $K/Ti\leq 0.140$) and enriched-type MORB (E-MORB, $K/Ti>0.140$), as well as a multitude of intraplate basalts, island arc volcanics, and back-arc basin basalts. Most of the rocks are oceanic basaltic glasses or fine-grained scoria, ranging from 40 to 59 wt.% SiO_2 and 3 to 10 wt.% MgO; thus, a range of magma compositions, from primitive to differentiated, are represented by this sample set. More information regarding the diversity of these samples, including a map showing their global distribution, is provided in the accompanying Supplementary materials.

3.2. Analytical method

Compared to rocks with coarser textures, glassy and/or fine-grained samples provide comparatively homogeneous surface compositions that can be analyzed via laser ablation mass spectrometry. This in-situ method of measuring trace element concentrations produces high-precision data and has been validated through numerous analytical studies (e.g., Pearce et al., 1997; Eggins et al., 1998; Norman et al., 1998; Eggins and Shelley, 2002; Jochum et al., 2005, 2006, 2007). Laser ablation mass spectrometry also allows for: i) analyses of fresh, unaltered materials, ii) low blanks, iii) millimeter-scale sample specimens, iv) spatially resolved, ng/g-level chemical measurements, and v) surface and grain-boundary contamination to be avoided. All samples examined in this study were analyzed using a New Wave