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 δ49Ti notation (deviation in permil of the 49Ti/47Ti ratio relative to the OL-Ti standard). No significant variation in δ49Ti is found among ordinary, enstatite, and carbonaceous chondrites, and the average chondritic δ49Ti value of +0.004 ± 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 δ49Ti value of komatiites of /C0 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 δ49Ti 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 δ49Ti, from −0.07 to +0.24‰. This is likely due to the uniquely reducing conditions under which the aubrite parent-body differentiated, allowing chalcophile Ti3+ and lithophile Ti4+ to co-exist. Consequently, the observed negative correlation between δ49Ti 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 Ti4+ was concentrated in the residual liquid during magmatic differentiation.

Finally, KREEPy impact melt breccia SaU 169 exhibits a heavy δ49Ti value of +0.330 ± 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 δ49Ti value of +0.330‰ is achieved after removal of 94% of Ti in ilmenite.

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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 δ49Ti value (part per mil deviation of the 49Ti/47Ti 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 δ49Ti 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 δ49Ti 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 δ49Ti correlates well with the SiO2 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 δ49Ti 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 δ49Ti 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, Chelabinsk), EH
(Sahara 97072), EL (Blithfield, Pilistfer), CO (Lancé), CM (Murray), CI (Orgueil) and CV (Allende) groups. All chondrites, except Kelly, Sahara 97072 and Blithfield, are observed falls. The Allende sample is a powder aliquot from the Smithsonian Allende standard (4 kg of homogenized and milled sample material, see Jarosewich et al. (1987)), which should provide a good estimate of the composition of Allende unaffected by nugget effects associated with the presence of large CAIs (Davis et al., 2016).

The HED-clan meteorites represent the best crustal samples from a differentiated asteroid; most likely Vesta (Consolmagno and Drake, 1977). They sampled lower crustal rocks (diogenites), gabbroic rocks formed within the crust (cumulate eucrites), shallow level rocks such as sills and lava flows (basaltic eucrites) and brecias consisting of a mixture of eucrite and diogenite (howardites) (e.g., Mandler and Elkins-Tanton, 2013; Mittlefehldt, 2015). We analyzed two diogenites (Johnstown, Tatabouine), one howardite (Kapota), two cumulate eucrites (Serra de Magé, Nagaria) and six basaltic eucrites for their Ti isotopic compositions. Except for Camel Donga, all HED-meteorites are falls. Basaltic eucrites can be further subdivided into three groups based on their chemical compositions. Using the terminology of Mittlefehldt (2015), the samples studied cover all three basaltic eucrite subgroups, namely, the Stannern-group (Stannern), the Nuevo-Laredo group (Lakangaon), and the main-group (Millbillilie, Camel Donga, Juvinas). Ibitira is an unusual eucrite, as it has a distinct oxygen isotopic composition (Wiechert et al., 2004), alkali element content and Ti/HF ratio (Mittlefehldt, 2005) compared to other HED meteorites. It plots, however, together with other HEDs in the $^{53}$Mn-$^{53}$Cr (Lugmair and Shukolyukov, 1998; Trinquier et al., 2008) and $^{60}$Fe-$^{60}$Ni (Tang and Dauphas, 2012) isochron diagrams. It is thus unclear whether this sample comes from a distinct parent-body than other HEDs (Wiechert et al., 2004; Mittlefehldt, 2005) or a mantle reservoir in Vesta that was never fully homogenized with the rest of the mantle (Dauphas and Schauble, 2016).

Angrites are uncommon achondrites as they are enriched in refractory elements, such as Ca and Ti and depleted in volatile elements such as Na, K or Rb (Keil, 2012). Based on their texture and mineralogy, they are divided into slowly cooled plutonic and rapidly cooled volcanic angrites. They consist mainly of anorthite, calcic olivine and Al-Ti bearing pyroxenes and contain as accessory minerals, (i) it affords complete dissolution of refractory accessory minerals, (ii) it avoids the creation of insoluble Ti-bearing fluoride that may cause mass-dependent Ti isotope fractionation, (iii) glass pellets are digested in HNO$_3$ avoiding the use of HF and HClO$_4$ and (iv) boron in the flux prevents fluorine in lab fumes to complex with Ti and, thus, ensures that Ti partitioning behavior on the ion-exchange chromatography columns is as expected. The flux fusion technique applied followed the protocol described in Pourmand et al. (2012), with some modifications. Sample powder and LiBO$_2$ were mixed in the proportions 1:6 and transferred to high purity graphite crucibles. Around 20 mg of a high-purity LiBr non-wetting solution was added per 100 mg of sample-flux mixture. The sample-flux mixture was subsequently fused in a furnace at 1100 °C for approximately 10 min. After the charge cooled, it was removed from the graphite crucible with tweezers and broken into pieces in a mortar. Afterwards, clean glass pellet pieces were separated by hand from those that were contaminated with graphite from the graphite crucible. Several millimeter-size basaltic shergottite, found in Morocco in 2016. Abundant secondary calcium indicates that NWA 11115 suffered from terrestrial alteration (Daswani et al., 2017).

The lunar KREEP sample analyzed for $\delta^{49}$Ti is an aliquot of the matrix of the impact melt breccia of meteorite Sayh al Uhaymir (SaU) 169. KREEP is an acronym for lunar material that is highly enriched in K,REE, P and other incompatible trace elements (Warren and Wasson, 1979). SaU 169 is the sample that shows the strongest enrichment in KREEP components known to date and was formed by impact melting of pre-existing KREEP-materials at 3.9 Ga (Gnos et al., 2004; Korotev, 2005; Lin et al., 2012). The mineralogy of the melt breccia matrix is dominated by Ca-poor pyroxene, plagioclase and ilmenite with accessory zircon and phosphates.

### 3. METHODS

All the meteorite and Alexo komatite sample powders were produced using agate mortar and pestle. Details of the sample preparation techniques for the Schapenburg, Komati, Belingwe and Weltevreden komatiites are reported in Puchtel et al. (2009, 2013, 2016). In contrast to previous studies that analyzed Ti isotopes by MC-ICP-MS (e.g. Leya et al., 2008; Trinquier et al., 2009; Zhang et al., 2011; Millet and Dauphas, 2014; Williams, 2014), samples for this work have been digested using alkali flux fusion. Alkali flux fusion with lithium metaborate (LiBO$_2$) is advantageous as (i) it affords complete dissolution of refractory accessory minerals, (ii) it avoids the formation of insoluble Ti-bearing fluoride that may cause mass-dependent Ti isotope fractionation, (iii) glass pellets are digested in HNO$_3$ avoiding the use of HF and HClO$_4$ and (iv) boron in the flux prevents fluorine in lab fumes to complex with Ti and, thus, ensures that Ti partitioning behavior on the ion-exchange chromatography columns is as expected. The flux fusion technique applied followed the protocol described in Pourmand et al. (2012), with some modifications. Sample powder and LiBO$_2$ were mixed in the proportions 1:6 and transferred to high purity graphite crucibles. Around 20 mg of a high-purity LiBr non-wetting solution was added per 100 mg of sample-flux mixture. The sample-flux mixture was subsequently fused in a furnace at 1100 °C for approximately 10 min. After the charge cooled, it was removed from the graphite crucible with tweezers and broken into pieces in a mortar. Afterwards, clean glass pellet pieces were separated by hand from those that were contaminated with graphite from the graphite crucible. Several millimeter-size
clean glass fragments containing more than ~2 μg total Ti were transferred to Savillex PFA beakers, spiked with a 48Ti-45Ti double spike and digested in 10 mL of 3 M HNO3 on a hot plate set at 130 °C, with repeated treatment in an ultrasonic bath. The amount of double-spike added was calculated based on the known sample Ti concentration and mass, and the fragment mass. For some low-Ti aubrites, the total Ti in the fragment was around 1 μg. The sample solution was subsequently evaporated and redigested at 150 °C in 12 M HNO3. Titanium was purified following the two-step ion-exchange chromatography protocol outlined in Millet and Dauphas (2014) and Zhang et al. (2011). During the first step, Ti was separated from the matrix on a 2 mL Eichrom TODGA column, and during the second step, the Ti fraction was purified using a 0.8 mL AG1-X8 Bio-Rad column. The second step is primarily used to remove molybdenum, whose doubly charged ions can interfere with Ti isotopes (Zhang et al., 2011). The second step was repeated twice. In each batch of ~15 samples, at least one USGS standard reference material, such as G3, BIR-1a or BHVO-2, was added as control that the measurements were accurate.

