



Titanium stable isotope investigation of magmatic processes on the Earth and Moon



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ABSTRACT

We present titanium stable isotope measurements of terrestrial magmatic samples and lunar mare basalts with the aims of constraining the composition of the lunar and terrestrial mantles and evaluating the potential of Ti stable isotopes for understanding magmatic processes. Relative to the OL-Ti isotope standard, the $\delta^{49}\text{Ti}$ values of terrestrial samples vary from -0.05 to $+0.55\%$, whereas those of lunar mare basalts vary from -0.01 to $+0.03\%$ (the precisions of the double spike Ti isotope measurements are ca. $\pm 0.02\%$ at 95% confidence). The Ti stable isotope compositions of differentiated terrestrial magmas define a well-defined positive correlation with SiO_2 content, which appears to result from the fractional crystallisation of Ti-bearing oxides with an inferred isotope fractionation factor of $\Delta^{49}\text{Ti}_{\text{oxide-melt}} = -0.23\% \times 10^6/T^2$. Primitive terrestrial basalts show no resolvable Ti isotope variations and display similar values to mantle-derived samples (peridotite and serpentinites), indicating that partial melting does not fractionate Ti stable isotopes and that the Earth's mantle has a homogeneous $\delta^{49}\text{Ti}$ composition of $+0.005 \pm 0.005$ (95% c.i., $n = 29$). Eclogites also display similar Ti stable isotope compositions, suggesting that Ti is immobile during dehydration of subducted oceanic lithosphere. Lunar basalts have variable $\delta^{49}\text{Ti}$ values; low-Ti mare basalts have $\delta^{49}\text{Ti}$ values similar to that of the bulk silicate Earth (BSE) while high-Ti lunar basalts display small enrichment in the heavy Ti isotopes. This is best interpreted in terms of source heterogeneity resulting from Ti stable isotope fractionation associated with ilmenite–melt equilibrium during the generation of the mantle source of high-Ti lunar mare basalts. The similarity in $\delta^{49}\text{Ti}$ between terrestrial samples and low-Ti lunar basalts provides strong evidence that the Earth and Moon have identical stable Ti isotope compositions.

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1. Introduction

Much of the stable isotope variation seen on Earth is mass-dependent in nature, scaling as a function of the difference in mass of the isotopes involved. Departures from such mass-dependent isotope fractionation are, however, commonplace in meteorites (Clayton, 1993; Dauphas et al., 2002) and one of the most intriguing features of the Earth–Moon system is the similarity of their mass-independent isotope signatures (e.g.: O: Clayton et al., 1973; Cr: Lugmair and Shukolyukov, 1998; Ti: Zhang et al., 2012). This similarity is difficult to reconcile with simple giant impact mod-

els that predict that most of the Moon's mass should consist of impactor material, because in this case lunar rocks should have inherited the isotope composition of the impactor, which Pahlevan and Stevenson (2007) argued should have been different from that of the Earth. Different scenarios were proposed to explain this similarity ranging from isotope equilibration between Earth's mantle and the protolunar disk (Pahlevan and Stevenson, 2007), impact of a Mars-size body with a fast-spinning Earth (Cúk and Stewart, 2012), impact between two similar-sized protoplanets (Canup, 2012), “hit-and-run” impact (Reufer et al., 2012), or an Earth-like impactor (Dauphas et al., 2014a; Mastrobuono-Battisti et al., 2015). The wide range of physical processes invoked in each of these different models highlights the need to develop new tools to evaluate the consequences of each model on the chemical and isotopic evolution of the Moon with respect to the Earth.

Interestingly, and in contrast to many mass-independent isotope systems, the *mass dependent* stable isotope compositions of a

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number of elements in terrestrial and lunar samples display significant variations (e.g.: O and Fe: Liu et al., 2010; Poitrasson et al., 2004; Weyer et al., 2005; Mg: Sedaghatpour et al., 2013; Zn: Paniello et al., 2012; Li: Seitz et al., 2006; Cl: Sharp et al., 2010; Cr: Bonnand et al., 2016). The stable isotope compositions of these elements have the potential to shed new light on the evolution of the Earth–Moon system as their variations are diagnostic features of a variety of processes such as volatile element depletion, core formation, and magma ocean crystallisation. However, many of these non-traditional stable isotope systems are affected by multiple processes, which complicate their interpretation.

Titanium has the advantage of being both lithophile and extremely refractory. It is therefore unlikely to have been affected by formation of the lunar and terrestrial cores, or volatile element depletion during the giant impact. It thus has the potential to provide unambiguous constraints on lunar magma ocean crystallisation. Despite its abundance in igneous rocks and the extensive use of TiO₂ concentrations in high-temperature geochemistry, Ti stable isotopes have received very limited attention to date (Millet and Dauphas, 2014; Zhang et al., 2014). Indeed, most of the studies so far focused on the detection of Ti isotopic anomalies to learn about nucleosynthetic processes, genetic relationships between planetary bodies, early solar system processes and/or cosmogenic effects (e.g.: Niederer et al., 1980; Niemeyer, 1988; Trinquier et al., 2009; Zhang et al., 2011, 2012). Titanium exists in several coordinations in magmatic systems: it is predominantly present in 5-fold coordination in all silicate melts but is also present in 4- and 6-fold coordinations in silicic and mafic melts respectively (Farges et al., 1996; Farges and Brown, 1997). In addition, 5-fold coordinated titanium transitions to 6-fold coordination during crystallisation of Ti-bearing oxides (Farges and Brown, 1997). As stable isotope theory (Schauble, 2004) predicts that stable isotope fractionation will be driven by major contrasts in elemental bonding environment, the coordination behaviour of Ti raises the possibility that Ti stable isotopes may serve as a tracer of magmatic processes. Furthermore, as Ti is refractory and comparably immobile in fluids, Ti stable isotopes are also likely to be comparatively resistant to overprinting. A potential complexity however, lies with the presence of Ti³⁺ in reduced magmas and planetary bodies such as the Moon. Oxygen fugacity estimates for the lunar mantle range from the iron–wüstite buffer to 2 log units below it (i.e. IW-2), with a most likely value of ~IW-1 (Wadhwa, 2008). Experimental work has shown that in these conditions, the lunar mantle could contain up to 10% Ti³⁺ (Krawczynski et al., 2009). However, direct measurements of Ti³⁺/ΣTi (Simon et al., 2014) in pyroxenes and olivines from lunar basalts have not detected any Ti³⁺.

