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Titanium stable isotopic variations in chondrites, achondrites and lunar rocks

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Abstract

Titanium isotopes are potential tracers of processes of evaporation/condensation in the solar nebula and magmatic differentiation in planetary bodies. To gain new insights into the processes that control Ti isotopic variations in planetary materials, 25 komatiites, 15 chondrites, 11 HED-clan meteorites, 5 angrites, 6 aubrites, a martian shergottite, and a KREEP-rich impact melt breccia have been analyzed for their mass-dependent Ti isotopic compositions, presented using the δ^{49}Ti notation (deviation in permil of the ^{49}Ti/^{47}Ti ratio relative to the OL-Ti standard). No significant variation in δ^{49}Ti is found among ordinary, enstatite, and carbonaceous chondrites, and the average chondritic δ^{49}Ti value of $+0.004 \pm 0.010$‰ is in excellent agreement with the published estimate for the bulk silicate Earth, the Moon, Mars, and the HED and angrite parent-bodies. The average δ^{49}Ti value of komatiites of -0.001 ± 0.019‰ is also identical to that of the bulk silicate Earth and chondrites. OL-Ti has a Ti isotopic composition that is indistinguishable from chondrites and is therefore a suitable material for reporting δ^{49}Ti values. Previously published isotope data on another highly refractory element, Ca, show measurable variations among chondrites. The decoupling between Ca and Ti isotope systematics most likely occurred during condensation in the solar nebula.

Aubrites exhibit significant variations in δ^{49}Ti, from -0.07 to $+0.24$‰. This is likely due to the uniquely reducing conditions under which the aubrite parent-body differentiated, allowing chalcophile Ti^{3+} and lithophile Ti^{4+} to co-exist. Consequently, the observed negative correlation between δ^{49}Ti values and MgO concentrations among aubrites is interpreted to be the result of isotope fractionation driven by the different oxidation states of Ti in this environment, such that isotopically heavy Ti^{4+} was concentrated in the residual liquid during magmatic differentiation.

Finally, KREEPy impact melt breccia SaU 169 exhibits a heavy δ^{49}Ti value of $+0.330 \pm 0.034$‰ which is interpreted to result from Ti isotopic fractionation during ilmenite precipitation in the late stages of lunar magma ocean crystallization. A Rayleigh distillation calculation predicts that a δ^{49}Ti value of $+0.330$‰ is achieved after removal of 94% of Ti in ilmenite.
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Keywords: Stable isotopes; Titanium; Bulk silicate Earth; Chondrite; Komatiite; HED; Angrite; Aubrite; Moon; Mars; Magma differentiation

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1. INTRODUCTION

In recent years, a growing number of non-traditional stable isotope systems have been used to study the evolution of the Earth and other solar system bodies (Teng et al., 2017). With advances in analytical techniques, non-traditional stable isotopes have seen increasing application to investigate high-temperature processes, such as magmatic differentiation, core formation, and early solar nebula evaporation and condensation. Titanium is a refractory and fluid immobile element, whose isotopic variations have seldom been measured.

The existence of mass-dependent Ti isotope fractionation in Ca-Al-rich inclusions (CAIs) had been detected by Niederer et al. (1985), who reported a shift towards heavier Ti isotopic compositions of CAIs compared to their host meteorite. More recent studies investigating CAIs of the Allende meteorite reported variations in the δ^{49}Ti value (part per mil deviation of the ^{49}Ti/^{47}Ti ratio in a sample from that of the OL-Ti standard) ranging from −4.0 to +4.0‰ (Zhang, 2012; Davis et al., 2016). This is most likely the result of kinetically driven isotope fractionation during condensation and evaporation processes.

Terrestrial rocks exhibit somewhat smaller variations in their Ti isotopic composition, with δ^{49}Ti values ranging between −0.07 and +0.55‰ (Millet and Dauphas, 2014; Millet et al., 2016). These variations are still significant, however, as the measurement precision achieved on δ^{49}Ti is better than ±0.03‰ (Millet and Dauphas, 2014). Titanium isotopes show little variation in mafic and ultramafic igneous rocks. Millet et al. (2016) used such rocks to estimate the Ti isotopic composition of the bulk Earth relative to the OL-Ti standard to be +0.005 ± 0.005‰ (95% c.i., n = 30). More evolved crustal rocks are enriched in heavy Ti isotopes and δ^{49}Ti correlates well with the SiO_2 concentration (Millet et al., 2016). This systematic shift towards heavier isotopic compositions has been interpreted to result from preferential incorporation of light Ti in Fe-Ti oxides during fractional crystallization, leaving behind a melt that is enriched in heavy Ti isotopes.