Blank levels were evaluated by measuring the Ti concentration by isotope dilution of fluxed LiBO2 that was subsequently treated in a similar manner as the samples. As the LiBO2 flux is the predominant blank source, the blank contribution to the sample is defined by the flux to sample ratio, i.e. 6.1. For 45 samples of melted and processed flux, which is higher than the amount of pellet sample aliquot used, the blank Ti amount is 18 ng, which is <0.5% of the total Ti present in the samples, except for some low-Ti aubrites (i.e. Shallowater, Cumberland Falls and Penã Blanca Spring), where the total analytical blank contribution was up to 2%.

The Ti isotopic composition was analyzed using a Neptune MC-ICP-MS at the University of Chicago, measuring simultaneously Ti isotopes at masses 46, 47, 48, 49, and 50, as well as 44Ca for correction of the interferences from 46Ca and 48Ca on 46Ti and 44Ti, respectively. Several of the analyzed isotopes suffer from polyatomic interferences: 44Ca (14N16O, 28Si16O), 46Ti (30Si16O), and 48Ti (36Ar14N). The measurements were therefore performed in high-resolution mode on the peak shoulder at a mass below the 38Ar14N interference on 50Ti, thus avoiding polyatomic interferences. The 44Ca and 46Ca interferences were corrected for each cycle using the exponential mass fractionation law,

\[ \delta^{48}\text{Ti}(%) = \left( \frac{48\text{Ti}_{\text{Sample}}}{48\text{Ti}_{\text{OL-Ti}}} \right) - 1 \times 1000. \]

Isotope mass fractionation during Ti purification and ICP-MS measurements was monitored and corrected for using the double-spike technique. Titanium-50 was not used in the double spike data reduction, as it suffers from 44Cr and 48V interferences and is also affected by the largest mass-independent Ti isotope anomalies (Leya et al., 2008; Trinquier et al., 2009; Zhang et al., 2012). Details of the 47Ti-48Ti double spike and the OL-Ti calibration and instrument setup are described in Millet and Dauphas (2014). Briefly, samples and standards were measured in 0.3 M HNO3+0.005 M HF and introduced into the mass spectrometer using an Apex HF or an Aridus I desolvating nebulizer system. The Ti isotopic compositions and measurement precisions are identical for the two introduction systems used. Each sample measurement was bracketed by measurements of the standards with 48Ti concentrations matched to within ±10%. After a block of six to eight samples, a clean solution, prepared from the same batches of acids used for preparing the standard and sample solutions, was measured and used for on-peak zero baseline correction.

The uncertainty on the Ti isotopic compositions has been evaluated according to Dauphas et al. (2009) and encompasses within-session as well as long term external reproducibility. The uncertainty is assumed to be the combination of the internal error (\(\sigma_{\text{MassSpec}}\); commonly around ±0.008‰), corresponding to repeated measurements of a single Ti solution and unknown errors (\(\sigma_{\text{Unknown}}\)), for example isotopic fractionation prior to spike-sample equilibration. The value of \(\sigma_{\text{Unknown}}\) was assessed by examining the long-term external reproducibility (±0.013‰; from rock digestion to isotopic analysis) of three different geostandards (G3, BHVO-2 and BIR-1a). The total uncertainty of a measurement is then defined as

\[ \epsilon_{\text{Data}} = 2 \cdot \sqrt{\sigma^2_{\text{Unknown}} + \sigma^2_{\text{MassSpec}}} \text{ with } \epsilon_{\text{Data}} \text{ being the 95% c.i.} \] (Dauphas et al., 2009).

Extraterrestrial samples suffer from isotopic anomalies on 46Ti and 48Ti so that one must correct for these anomalies to obtain purely mass-dependent Ti isotope variations. This correction is further explained in section 3.2; as a result of the corrections, the uncertainty on the \(\delta^{48}\text{Ti}\) for extraterrestrial samples is estimated to increase up to ±0.042‰.

3.1. Test of the accuracy

One potential difficulty of using flux fusion samples to analyze Ti isotopes is that Li could theoretically cause ArLi molecular interferences on masses 48Ti and 47Ti. Even though mass scans over the masses of Li of samples and blanks were identical and did not indicate the presence of Li, several tests were performed to check if the newly developed digestion technique resulted in accurate isotopic compositions.
(i) As a first test, BIR-1a and BHVO-2, as well as four komatiite samples, were prepared following the methodology (i.e., conventional acid attack digestion) described in Millet and Dauphas (2014) (labeled with the suffix “acid”, as in “BIR-1a acid” in Appendix Table B.1). The total Ti blank for the acid attack method was \(< 10 \text{ ng} \). 

(ii) The second test used Ti-free matrix cuts of the first-step of column chemistry of three fluxed samples (M712, BV05 and 501-2) mixed with spiked standards (labeled with the suffix “Matrix doped”, as in M712 Matrix doped in appendix Table B.1). 

(iii) The third test used pure fluxed LiBO\(_2\) mixed with double spiked OL-Ti standard (Flux Blank doped). 

(iv) The fourth test was conducted by adding the Ti double-spike to the sample powder-flux mixture of ordinary chondrite sample Chelyabinsk prior to flux fusion (for other samples, the double-spike is added when a fragment of the solidified flux-sample melt is digested).

The Ti isotopic compositions of the four tests are shown in Table 1 and Appendix Table B.1. The first test resulted in identical \(\delta^{49}\text{Ti}\) values, independent of the digestion technique applied. In addition, BIR-1a and BHVO-2 have the same Ti isotopic compositions as those reported in Millet and Dauphas (2014). The matrix cuts and pure LiBO\(_2\) samples mixed with spiked standard from tests (ii) and (iii) exhibit, as expected, a \(\delta^{49}\text{Ti}\) value that is within error of 0‰. The fourth test (iv) gave an identical \(\delta^{49}\text{Ti}\) value for the two aliquots of Chelyabinsk, irrespective of when the Ti double-spike was added. Thus, the performed tests indicate that the change in the analytical technique involving flux fusion rather than acid digestion yields accurate Ti isotopic data.

To evaluate the accuracy and effectiveness of our correction of Ca isotope interference on \(^{46}\text{Ti}\) and \(^{48}\text{Ti}\), Ca doping tests were performed, where different amounts of Ca were added to the spiked OL-Ti standard. The percent of Ca relative to Ti ranged from 3% to 21% (Fig. 1 and appendix Table B.2). As evident from Fig. 1, if no Ca correction is applied, the Ti isotopic composition increases linearly with the Ca/Ti ratio, reaching a \(\delta^{49}\text{Ti}\) value of \(+0.6\text{%e} \) at 20% Ca contamination. However, when the Ca correction is applied, samples with \(<10\% \text{Ca}\) do not show any significant departure from the standard value (i.e., 0‰). At around 20% Ca contamination, the \(\delta^{49}\text{Ti}\) value increases just slightly outside our measurement precision of \(\pm0.03\text{%e} \). Most samples measured contained less than 1% Ca and no sample had more than 5% Ca. Thus, we conclude that any Ca interference present was adequately corrected for.

An additional test was performed to determine the efficiency with which Ti was purified during each of the different ion-exchange chromatography steps. From each of the three reference materials BHVO-2, BIR-1a and G3, an aliquot of the sample solution was taken after each ion-exchange chromatography step, named cut1, cut2 and cut3. For all three reference materials, the \(\delta^{49}\text{Ti}\) value obtained for different cuts were identical within uncertainty, meaning that the level of purity of the final solutions exceeded the requirements to achieve accurate Ti isotopic measurements.

