

## Durham Research Online

---

### Deposited in DRO:

24 June 2016

### Version of attached file:

Accepted Version

### Peer-review status of attached file:

Peer-reviewed

### Citation for published item:

Millet, M.-A. and Dauphas, N. and Greberb, N.D. and Burton, K.W. and Dale, C.W. and Debret, B. and Macpherson, C.G. and Nowell, G.M. and Williams, H.M. (2016) 'Titanium stable isotope investigation of magmatic processes on the Earth and Moon.', *Earth and planetary science letters.*, 449 . pp. 197-205.

### Further information on publisher's website:

<http://dx.doi.org/10.1016/j.epsl.2016.05.039>

### Publisher's copyright statement:

© 2016 This manuscript version is made available under the CC-BY-NC-ND 4.0 license  
<http://creativecommons.org/licenses/by-nc-nd/4.0/>

### Additional information:

## Use policy

---

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a [link](#) is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full DRO policy](#) for further details.

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

3

4

5 Marc-Alban Millet<sup>1,2\*</sup>, Nicolas Dauphas<sup>2</sup>, Nicolas D. Greber<sup>2</sup>, Kevin W.

6 Burton<sup>1</sup>, Chris W. Dale<sup>1</sup>, Baptiste Debret<sup>1</sup>, Colin Macpherson<sup>1</sup>, Geoffrey M.

7 Nowell<sup>1</sup> and Helen M. Williams<sup>1</sup>

8

9

10 <sup>1</sup> Durham University, Department of Earth Sciences, South Road, Durham DH1 3LE,  
11 United Kingdom

12

13 <sup>2</sup> Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi  
14 Institute, University of Chicago, 5734 S Ellis Avenue, Chicago IL, 60637, USA.

15

16 \* Corresponding author: [m.a.millet@durham.ac.uk](mailto:m.a.millet@durham.ac.uk)

17

18

19

20

21 Keywords: Stable Isotopes, Magma differentiation, Bulk Silicate Earth, Lunar basalts

22 **Abstract**

23

24 We present titanium stable isotope measurements of terrestrial magmatic samples  
25 and lunar mare basalts with the aims of constraining the composition of the lunar and  
26 terrestrial mantles and evaluating the potential of Ti stable isotopes for understanding  
27 magmatic processes. Relative to the OL-Ti isotope standard, the  $\delta^{49}\text{Ti}$  values of  
28 terrestrial samples vary from -0.05 to +0.55‰, whereas those of lunar mare basalts  
29 vary from -0.01 to +0.03‰ (the precisions of the double spike Ti isotope  
30 measurements are ca.  $\pm 0.02\%$  at 95% confidence). The Ti stable isotope  
31 compositions of differentiated terrestrial magmas define a well-defined positive  
32 correlation with  $\text{SiO}_2$  content, which appears to result from the fractional  
33 crystallisation of Ti-bearing oxides with an inferred isotope fractionation factor of  
34  $\Delta^{49}\text{Ti}_{\text{oxide-melt}} = -0.23\text{‰} \times 10^6/T^2$ . Primitive terrestrial basalts show no resolvable

35 Ti isotope variations and display similar values to mantle-derived samples (peridotite  
36 and serpentinites), indicating that partial melting does not fractionate Ti stable  
37 isotopes and that the Earth's mantle has a homogeneous  $\delta^{49}\text{Ti}$  composition of  
38  $+0.005 \pm 0.005$  (95% c.i.,  $n=30$ ). Eclogites also display similar Ti stable isotope  
39 compositions, suggesting that Ti is immobile during dehydration of subducted  
40 oceanic lithosphere. Lunar basalts have variable  $\delta^{49}\text{Ti}$  values; low-Ti mare basalts  
41 have  $\delta^{49}\text{Ti}$  values similar to that of the bulk silicate Earth (BSE) while high-Ti lunar  
42 basalts display small enrichment in the heavy Ti isotopes. This is best interpreted in  
43 terms of source heterogeneity resulting from Ti stable isotope fractionation  
44 associated with ilmenite-melt equilibrium during the generation of the mantle source  
45 of high-Ti lunar mare basalts. The similarity in  $\delta^{49}\text{Ti}$  between terrestrial samples and  
46 low-Ti lunar basalts provides strong evidence that the Earth and Moon have identical  
47 stable Ti isotope compositions.

48 **1. Introduction**

49 Much of the stable isotope variation seen on Earth is mass-dependent in nature,  
50 scaling as a function of the difference in mass of the isotopes involved. Departures  
51 from such mass-dependent isotope fractionation are, however, commonplace in  
52 meteorites (Clayton, 1993; Dauphas et al., 2002) and one of the most intriguing  
53 features of the Earth-Moon system is the similarity of their mass-independent isotope  
54 signatures (e.g.: O: Clayton et al., 1973; Cr: Lugmair and Shukolyukov, 1998 Ti:  
55 Zhang et al., 2012;). This similarity is difficult to reconcile with simple giant impact  
56 models that predict that most of the Moon's mass should consist of impactor material,  
57 because in this case lunar rocks should have inherited the isotope composition of the  
58 impactor, which Pahlevan and Stevenson (2007) argued should have been different  
59 from that of the Earth. Different scenarios were proposed to explain this similarity  
60 ranging from isotope equilibration between Earth's mantle and the protolunar disk  
61 (Pahlevan and Stevenson, 2007), impact of a Mars-size body with a fast-spinning  
62 Earth (Cúk and Stewart, 2012), impact between two similar-sized protoplanets  
63 (Canup, 2012), "hit-and-run" impact (Reufer et al., 2012), or an Earth-like impactor  
64 (Dauphas et al., 2014a, Mastrobuono-Battisti et al., 2015). The wide range of  
65 physical processes invoked in each of these different models highlights the need to  
66 develop new tools to evaluate the consequences of each model on the chemical and  
67 isotopic evolution of the Moon with respect to the Earth.