Previous work has revealed variations in the stable isotopic composition of Ca among bulk chondrites, demonstrating that refractory elements can be fractionated isotopically by nebular processes. Documenting whether such variations also exist for Ti is important to assess whether the bulk silicate Earth has the same isotopic composition as chondrites, and evaluate possible genetic relationships between the Earth and meteorites.

Titanium isotopes can also be used to constrain the igneous history of differentiated planetesimals. For example, Millet et al. (2016) reported small variations in the Ti isotopic composition of low-Ti and high-Ti lunar mare basalts, whereby the latter have a heavier δ^{49}Ti value. It is generally thought that ilmenite cumulates in the lunar mantle are involved in the production of high-Ti lunar mare basalts. Taking Ti isotope variation in evolved terrestrial silicic rocks as a guide, ilmenite is expected to have a light Ti isotopic composition relative to the melt. To explain the heavy δ^{49}Ti value in high-Ti mare basalts, Millet et al. (2016) argued that they were likely sourced from mantle regions fertilized by negatively buoyant partial melts of ilmenite cumulates or that ilmenite was not exhausted during the melting process. In both cases, high-Ti lunar mare basalt melt would have become enriched in heavy Ti isotopes by equilibrating with isotopically light ilmenite. The model proposed by Millet et al. (2016) for the Ti isotope evolution during the lunar magma ocean predicts that the residual liquid after ilmenite crystallization would be strongly enriched in heavy Ti isotopes. Accordingly, KREEP-rich lunar samples, rocks highly enriched in incompatible trace elements and thought to represent left-over melt after major ilmenite crystallization in the lunar magma ocean (e.g., Warren and Wasson, 1979), are expected to have a heavy Ti isotope signature.

The main objectives of the present study are to (1) determine the Ti isotopic composition of the major groups of chondrites and (2) analyze the Ti isotopic composition of a comprehensive set of terrestrial komatiites, howardite-eucrite-diogenite (HED) meteorites, aubrites, angrites, a martian shergottite and a lunar KREEP-rich impact melt breccia to constrain the igneous history of these planetary objects.

2. SAMPLES

2.1. Komatiites

Komatiites are high-MgO volcanic rocks formed via high degrees of partial melting (*i.e.*, between 30 and 50%; Arndt et al., 1977) of the mantle. This type of melting regime commonly leads to almost complete removal of incompatible elements, such as Ti, from the source into the melt. Komatiites are therefore well suited to characterize the isotopic composition of the mantle and have been used previously for that purpose in studies of Mg, Fe, Mo, Ga and Ni isotope systematics (Dauphas et al., 2010; Greber et al., 2015; Gall et al., 2016; Kato et al., 2016). The samples studied are komatiites from the 3.55 Ga Schapenburg Greenstone Remnant (6 samples), the 3.48 Ga Komati (5) and the 3.26 Ga Weltevreden (6) Formations of the Barberton Greenstone Belt, the 2.72 Ga Alexo locality in the Abitibi Greenstone Belt (4) and the 2.7 Ga Reliance Formation of the Belingwe Greenstone Belt (5). Details of the petrology and geochemistry of the samples studied can be found in Puchtel et al. (2013) and Puchtel et al. (2014) for the Komati and Weltevreden systems, in Puchtel et al. (2016) for the Schapenburg system, in Puchtel et al. (2009) for the Belingwe samples and in Lahaye and Arndt (1996) and Dauphas et al. (2010) for the Alexo system.

2.2. Meteorites

Titanium isotopic compositions were measured in 15 chondrites, 11 achondrites from the howardite-eucrite-diogenite (HED) clan, 6 aubrites, 5 angrites, a martian shergottite, and one lunar KREEP meteorite sample. The analyzed chondrites include meteorites from the H (Ste Marguerite, Queen‘s Mercy, Pultusk), L (Bald Mountain, Farmington), LL (Kelly, Dhurmsala, Chelyabinsk), EH

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