Table 1
Titanium isotopic compositions of chondrites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Group</th>
<th>(\delta^{46}\text{Ti})</th>
<th>95% c.i.</th>
<th>(\delta^{48}\text{Ti})</th>
<th>95% c.i.</th>
<th>(\delta^{49}\text{Ti}*) (%)</th>
<th>(\delta^{49}\text{Ti}^\text{a}) (%)</th>
<th>95% c.i.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ste Marguerite</td>
<td>H4</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>0.029</td>
<td>0.022</td>
<td>0.033</td>
<td>4</td>
</tr>
<tr>
<td>Queen’s Mercy</td>
<td>H6</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>0.002</td>
<td>-0.005</td>
<td>0.033</td>
<td>4</td>
</tr>
<tr>
<td>Pultrusk</td>
<td>H5</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>-0.008</td>
<td>-0.015</td>
<td>0.033</td>
<td>4</td>
</tr>
<tr>
<td>Bald Mountain</td>
<td>L4</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>-0.020</td>
<td>-0.027</td>
<td>0.033</td>
<td>4</td>
</tr>
<tr>
<td>Farmington</td>
<td>L5</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>0.012</td>
<td>0.005</td>
<td>0.033</td>
<td>4</td>
</tr>
<tr>
<td>Kelly</td>
<td>LL4</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>0.014</td>
<td>0.007</td>
<td>0.033</td>
<td>4</td>
</tr>
<tr>
<td>Dhurmsala</td>
<td>LL6</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>0.021</td>
<td>0.014</td>
<td>0.033</td>
<td>4</td>
</tr>
<tr>
<td>Chelyabinsk</td>
<td>LL5</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>0.018</td>
<td>0.011</td>
<td>0.033</td>
<td>4</td>
</tr>
<tr>
<td>Chelyabinsk*</td>
<td>LL5</td>
<td>-0.08</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.12</td>
<td>0.022</td>
<td>0.015</td>
<td>0.037</td>
<td>4</td>
</tr>
<tr>
<td>Sahara 97072</td>
<td>EH3</td>
<td>0.01</td>
<td>0.02</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.023</td>
<td>0.026</td>
<td>0.034</td>
<td>4</td>
</tr>
<tr>
<td>Blithfield</td>
<td>EL6</td>
<td>0.01</td>
<td>0.02</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.024</td>
<td>0.027</td>
<td>0.034</td>
<td>4</td>
</tr>
<tr>
<td>Pillistfer</td>
<td>EL6</td>
<td>0.01</td>
<td>0.02</td>
<td>-0.02</td>
<td>0.06</td>
<td>-0.022</td>
<td>-0.019</td>
<td>0.034</td>
<td>4</td>
</tr>
<tr>
<td>Lancé</td>
<td>CO</td>
<td>0.61</td>
<td>0.05</td>
<td>-0.07</td>
<td>0.16</td>
<td>-0.075</td>
<td>0.002</td>
<td>0.036</td>
<td>4</td>
</tr>
<tr>
<td>Murray</td>
<td>CM</td>
<td>0.56</td>
<td>0.05</td>
<td>-0.08</td>
<td>0.16</td>
<td>-0.075</td>
<td>-0.002</td>
<td>0.036</td>
<td>4</td>
</tr>
<tr>
<td>Orgueil</td>
<td>CI</td>
<td>0.35</td>
<td>0.04</td>
<td>0.00</td>
<td>0.15</td>
<td>-0.032</td>
<td>0.009</td>
<td>0.034</td>
<td>4</td>
</tr>
<tr>
<td>Allende</td>
<td>CV</td>
<td>0.72</td>
<td>0.02</td>
<td>0.02</td>
<td>0.08</td>
<td>-0.028</td>
<td>0.052</td>
<td>0.032</td>
<td>4</td>
</tr>
</tbody>
</table>

Average (excluding Allende):

\(\delta^{49}\text{Ti}^\text{a}\) = Ti isotopic composition prior to correction for isotopic anomalies on \(^{46}\text{Ti}\) and \(^{48}\text{Ti}\).

\(\delta^{49}\text{Ti}\) and \(\delta^{49}\text{Ti}\) isotope anomalies from Zhang et al. (2012)

95% c.i. = 95% confidence interval.

n is the number of repeat measurements of the purified Ti solution.

Sample spiked prior to flux fusion.
unknowns; topic mass fractionation. This equation has three ratio constant to correct for natural and lab-induced iso-
e masses of isotopes $i$.

We can make on solutions that contain up to 20% Ca, while the samples measured in this study have Ca at a level of less than 5%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 3.2. Data reduction and correction for Ti isotope anomalies

The Ti isotope data reduction was done in Mathematica following the method outlined in Millet and Dauphas (2014) and Tissot and Dauphas (2015). A complication arises with meteorites in that some isotopes are affected by the presence of nucleosynthetic anomalies. When no such anomalies are present, the ratio in the sample is assumed to be related to that of a standard by the laws of mass-dependent fractionation (an exponential law is often assumed), so we have $R_{\text{sample}} = R_{\text{Standard}} \cdot \left( \frac{m_i}{m_j} \right)^\beta$. If isotopic anomalies are present (noted $\epsilon_i^{\text{measured}}$), this assumption is not warranted and the formula is modified accordingly (see Appendix A for details),

$$
R_{\text{measured}}^{i/j} = \left[ p \cdot R_{\text{spike}}^{i/j} + (1 - p) \cdot R_{\text{standard}}^{i/j} \cdot \left( \frac{m_i}{m_j} \right)^\beta \cdot \epsilon_i^{\text{measured}} / 10^6 \right],
$$

where $R_{\text{measured}}^{i/j}$, $R_{\text{spike}}^{i/j}$, and $R_{\text{standard}}^{i/j}$ are the ratios of the measured sample, the standard and spike; $m_i$ and $m_j$ are the masses of isotopes $i$ and $j$ and, $p$ is the proportion of isotope $j$ in the sample-spike mixture, $\beta$ is the extent of natural mass fractionation, and $\epsilon_i^{\text{measured}}$ denotes isotopic anomalies (departure in part per 10,000 relative to terrestrial composition) measured by internal normalization by fixing the $^{46}$Ti/$^{48}$Ti ratio constant to correct for natural and lab-induced isotopic mass fractionation. This equation has three unknowns; $p$, $\beta$, and $\epsilon$. To solve it, three independent equa-
tions are written using the three isotopic ratios $^{46}$Ti/$^{48}$Ti, $^{48}$Ti/$^{50}$Ti and $^{46}$Ti/$^{47}$Ti.

Average $\epsilon^{46}$Ti and $\epsilon^{48}$Ti data published in Trinquier et al. (2009) and Zhang et al. (2012) were used for correcting the mass-dependent Ti isotopic compositions of ordinary chondrites ($\epsilon^{46}$Ti = $-0.08 \pm 0.01$; $\epsilon^{48}$Ti = $-0.02 \pm 0.12$), enstatite chondrites ($\epsilon^{46}$Ti = $0.01 \pm 0.02$; $\epsilon^{48}$Ti = $-0.02 \pm 0.06$), HED meteorites ($\epsilon^{46}$Ti = $-0.22 \pm 0.03$; $\epsilon^{48}$Ti = $-0.05 \pm 0.06$), angrites ($\epsilon^{46}$Ti = $-0.21 \pm 0.04$; $\epsilon^{48}$Ti = $0.06 \pm 0.20$),aubrites ($\epsilon^{46}$Ti = $0.01 \pm 0.03$; $\epsilon^{48}$Ti = $-0.05 \pm 0.16$) and martian shergottite NWA 1115 ($\epsilon^{46}$Ti = $-0.17 \pm 0.04$; $\epsilon^{48}$Ti = $-0.07 \pm 0.07$), while individual meteorite $\epsilon^{46}$Ti and $\epsilon^{48}$Ti data were used for correcting $\delta^{49}$Ti of carbonaceous chondrites. The Moon and aubrite parent-body have the same $\epsilon^{46}$Ti and $\epsilon^{48}$Ti as the Earth (Zhang et al., 2012). Aubrites and lunar soil samples can have high exposure ages and thus, the Ti isotopic composition might be affected by cosmogenic effects. The impact on $\epsilon^{46}$Ti and $\epsilon^{48}$Ti due to cosmogenic effects is, however, 2–4 times lower than for $\epsilon^{46}$Ti and $\epsilon^{48}$Ti, and both, aubrites and lunar meteorites have identical or almost identical $\epsilon^{46}$Ti, $\epsilon^{48}$Ti and $\epsilon^{46}$Ti as the Earth (see appendix of Zhang et al., 2012). Because we do not use $\delta^{48}$Ti in our double spike reduction, the impact on the mass-dependent Ti isotopic composition of cosmogenic effects for these meteorite groups is insignificant given the current measurement precision.

The additional error on the $\delta^{49}$Ti value arising from the correction of isotope anomalies was estimated using a Monte Carlo approach ($n = 10,000$ simulations) by generating normally distributed $\epsilon^{46}$Ti and $\epsilon^{48}$Ti values with the mean and error of each meteorite. The uncertainty resulting from the correction for Ti isotope anomalies ranges from $\pm 0.007/\epsilon$ for enstatite chondrites to $\pm 0.024/\epsilon$ for angrites. The total error (95% c.i.) on the $\delta^{49}$Ti value was then calculated as $\epsilon_{\text{Total}} = \sqrt{\epsilon_{\text{anomalies}}^2 + \epsilon_{\text{Data}}^2}$.