In this contribution, high precision Ti stable isotope measurements are presented for a range of terrestrial and lunar magmatic rocks with three aims. The objectives of this contribution are to (i) evaluate the effect of fractional crystallisation and magma differentiation on the Ti stable isotope composition of silicate melts; (ii) determine the Ti stable isotope composition of the terrestrial mantle and assess its homogeneity and (iii), use the Ti stable isotope composition of lunar basalts to investigate the magmatic evolution of the Moon.

2. Samples and methods

2.1. Samples

In addition to the dataset already presented in Millet and Dauphas (2014), we have analysed 36 terrestrial samples reflecting a global coverage from a diverse range of geodynamic contexts. We have also analysed 9 primitive lunar basalts covering the range of TiO₂ concentrations observed in lunar rocks.

Mid-Ocean Ridge Basalts (MORB). Seven MORB samples were analysed in order to constrain the composition of the upper mantle. The sample suite includes glasses from the mid-Atlantic ridge, the East-Pacific Rise (Batiza and Niu, 1992), the Pacific–Cocos–Nazca triple junction (Puchelt and Emmermann, 1983) as well as the South–West Indian Ridge (Escrig et al., 2004), including a single MORB sample displaying Sr, Pb and Os isotope compositions characteristic of the Dupal anomaly (MD57 9-1).

Island arc basalts. The island arc basalts studied here mainly comprise basalts sampled from oceanic arcs in order to limit the potential for crustal contamination and assimilation processes. In addition to the New Britain basalt data published by Millet and Dauphas (2014), 3 arc lavas from the Mariana arc were studied that were previously analysed for major and trace elements by Yi et al. (2000). A single basalt from the Izu–Bonin arc, rock standard JB-2, was also analysed.

Intraplate basalts. The intraplate basalts mainly comprise ocean island basalts (OIBs) from four different localities. Single samples from Hawaii (BHVO-2 rock standard) and Easter Island (sample 17678, Baker et al., 1974) were analysed as well as samples from the Cape Verde (São Nicolau island; Millet et al., 2008) and Azores archipelagos (São Miguel island: Turner et al., 1997; São Jorge island: Millet et al., 2009). In addition, a single continental flood basalt (the USGS rock standard BCR-2) was also analysed.

Eclogites. The three eclogites measured here were collected from the Zermatt-Saas Fee ophiolite, Switzerland. They consist of 2 basaltic eclogites and 1 gabbroic eclogite, based on their mineralogy (Dale et al., 2007). Estimates of peak metamorphic conditions for these samples range between 2 and 3 GPa and from 550 to 630 °C (Barnicoat and Fry, 1986; Reinecke, 1991). Major and trace element data (Dale et al., 2007) show that all the samples selected suffered loss of volatile and fluid-mobile elements during metamorphic dehydration.

Mantle samples. The mantle-derived samples are of two types. First, a single orogenic peridotite from the Beni Bousera massif was analyzed (GP13, Pearson et al., 2004). The other 3 mantle-derived samples are serpentinites from various Western Alps ophiolites. These samples originate from the lithospheric mantle section of a subducted slab and have been chosen because they record different metamorphic conditions during subduction. These have partly (BCh9, MM15) to fully (LZ14b) re-equilibrated in the antigorite (high temperature and pressure variety of serpentine) stability field during subduction (see Debret et al., 2014 for details).

Differentiated magmas. In order to assess the effect of magmatic differentiation, rock standards of varying SiO₂ content (AGV-1 andesite: 58.8 wt%, G-2 granite: 69.1 wt%, RGM-1 rhyolite: 73.4 wt%) and a basaltic andesite from São Miguel Island (54.5 wt% SiO₂, Azores archipelago) were analysed. Although not cogenetic, these samples span almost the full range of silica content observed in terrestrial rocks and show a continuous decrease in TiO₂ content with increasing SiO₂. To complement this sample set, 6 cogenetic samples from Agung volcano (Bali, Indonesia) related to each other by fractional crystallisation were analysed. The SiO₂ concentration of these samples ranges from 54 to ca. 63 wt% and TiO₂ shows a continuous decrease from 0.92 to 0.60 wt% over that range (Dempsey, 2012).

Lunar samples. Nine lunar samples were analysed. Specifically, we selected 5 high-Ti basalts (TiO₂ ranging from 12.2 to 13.4 wt%) and 3 low-Ti basalts (TiO₂ ranging from 1.9 to 3.3 wt%). A single green glass sample was also analysed (sample 15426, TiO₂ = 0.5 wt%).

2.2. Methods

Samples were processed and measured using the double-spike method of Millet and Dauphas (2014), which is briefly outlined

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