### 3.3. Recommended data representation of titanium isotopic compositions

To facilitate inter-laboratory comparison of Ti isotope data, we recommend that $\delta^{49}$Ti data is published normalized to the Origins Laboratory Ti standard (OL-Ti), which can be requested at SARM (Service d’Analyses des Roches et des Minéraux, Nancy, France). The OL-Ti standard fulfills the guidelines for a suitable reference material as put forward by Teng et al. (2017). It also has an ideal Ti isotopic composition, which is within current measurement precision identical to the bulk silicate Earth (Millet et al., 2016). The $\delta^{49}$Ti value of NIST SRM 3162a relative to OL-Ti is $+1.056 \pm 0.026/\epsilon$ (Table B.1). If in-house Ti reference materials other than the OL-Ti standard are used, it is suggested to calibrate them against the OL-Ti standard and to subsequently correct the $\delta^{49}$Ti data for the offset between the two Ti reference materials. For example, $\delta^{49}$Ti data measured relative to standard reference material 3162a from NIST can be recalculated to the OL-Ti standard with $\delta^{49}$Ti$_{\text{OL-Ti}} = \delta^{49}$Ti$_{\text{SRM3162a}} + 1.056/\epsilon$. 

![Fig. 1. Titanium isotopic compositions of Ca doping experiment of data left uncorrected (blue diamonds) and data corrected for Ca interference on $^{46}$Ti and $^{48}$Ti (red squares).](Image)
Table 2
Titanium isotopic composition of komatiite samples and selected USGS rock reference standards.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Facies</th>
<th>δ⁴⁹Ti (%)</th>
<th>95% c.i.</th>
<th>n</th>
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<tr>
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</tr>
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<td>G3</td>
<td>USGS</td>
<td>0.429</td>
<td>0.025</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

95% c.i. = 95% confidence interval.
USGS: USGS powder rock reference standards, agree well with those published in Millet and Dauphas (2014) and Millet et al. (2016).
n is the number of repeat measurements of the purified Ti solution.
b Duplicate measurement, prepared from new pellet aliquot.

4. RESULTS

The Ti isotopic compositions of various terrestrial and extraterrestrial materials analyzed in this study are presented in Tables 1–3. Unless otherwise stated, all uncertainties are given as 95% confidence intervals (c.i. hereafter). No significant variation is found in the Ti isotopic composition of chondrites, except possibly for a slightly heavier δ⁴⁹Ti value in the Allende CV chondrite. The heavy δ⁴⁹Ti value of Allende is presumably due to the large modal fraction of refractory dust in this sample relative to other chondrites (Hezel et al., 2008; Dauphas and Pourmand, 2015). Excluding this sample, chondrites define a mean δ⁴⁹Ti value of +0.004 ± 0.010‰, which is in excellent agreement with the proposed composition of the bulk silicate Earth (Fig. 2 and Table 1; Millet et al., 2016). The very consistent δ⁴⁹Ti observed among all investigated chondrite groups is in contrast to the isotope pattern of the similarly refractory and lithophile Ca, where carbonaceous chondrites have lighter δ⁴⁴Ca than enstatite and ordinary chondrites (Fig. 3; Simon and DePaolo, 2010; Valdes et al., 2014).

The range in δ⁴⁹Ti values of komatiites is similar to that observed among post-Archean mafic and ultramafic rocks (Millet et al., 2016). Individual samples from the Schapenburg, Komati, Belingwe and Alexo komatiites are within error identical and define average Ti isotopic compositions of +0.025 ± 0.020‰, +0.002 ± 0.024‰, +0.016 ± 0.012‰ and +0.035 ± 0.016‰, respectively. In the Weltevreden system, measurements of samples 501-1, 501-8 were shifted towards lighter δ⁴⁹Ti values (−0.072 ± 0.030‰ and −0.102 ± 0.030‰, respectively) compared to the other samples from that locality. Replica analyses of newly prepared aliquots from the fluxed pellets of samples 501-1 and 501-8 yielded δ⁴⁹Ti values of +0.004 ± 0.033‰ and −0.001 ± 0.033‰, respectively, which are identical within errors to the rest of the Weltevreden samples. It is likely that the light δ⁴⁹Ti compositions from the first measurements of samples 501-1 and 501-8 from Weltevreden are incorrect. The calculated Ti concentrations with isotope dilution for these two samples resulted in around 12% higher Ti concentrations for the second measurement. This could indicate that an error occurred during the spiking procedure or the spike-sample mixture did not completely equilibrate. Excluding the two light outliers, the average δ⁴⁹Ti of the Weltevreden komatiites is −0.015 ± 0.012‰. No correlation between age and the Ti isotopic composition of komatiites is observed. The overall average Ti isotopic composition of all komatiites (i.e., δ⁴⁹Ti = −0.001 ± 0.019‰) is identical within uncertainties to the bulk silicate Earth δ⁴⁹Ti value of +0.005 ± 0.005‰ reported by Millet et al. (2016).

The δ⁴⁹Ti values of the HED meteorites studied vary between −0.04 and +0.04‰ and thus span a similar range as that observed for terrestrial basalts (Millet et al., 2016). No difference in the Ti isotopic composition of diogenites, howardites and eucrites is observed and the overall average δ⁴⁹Ti is +0.011 ± 0.015‰. Four out of the five studied angrites have a Ti isotopic composition similar to chondrites, with values ranging from −0.010 ± 0.042 to +0.042 ± 0.042‰. Plutonic angrite NWA 4590 has a significantly lighter δ⁴⁹Ti of −0.111 ± 0.042‰. No systematic difference in the Ti isotopic composition can be observed between volcanic and plutonic angrites and no correlation between the Ti isotopic composition and major or trace element concentrations of angrites exists, except that the sample most enriched in TiO₂ (NWA 4590 = 1.42 wt.%; Shirai et al., 2009; Keil, 2012) has the lightest δ⁴⁹Ti. The martian
Table 3
Titanium isotopic compositions of lunar and achondrite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Classification</th>
<th>$\varepsilon^{46}\text{Ti}$</th>
<th>95% c.i.</th>
<th>$\varepsilon^{48}\text{Ti}$</th>
<th>95% c.i.</th>
<th>$\delta^{49}\text{Ti}$ (%)</th>
<th>95% c.i.</th>
<th>n</th>
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</thead>
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$\delta^{49}\text{Ti}$: Ti isotopic composition prior to correction for isotopic anomalies on $^{46}\text{Ti}$ and $^{48}\text{Ti}$.
$\varepsilon^{46}\text{Ti}$ and $\varepsilon^{48}\text{Ti}$, isotopic anomalies from Zhang et al. (2012) except Mars, which is from Trinquier et al. (2009).
95% c.i. = 95% confidence interval.
CM = cumulate; MG = main group; NL = Nuevo Laredo group; ST = Stannern group.
n is the number of repeat measurements of the purified Ti solution.
$^b$ Duplicate measurement, prepared from new pellet aliquot.
$^c$ Shallowater may originate from a distinct parent-body than the rest of group; see text for details.

Fig. 2. Titanium isotope compositions of ordinary, enstatite and carbonaceous chondrites. The shaded area shows the average $\delta^{49}\text{Ti}$ value (±95% c.i.) of measured chondrites; +0.004 ± 0.010‰ (CV chondrite Allende not included, see text).
shergottite has a $\delta^{49}\text{Ti}$ value of $+0.021 \pm 0.038\%e$, consistent with the Ti isotopic composition of chondrites.

The variation in the Ti isotopic composition among chondrites is over 0.30%e (Table 3) and, thus, is much higher than what is observed in terrestrial basalts and HED meteorites. Bishopville and North County have the heaviest (+0.242 ± 0.034%e) and lightest (−0.069 ± 0.034%e) $\delta^{49}\text{Ti}$ values, respectively. The $\delta^{49}\text{Ti}$ of enstatite and ordinary chondrites (Simon and DePaolo, 2010; Valdes et al., 2014; Huang and Jacobsen, 2017) is lighter than that of the bulk silicate Earth, ordinary carbonaceous chondrites, except those of the CO group, and CV3 chondrites. This idea is corroborated by the REE signature of CV3 chondrites, where the presence of an extraneous CAI/refractory dust component is manifested as a Tm excess relative to other meteorite groups, Earth, Mars, and Vesta (Dauphas and Pourmand, 2015; Barrat et al., 2016). An important difference between Ca and Ti in CAIs is that while Ca isotopes show overall light compositions, Ti isotopes show variations that are centered on the chondritic composition (Davis et al., 2016; Simon et al., 2016a). The effect on the Ti and Ca isotopic compositions of mixing a CAI/refractory component with an ordinary chondrite was calculated using published Ca and Ti isotopic compositions and concentrations. For the Ca and Ti concentrations of the refractory dust, the suggested average values for type II CAIs by Dauphas and Pourmand (2015) are used (i.e. Ti = 4065 μg/g, Ca = 8.4 wt.%).

Finally, lunar KREEP sample SaU 169 has a composition highly enriched in heavy Ti isotopes (+0.330 ± 0.034%e), a signature that is well resolved from the $\delta^{49}\text{Ti}$ values of low-Ti and high-Ti mare basalts (ranging from −0.008 to +0.033%e), as reported by Millet et al. (2016).

5. DISCUSSION

5.1. Titanium isotopic composition of chondrites and comparison with calcium isotopes

The Ti isotopic compositions of ordinary, enstatite, and carbonaceous chondrites are identical within their respective uncertainties (Fig. 2) and define an average of +0.004 ± 0.010%e. This observation contrasts with the documented heterogeneity in Ca isotopes among chondrites (Fig. 3; refs). Calcium is slightly less refractory than Ti with 50% condensation temperatures of 1517 and 1582 K, respectively (at 10$^{-4}$ bar total pressure in a gas of solar composition) (Grossman and Larimer, 1974; Lodders, 2003). Both Ca and Ti are lithophile and do not partition in either metal or sulfide except under highly reducing conditions. One might thus expect that isotopic variations of Ti would mirror those documented for Ca. However, unlike $\delta^{49}\text{Ti}$, the calcium isotope compositions ($\delta^{44}\text{Ca}$) of most carbonaceous chondrites, except those of the CO group, are lighter than that of the bulk silicate Earth, ordinary and enstatite chondrites (Simon and DePaolo, 2010; Valdes et al., 2014; Huang and Jacobsen, 2017). The reason for the $\delta^{44}\text{Ca}$ variation among carbonaceous chondrites is not yet well understood. Recently, it was suggested that the light Ca isotopic composition of carbonaceous chondrites may be linked to the amount of incorporated calcium-aluminum rich inclusions (CAI) and refractory dust (Dauphas and Pourmand, 2015; Huang and Jacobsen, 2017). CAIs are among the earliest solar nebula condensates and, as a result of kinetically driven isotope fractionation during condensation and/or evaporation (Huang et al., 2012), they carry a very light Ca isotope signature, reaching −11%e (Niederer and Papanastassiou, 1984; Huang et al., 2012; Simon et al., 2016a). The high Ca concentration and low $\delta^{44}\text{Ca}$ value of refractory dust can influence the Ca budget and isotopic composition of chondrites. This idea is corroborated by the REE signature of carbonaceous chondrites, where the presence of an extraneous CAI/refractory dust component is manifested as a

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**Fig. 3.** Average Ti isotopic composition versus Ca isotopic composition of various chondrite groups (OC, EC, CO, CM, CI and CV) and the bulk silicate Earth (BSE) in ppm per atomic mass unit ($\delta^{49}\text{Ti} = \delta^{49}\text{Ti}/(49–47)$ and $\delta^{44}\text{Ca} = \delta^{44}\text{Ca}/(44–40)$). Ti isotope data is from this study (Table 1) and Ca isotope data from Valdes et al. (2014). Carbonaceous chondrites have a significantly lighter Ca isotopic composition than the Earth, ordinary and enstatite chondrites. In contrast, all chondrite groups have the same Ti isotopic composition within uncertainty. The dotted line with white diamonds is the mixing curve between an ordinary chondrite and refractory dust (CAIs) in 0.5% increments (see text for details). Because CAIs have on average chondritic Ti isotopic composition, their removal or addition does not affect the Ti isotopic composition of bulk meteorites significantly, while it affects the Ca isotopic composition (see text for details).
not yet well understood. One reason for the higher 50% condensation temperature of Ti relative to Ca is that Ti condenses as perovskite whose stoichiometry (CaTiO$_3$) dictates that for every Ti that condenses one atom of Ca also condenses. Because the Ca/Ti ratio of solar gas is ~25, only a small fraction is Ca is condensed when Ti is fully condensed in perovskite (Grossman and Larimer, 1974). The fact that the average Ti isotopic composition of CAIs is similar to that of chondrites, despite displaying a significant range in $\delta^{49}$Ti values, suggests that CAIs as a whole behaved as a closed-system for Ti. Some CAIs were enriched in the light isotope by kinetic isotope fractionation associated with condensation from supersaturated gas but the isotopically heavy Ti left behind in the gas was eventually condensed in other CAIs and no net loss of Ti from the CAI-forming region took place. Calcium on the other hand is slightly less refractory and is enriched in the light isotopes. Following condensation of isotopically light Ca, the residual isotopically heavy Ca gas was driven off from the CAI-forming region but Ti was already all in the solid, so its isotopic composition was unaffected. Further work on CAIs is needed to understand what caused the isotopic decoupling between Ca and Ti but their distinct condensation behaviors apparently affected the compositions of bulk chondrites.

5.2. Titanium isotopic variability in terrestrial mafic and ultramafic rocks

As was discussed earlier, the average chondritic Ti isotopic composition of +0.004 ± 0.010‰ obtained in this study agrees well with the proposed value for the bulk silicate Earth (+0.005 ± 0.005‰; Millet et al., 2016), implying that the Earth has a chondritic $\delta^{49}$Ti value. Titanium is a lithophile element, so the only mechanism that could have conceivably fractionated the isotopic composition of the Earth at a large scale, after its accretion, is continental crust extraction. Indeed, evolved crustal rocks have a heavier Ti isotopic composition than basalts or peridotites (Millet et al., 2016). However, Millet et al. (2016) did not observe significant Ti isotope fractionation during mantle melting processes and, thus, it is more likely that the isotopically light counterpart to the heavier upper continental crust is the lower continental crust. In addition, a first order calculation of the effect of crust extraction on the $\delta^{49}$Ti of the terrestrial mantle indicates that this process is unlikely to change the Ti isotopic composition of the mantle. The average Ti concentration of the bulk silicate Earth is estimated to be ~1205 µg/g (McDonough and Sun, 1995) and that of the average continental crust is ~4316 µg/g (Rudnick and Gao, 2003). The mass of the continental crust is around 0.6 wt.% of that of the bulk silicate Earth (Helffrich and Wood, 2001). Hence, around 2.2 wt.% of the total Ti in the bulk silicate Earth is stored in the continental crust. An estimate of the average continental crust $\delta^{49}$Ti value can be obtained by interpolating the $\delta^{49}$Ti vs. SiO$_2$ correlation from Millet et al. (2016) to 60.6 wt.% SiO$_2$, the estimated average SiO$_2$ concentration of the bulk continental crust after Rudnick and Gao (2003). This yields an average continental crust $\delta^{49}$Ti value of +0.21‰. The mass-balance would therefore predict that the mantle should have been shifted by ~0.005% by continental crust extraction. The effect of crustal extraction on the Ti isotopic composition of the depleted mantle depends on the mantle volume that was depleted. Mass balance calculations of K, U and Th suggest that around 50% of Earth’s mantle is depleted (Helffrich and Wood, 2001). If correct, the $\delta^{49}$Ti of the depleted mantle would have been shifted by around ~0.010‰ from the chondritic value. Crustal extraction therefore had little influence on the bulk mantle Ti isotopic composition, consistent with the fact that terrestrial mafic and ultramafic rocks have Ti isotopic compositions similar to chondrites.

Komatiites have experienced extensive alteration. Titanium, which is highly insoluble in most aqueous fluids, was not mobilized by this alteration. Indeed, the TiO$_2$ concentration of the samples all plot on olivine control lines, meaning that Ti concentration variations in komatiites are entirely explainable by magmatic processes (see Puchtel et al., 2009, 2013, 2016 and Appendix Fig. C.1). Among komatiites, one needs to distinguish between the bulk Ti isotopic composition of a lava flow and individual samples. The $\delta^{49}$Ti of the latter might have been affected by isotope fractionation induced by fractional crystallization after lava emplacement. For Komati, Weltevreden, Belingwe and Alexo komatiite lava flows, we analyzed olivine cumulates and spinifex textured rocks, which represent end members of in situ lava differentiation. However, no systematic difference in the Ti isotopic composition between olivine cumulates and spinifex textured rocks is observed. Also, the analyzed Schapenburg samples are identical within error, with the caveat that only spinifex-textured rocks were analyzed. Therefore, the bulk lava $\delta^{49}$Ti of a komatiite system is estimated using the average Ti isotopic compositions of the samples from the respective komatiite location (see Table 2). Based on these considerations, the Komati, Schapenburg, Weltevreden (excluding measurements 501-1 and 501-8 with unusual light $\delta^{49}$Ti values) and Belingwe suites have a chondritic $\delta^{49}$Ti (average = +0.007 ± 0.011‰) and the Alexo komatiites a slightly sub-chondritic $\delta^{49}$Ti of ~0.035 ± 0.016‰ but this is at the limit of precision (Fig. 4). While the shift towards heavier Ti isotopic compositions in basalts can be explained by an early onset of Fe-Ti-oxide crystallization (Millet et al., 2016), the shift towards a lighter than chondritic Ti isotopic composition is more difficult to explain. Indeed, no mineral phase has yet been identified that preferentially incorporates heavy Ti isotopes, which would result in a melt enriched in light Ti isotopes. Mantle derived rocks with a sub-chondritic $\delta^{49}$Ti have been identified in island-arc basalts (JB-2, $\delta^{49}$Ti = ~0.046 ± 0.009; Millet et al., 2016), ocean island basalts (BIR-1a) and the Alexo komatiites. As Ti behaves as an incompatible element, one possible mechanism that could affect its isotopic composition is extensive depletion of the mantle. In such a process, one would expect to observe the strongest effect on the $\delta^{49}$Ti in the Ti residue corresponding to the strongly depleted mantle. REE behave as a coherent series of elements whose incompatibility during mantle melting decreases with increasing atomic number (Winter, 2001). The REE pattern
Samples with a subchondritic Si$^{4+}$ into tetrahedral sites, in the presence of water Ti enters complex. While in anhydrous olivine, Ti $^{4+}$ substitutes for

rate 6-fold Ti in their structure (O’Neill and Navrotsky, 1983; Waychunas, 1987). The situation with olivine is more

als like pyroxene, garnet and spinel, preferentially incorpo-

rations of the mantle, then a mechanism is needed that extracts preferentially heavy Ti isotopes during mantle melting, leaving behind a residue enriched in light Ti isotopes. Titanium in mafic melts is predominantly in 5-fold, but also 4- and 6-fold coordinations are present (Farges et al., 1996; Farges and Brown, 1997). Titanium-bearing mineral phases like pyroxene, garnet and spinel, preferentially incorporate 6-fold Ti in their structure (O’Neill and Navrotsky, 1983; Waychunas, 1987). The situation with olivine is more complex. While in anhydrous olivine, Ti$^{4+}$ substitutes for Si$^{4+}$ into tetrahedral sites, in the presence of water Ti enters in sixfold coordination as Ti-clinohumite-like point or planar defects (Berry et al., 2007; Hermann et al., 2007). Olivine is, however, not expected to be an important host for Ti in the mantle (McDonough et al., 1992; Green, 1994) and thus, from a mass balance point of view, should not significantly affect the Ti isotopic signature. Because low coordination is usually associated with stiffer bonds and heavy isotope enrichment, one would predict that depleted mantle would be shifted towards light $\delta^{49}$Ti (Schauble, 2004; Millet et al., 2016), consistent with the observed low $\delta^{49}$Ti values in magmas from strongly depleted sources.

Depleted sources are also more prone to metasomatism, which taking Fe isotope systematics as a guide, can produce light Ti isotope signatures in some contexts (Weyer and Ionov, 2007). A possible scenario is that metasomatism of a depleted source by Ti-rich melts was accompanied by diffusion of Ti from the melt to the solid. Because light Ti isotopes diffuse faster than heavier ones (Richter et al., 2009 and references therein), the metasomatized solid would be expected to be enriched in the light Ti isotopes during such a re-fertilization event.

An open question is to what extent a mantle source needs to be depleted to become significantly biased in its Ti isotopic composition. As seen in Fig. 4 and published Ti isotope data on eclogites, peridotites and N-MORB data (Millet et al., 2016), many rocks exhibiting a depleted LREE pattern and thus derived from a depleted mantle source have a $\delta^{49}$Ti identical within errors to the bulk silicate Earth. To more rigorously explain and address the occurrence of subchondritic $\delta^{49}$Ti among terrestrial mafic and ultramafic rocks, more data describing the Ti isotopic composition of important major minerals, such as garnet, pyroxene, spinel, and olivine, are needed. Studies targeting peridotites that have experienced re-fertilization and metasomatism should also help elucidate whether such processes can explain the light Ti isotope signature of depleted sources.

5.3. Titanium isotopic fractionation in aubrites

The variation in the Ti isotopic composition among aubrites is over 0.3‰ and is three times larger than what is observed for terrestrial basalts and HED meteorites. The $\delta^{49}$Ti value of aubrites correlates well with their estimated MgO/SiO$_2$ ratio and the MgO concentration (compiled from the MetaBase database), with the exception of Shallowater (Fig. 5). Shallowater has a distinct metal content compared to other aubrites and a complex and unique three stage cooling history, suggesting that it was derived from a distinct parent-body (Keil, 1989). Its outlier Ti isotopic composition relative to other aubrites further confirms the unusual nature of Shallowater in this meteorite group and consequently, it will be omitted from further discussion.

The unusually large spread in $\delta^{49}$Ti values in rocks with similar compositions is most probably the result of the very low O$_2$ under which aubrite meteorites evolved. By analogy with enstatite chondrites, Ti likely exists in aubrites in the oxidation states Ti$^{3+}$ and Ti$^{4+}$ (Simon et al., 2016b), which favors a higher degree of isotopic fractionation (Schauble, 2004; Dauphas et al., 2014b). In these conditions, the nominally lithophile element Ti becomes chalcophile and is enriched in troilite (Watters and Prinz, 1979). The TiO$_2$ concentration in aubritic meteorites is low, with values between 0.01 and 0.2 wt% (Watters and Prinz, 1979), a likely result of the removal of Ti from the mantle in a sulfide melt during core formation (Lodders et al., 1993). The good correlation between $\delta^{49}$Ti and MgO/SiO$_2$ ratio and the MgO concentration, two indexes of magmatic differentiation, suggests that an igneous process, such as fractional crystallization or partial melting is
responsible for the fractionated Ti isotopic composition. Partitioning of Ti between sulfide and silicate melt, as well as its presence in different oxidation states (Ti\(^{3+}\) vs. Ti\(^{4+}\)), are likely mechanisms to fractionate its isotopes in this reducing environment. Titanium-rich troilite is one of the major hosts of Ti in aubrites and most likely favors Ti\(^{3+}\) over Ti\(^{4+}\). No data are yet available regarding the partitioning behavior of Ti\(^{4+}\) vs. Ti\(^{3+}\) in silicate minerals from aubrites. In refractory inclusions, however, Ti\(^{3+}\) is preferentially incorporated into pyroxenes over Ti\(^{4+}\) and the melt from which they crystallize gets progressively depleted in Ti\(^{4+}\) and enriched in Ti\(^{3+}\) (Simon et al., 1991; Papike et al., 2016). Thus, sulfides and silicate minerals are likely mechanisms to fractionate its isotopes in this reducing environment. Titanium-rich troilite is one of the major hosts of Ti in aubrites and most likely favors Ti\(^{3+}\) over Ti\(^{4+}\). No data are yet available regarding the partitioning behavior of Ti\(^{4+}\) vs. Ti\(^{3+}\) in silicate minerals from aubrites. In refractory inclusions, however, Ti\(^{3+}\) is preferentially incorporated into pyroxenes over Ti\(^{4+}\) and the melt from which they crystallize gets progressively depleted in Ti\(^{4+}\) and enriched in Ti\(^{3+}\) (Simon et al., 1991; Papike et al., 2016). Thus, sulfides and silicate minerals are expected to prefer Ti\(^{3+}\) over Ti\(^{4+}\) in their mineral structures, making it likely that with increasing fractionation of the system, the Ti\(^{4+}/Ti^{3+}\) ratio in the melt would increase. Following Schaubel (2004) and Dauphas et al. (2014b), we can assume, as the first order approximation, that species containing Ti\(^{3+}\) have a heavier Ti isotopic composition than those hosting Ti\(^{4+}\). In addition, Ti-S bond length in Ti sulfides like TiS\(_2\) (≈2.4 Å; Chianelli et al., 1975) or heideite (≈2.5 Å; Takahashi and Yamada, 1973) are longer than Ti-O bonds observed in silicate minerals like e.g. enstatite (≈2.1 Å; Tarantino et al., 2002) or silicate glass (≈1.9 Å; Cormier et al., 2001). The difference in bond length results in lower force constants of Ti-S bonds than in Ti-O bonds (Young et al., 2015). Weaker bonds favor light isotopes and thus, one can predict that sulfide minerals are enriched in light Ti isotopes. Therefore, silicate and sulfide minerals should preferentially incorporate light Ti isotopes. Following this line of argument, increasing fractionation of the magmatic system should result in a progressively higher Ti\(^{3+}/Ti^{4+}\) ratio and thus a heavier \(\delta^{49}\)Ti in the residual melt. This is consistent with the observed correlations between \(\delta^{49}\)Ti and indices of magmatic differentiation.

Although there are still substantial gaps in our understanding of the geochemical behavior of Ti under these reducing conditions, the argument presented above at least qualitatively explains the observed \(\delta^{49}\)Ti signatures in aubrites. The extraction of Ti from the mantle by a sulfide melt during core formation (Lodders et al., 1993) could have shifted the bulk silicate Ti isotopic composition of the aubrite parent-body towards a \(\delta^{49}\)Ti value heavier than the chondritic average.

### 5.4. Titanium isotope fractionation in the lunar magma ocean

One of the remarkable features of lunar mare basalts is their highly variable and sometimes high Ti concentrations. One interpretation of this observation is that accumulated ilmenite from the latest stages of the lunar magma ocean crystallization (e.g. Snyder et al., 1992; Shearer and Papike, 1999) was involved in the generation of high-Ti mare basalts (e.g. Wagner and Grove, 1997; van Orman and Grove, 2000). Following the argument of Millet et al. (2016) that the heavy Ti isotopic composition in evolved silicic crustal rocks on Earth is the result of light Ti isotopic fractionation into Fe-Ti oxides, the crystallization of ilmenite in the lunar magma ocean should have shifted the residual liquid towards a heavy Ti isotopic composition, too. Accordingly, KREEP-rich rocks (material that is highly enriched in K, REE, P and other incompatible trace elements) that represent the residual liquid from lunar magma ocean crystallization (Warren and Wasson, 1979) may show enrichments in the heavy isotopes of titanium. The significantly distinct \(\delta^{49}\)Ti value (\(+0.330 \pm 0.034\)‰) of the KREEPy impact melt breccia part of SaU 169 therefore supports Ti isotope fractionation due to ilmenite crystallization in the lunar magma ocean. Using the Rayleigh distillation modelling approach of Millet et al. (2016) and a Ti isotope fractionation value between melt and ilmenite of \(-0.118\)‰ (at \(T = 1125\) °C; van Orman and Grove, 2000), a \(\delta^{49}\)Ti of \(+0.330\)‰ in the melt is achieved when approximately 94% of Ti has been removed in ilmenite (Fig. 6). At this point, the bulk ilmenite cumulate would have a \(\delta^{49}\)Ti of \(-0.017\)‰ (Fig. 6).
It is generally thought that the source of the high-Ti lunar mare basalts is linked to ilmenite-bearing cumulates, either by assimilation of ilmenite during magma ascent or by fertilization of ilmenite free mantle layers by sinking ilmenite-bearing cumulates or negatively buoyant partial melts from ilmenite-rich zones (e.g., Snyder et al., 1992; Wagner and Grove, 1997; van Orman and Grove, 2000; Elkins-Tanton et al., 2011; Hallis et al., 2014). However, high-Ti mare basalts have \( \delta^{49}\text{Ti} \) ranging from +0.011 to +0.033 ‰ (Millet et al., 2016) and are thus heavier than the estimated bulk ilmenite cumulate \( \delta^{49}\text{Ti} = 0.017 \) ‰. This discrepancy suggests that either (i) preferentially late ilmenite cumulates which host a heavier \( \delta^{49}\text{Ti} \) were the predominant Ti source of the high-Ti mare basalts, or (ii) that ilmenite was not exhausted during the melting process, so that significant fractionation was imparted to the melt upon melting of the source of high-Ti mare basalts. The first option is somewhat \textit{ad hoc} and difficult to test. The second process could have occurred during melting of ilmenite-bearing cumulates in the lunar mantle (Hess and Parmentier, 1995; Beard et al., 1998; Hallis et al., 2014) or during the production of a buoyant partial melt from an ilmenite-bearing layer that then subsequently sunk and fertilized parts of the lunar mantle with Ti (van Orman and Grove, 2000; Elkins-Tanton et al., 2004). It is currently not possible to evaluate which of the two latter processes was more likely to generate high-Ti mare basalts based on the Ti isotopic compositions of lunar rocks.

5.5. Titanium isotope signature of angrites, HED meteorites and Mars

The angrites NWA 2999, D’Orbigny, NWA 1670 and Sahara 99555 have Ti isotopic compositions that are identical within uncertainties. The average \( \delta^{49}\text{Ti} \) value of these samples is +0.007 ± 0.038 ‰, which is indistinguishable from the chondritic value. Angrite NWA 4590, however, has a significantly lighter \( \delta^{49}\text{Ti} = -0.111 \pm 0.042 \) ‰. Angrites are enriched in refractory elements, such as Ti and Ca, and thus contain minerals with high Ti concentrations, such as Al-Ti-rich diopside, ilmenite, magnetite and ulvöspinel (e.g. Keil, 2012), which increases the possibility of Ti isotope fractionation via crystallization of these mineral phases. Published CaO and TiO2 concentrations of angrites correlate well (appendix Fig. C.2), with exception of sample NWA 4590 that plots at too high TiO2 concentration relative to its CaO concentration, which likely is the result of the high abundance of ulvöspinel in that meteorite (>18 vol.%; Kuehner and Irving, 2007). Angrite NWA 4590 has also an unusual coarse grained mineral texture that resembles cumulate rocks (Kuehner and Irving, 2007). Assuming that (i) ulvöspinel is the major host of Ti in angrite NWA 4590 and thus defines its \( \delta^{49}\text{Ti} \) composition and (ii) NWA 4590 equilibrated with a melt with chondritic \( \delta^{49}\text{Ti} \), then the Ti isotopic fractionation between the melt and ulvöspinel is approximately −0.115 ± 0.042 ‰. Such fractionation is consistent with the expected equilibrium fractionation between silicate melt and oxide of around −0.106 ‰ (Millet et al., 2016) assuming a crystallization temperature around the liquidus of a basaltic melt of ~1200 °C. Therefore, the light \( \delta^{49}\text{Ti} \) value of NWA 4560 is likely the result of accumulation of ulvöspinel and is thus not representative of the bulk angrite parent-body. Consequently, the best estimate of the bulk angrite parent-body \( \delta^{49}\text{Ti} \) is calculated as the average for angrites NWA 2999, D’Orbigny, NWA 1670 and Sahara 99555 only. This average \( \delta^{49}\text{Ti} = +0.007 \pm 0.038 \) ‰ is indistinguishable from the chondritic value.

A similar picture emerges from the analyzed HED meteorites. No systematic difference in the \( \delta^{49}\text{Ti} \) values between diogenites, eucrites and howardites is observed and the overall average of +0.011 ± 0.015 ‰ is identical to the
chondritic value. The similar Ti isotopic composition between diogenites (lower crust samples), cumulate eucrites (gabbroic rocks formed within the crust) and basaltic eucrites (sills and lava flows) (Mandler and Elkins-Tanton, 2013; Mittlefehldt, 2015) further indicates that Ti isotope fractionation in mafic systems is limited unless Ti exists in different oxidation states (as discussed for aubrites) or an Fe-Ti oxide like ilmenite reaches saturation (as discussed for the Moon).

The estimated Ti isotopic compositions of the parent-bodies of angrites (+0.007 ± 0.038‰) and HEDs (+0.011 ± 0.015‰), Mars (+0.021 ± 0.038‰; based on a single martian shergottite), the Moon (−0.003 ± 0.014‰; Millet et al., 2016) and the bulk silicate Earth (+0.005 ± 0.005‰; Millet et al., 2016), are all within error identical to the chondritic value of +0.004 ± 0.010‰, which argues for a widespread homogeneous δ⁴⁹Ti signature among solar system objects (Fig. 7 and Table 4).

5.6. Comparison with previously published data

Comparison of our data with previous work on the mass-dependent Ti isotopic composition of meteorites of Williams (2014) (PhD Thesis, Table 5.1, page 156) is complicated by the fact that different isotopic ratios and standards were used. Thus, the data of Williams (2014) was renormalized to the OL-Ti standard by applying an offset δ⁴⁹Ti value of solar system objects than observed in our study. Based on our set of samples, including chondrites, various acondrites and terrestrial komatiites (Fig. 7, Table 4), we argue that solar objects are defined by a homogeneous Ti isotopic composition.

Table 4

<table>
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</tr>
<tr>
<td>Bulk silicate Earth</td>
<td>0.005</td>
<td>0.005</td>
</tr>
</tbody>
</table>

* Data from Millet et al. (2016).

![Fig. 7. Estimated average Ti isotopic compositions of the angrite and HED parent bodies, Mars, the Moon and the bulk silicate Earth (BSE), compared to the chondritic composition. The lack of variations indicates that given current analytical precision, solar system objects have uniform Ti isotopic compositions. Magmatic fractionation of Ti isotopes in the Aubrite parent-body prevents us from accessing its bulk composition.](image-url)

1. A new sample preparation technique for measuring the stable isotopic composition of titanium is presented. Samples are digested using LiBO₂ flux fusion, which leads to complete dissolution of chemically resistant accessory minerals and avoids the creation of insoluble Ti-bearing fluorides that may fractionate Ti isotopes.

2. No difference in the Ti isotopic composition among ordinary, enstatite, and carbonaceous chondrites is observed, except possibly for the CV chondrite Allende, which is rich in CAIs. The average chondritic δ⁴⁹Ti value of +0.004 ± 0.010‰ is identical to that of the HED parent-body (+0.011 ± 0.021‰) the angrite parent-body (+0.007 ± 0.038‰), Mars (+0.021 ± 0.038‰) and published estimates for the Moon (−0.003 ± 0.014‰) and the bulk silicate Earth (+0.005 ± 0.005‰). The homogeneous Ti isotopic composition among all classes of chondrites contrasts with published Ca isotope data showing that carbonaceous chondrites are shifted towards lighter Ca isotopic compositions compared to Earth, ordinary, and enstatite chondrites. The decoupling of the Ti and Ca isotope systems likely originated from differences in behaviors between Ca and Ti during condensation in the solar nebula.

3. The Ti isotopic variations observed among aubrite meteorites span about ~0.3‰, which is much larger than the range found in terrestrial basalts and HED meteorites. The reason for the more fractionated isotopic compositions is that differentiation and magmatic fractionation
on the aubrite parent-body occurred under highly reducing conditions, allowing partially chalcophile Ti$^{3+}$ and lithophile Ti$^{4+}$ to co-exist. The good negative correlation between $\delta^{49}$Ti values and the MgO/SiO$_2$ ratios and MgO concentrations is interpreted to be due to redox isotope fractionation, whereby magmatic differentiation results in enrichment of isotopically heavy Ti$^{4+}$ in the residual melt.

4. Titanium isotopic fractionation during ilmenite precipitation during late stages of lunar magma ocean crystallization resulted in a progressive enrichment of heavy Ti isotopes in the residual melt, as is evident from the observed heavy $\delta^{49}$Ti value of KREEPy impact melt breccia SaU 169 (+0.330 ± 0.034‰).

ACKNOWLEDGMENTS

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APPENDIX A. DOUBLE-SPIKE CORRECTION IN THE PRESENCE OF ISOTOPIC ANOMALIES.

Let us write $R_{\text{standard}}^{47}$ and $R_{\text{sample}}^{47}$ the ‘Ti$^{47}$/Ti$^{49}$ ratios in the standard and sample. The manner in which isotopic anomalies are calculated is usually by internal normalization, which consists in arbitrarily correcting one ratio for apparent mass fractionation and applying the same mass fractionation correction to all isotope ratios. For a sample, the internally normalized corrected value $R_{\text{sample}}^{47}$ would be $R_{\text{sample}}^{47} = R_{\text{sample}}^{47}/(m^3/m^4)^{\alpha}$, where $\alpha$ is calculated

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{49}$Ti (%)</th>
<th>95% c.i.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST SRM 3162a</td>
<td>1.056</td>
<td>0.026</td>
<td>12</td>
</tr>
<tr>
<td>BHVO acid</td>
<td>0.017</td>
<td>0.029</td>
<td>4</td>
</tr>
<tr>
<td>BHVO Flux</td>
<td>0.015</td>
<td>0.025</td>
<td>44</td>
</tr>
<tr>
<td>BHVO Flux cut1</td>
<td>−0.001</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>BHVO Flux cut2</td>
<td>0.003</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>BHVO Flux cut3</td>
<td>0.009</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>BIR-1a acid</td>
<td>−0.054</td>
<td>0.029</td>
<td>4</td>
</tr>
<tr>
<td>BIR-1a Flux</td>
<td>−0.065</td>
<td>0.025</td>
<td>40</td>
</tr>
<tr>
<td>BIR-1a Flux cut1</td>
<td>−0.103</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>BIR-1a Flux cut2</td>
<td>−0.092</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>BIR-1a Flux cut3</td>
<td>−0.070</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>G3 Flux</td>
<td>0.429</td>
<td>0.025</td>
<td>25</td>
</tr>
<tr>
<td>G3 Flux cut1</td>
<td>0.412</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>G3 Flux cut2</td>
<td>0.419</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>G3 Flux cut3</td>
<td>0.431</td>
<td>0.029</td>
<td>2</td>
</tr>
<tr>
<td>Flux Blank doped</td>
<td>0.008</td>
<td>0.029</td>
<td>4</td>
</tr>
<tr>
<td>M712 Matrix doped</td>
<td>0.009</td>
<td>0.029</td>
<td>4</td>
</tr>
<tr>
<td>BV05 Matrix doped</td>
<td>0.009</td>
<td>0.029</td>
<td>4</td>
</tr>
<tr>
<td>501-2 Matrix doped</td>
<td>−0.001</td>
<td>0.029</td>
<td>4</td>
</tr>
<tr>
<td>M712 acid</td>
<td>−0.029</td>
<td>0.030</td>
<td>4</td>
</tr>
<tr>
<td>M712 Flux</td>
<td>−0.022</td>
<td>0.030</td>
<td>8</td>
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<tr>
<td>SCH2.1 acid</td>
<td>0.007</td>
<td>0.030</td>
<td>4</td>
</tr>
<tr>
<td>SCH2.1 Flux</td>
<td>−0.006</td>
<td>0.030</td>
<td>4</td>
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<tr>
<td>BV03 acid</td>
<td>0.022</td>
<td>0.030</td>
<td>4</td>
</tr>
<tr>
<td>BV03 Flux</td>
<td>−0.005</td>
<td>0.030</td>
<td>4</td>
</tr>
<tr>
<td>501-2 acid</td>
<td>−0.016</td>
<td>0.030</td>
<td>4</td>
</tr>
<tr>
<td>501-2 Flux</td>
<td>−0.029</td>
<td>0.030</td>
<td>4</td>
</tr>
</tbody>
</table>

95% c.i. = 95% confidence interval.
Acid: the sample was digested using acid attack.
Flux: the sample was digested using flux fusion.
cut1, cut2, cut3: Aliquot of sample was measured after first, second or third ion-exchange chromatography.
n is the number of repeat measurements of the purified Ti solution.
independently by fixing the $^{48}\text{Ti}/^{47}\text{Ti}$ ratio of the sample to the standard ratio by applying the same formula. Isotopic anomalies are usually expressed as,

$$\delta^{49}\text{Ti} = \frac{R_i^{49}\text{Sample}}{R_i^{49}\text{Standard}} - 1 \cdot 10^4 \approx 10^4 \ln \left( \frac{R_i^{49}\text{Sample}}{R_i^{49}\text{Standard}} \right).$$

We therefore can write $R_i^{47}\text{Sample}$ as,

$$R_i^{47}\text{Sample} = R_i^{47}\text{Standard} \left( \frac{m_i^{47}}{m_i^{48}} \right)^{\delta^{49}\text{Ti}} \left( 1 + \frac{\delta^{49}\text{Ti}}{10^4} \right).$$

This formula is used in double spike data reduction to calculate $R_i^{47}\text{Sample}$.

**APPENDIX B**

See Tables B.1 and B.2.

**APPENDIX C**

See Figs. C.1 and C.2.

**REFERENCES**