68 Interestingly, and in contrast to many mass-independent isotope systems, the  
69 *mass dependent* stable isotope compositions of a number of elements in terrestrial  
70 and lunar samples display significant variations (e.g.: O and Fe: Liu et al., 2010;  
71 Poitrasson et al., 2004; Weyer et al., 2005; Mg: Sedaghatpour et al., 2013; Zn:  
72 Paniello et al., 2012; Li: Seith et al., 2006; Cl: Sharp et al., 2010; Cr: Bonnand et al.,  
73 2016). The stable isotope compositions of these elements have the potential to shed  
74 new light on the evolution of the Earth-Moon system as their variations are diagnostic  
75 features of a variety of processes such as volatile element depletion, core formation,

76 and magma ocean crystallization. However, many of these non-traditional stable  
77 isotope systems are affected by multiple processes, which complicate their  
78 interpretation.

79 Titanium has the advantage of being both lithophile and extremely refractory.  
80 It is therefore unlikely to have been affected by formation of the lunar and terrestrial  
81 cores, or volatile element depletion during the giant impact. It thus has the potential  
82 to provide unambiguous constraints on lunar magma ocean crystallization. Despite  
83 its abundance in igneous rocks and the extensive use of TiO<sub>2</sub> concentrations in high-  
84 temperature geochemistry, Ti stable isotopes have received very limited attention to  
85 date (Millet and Dauphas 2014; Zhang et al., 2014). Indeed, most of the studies so  
86 far focused on the detection of Ti isotopic anomalies to learn about nucleosynthetic  
87 processes, genetic relationships between planetary bodies, early solar system  
88 processes and/or cosmogenic effects (e.g.: Niederer et al., 1980; Niemeier, 1988;  
89 Trinquier et al., 2009; Zhang et al., 2011; 2012). Titanium exists in several  
90 coordinations in magmatic systems: it is predominantly present in 5-fold coordination  
91 in all silicate melts but is also present in 4- and 6-fold coordinations in silicic and  
92 mafic melts respectively (Farges et al., 1996; Farges and Brown, 1997). In addition,  
93 5-fold coordinated titanium transitions to 6-fold coordination during crystallisation of  
94 Ti-bearing oxides (Farges and Brown, 1997). As stable isotope theory (Schauble,  
95 2004) predicts that stable isotope fractionation will be driven by major contrasts in  
96 elemental bonding environment, the coordination behaviour of Ti raises the possibility  
97 that Ti stable isotopes may serve as a tracer of magmatic processes. Furthermore,  
98 as Ti is refractory and comparably immobile in fluids, Ti stable isotopes are also likely  
99 to be comparatively resistant to overprinting. A potential complexity however, lies  
100 with the presence of Ti<sup>3+</sup> in reduced magmas and planetary bodies such as the  
101 Moon. *f*O<sub>2</sub> estimates for the lunar mantle range from the iron-wüstite buffer to 2 log  
102 units below it (i.e. IW-2), with a most likely value of ~IW-1 (Wadhwa, 2008).  
103 Experimental work has shown that in these conditions, the lunar mantle could contain

104 up to 10%  $Ti^{3+}$  (Krawczynski et al., 2009). However, direct measurements of  $Ti^{3+}/\Sigma Ti$   
105 (Simon et al., 2014) in pyroxenes and olivines from lunar basalts have not detected  
106 any  $Ti^{3+}$ .

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

114

## 115 **2. Samples and methods**

### 116 **2.1 Samples**

117 In addition to the dataset already presented in Millet and Dauphas (2014), we have  
118 analysed 34 terrestrial samples reflecting a global coverage from a diverse range of  
119 geodynamic contexts. We have also analysed 8 primitive lunar mare basalts covering  
120 the range of  $TiO_2$  concentrations observed in lunar rocks.

121

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

128

129 *Island Arc Basalts*. The island arc basalts studied here mainly comprise basalts  
130 sampled from oceanic arcs in order to limit the potential for crustal contamination and  
131 assimilation processes. In addition to the New Britain basalt data published by Millet

132 and Dauphas (2014), 3 arc lavas from the Mariana arc were studied that were  
133 previously analysed for major and trace elements by Yi et al. (2000). A single basalt  
134 from the Izu-Bonin arc, rock standard JB-2, was also analysed.

135

136 *Intraplate basalts.* The intraplate basalts mainly comprise ocean island basalts (OIBs)  
137 from four different localities. Single samples from Hawaii (BHVO-2 rock standard)  
138 and Easter Island (sample 17678, Baker et al., 1974) were analysed as well as  
139 samples from the Cape Verde (São Nicolau island; Millet et al., 2008) and Azores  
140 archipelagos (São Miguel island: Turner et al., 1997; São Jorge island: Millet et al.,  
141 2009). In addition, a single continental flood basalt (the USGS rock standard BCR-2)  
142 was also analysed.

143

144 *Eclogites.* The three eclogites measured here were collected from the Zermatt-Saas  
145 Fee ophiolite, Switzerland. They consist of 2 basaltic eclogites and 1 gabbroic  
146 eclogite, based on their mineralogy (Dale et al., 2007). Estimates of peak  
147 metamorphic conditions for these samples range between 2-3 GPa and 550 to 630  
148 °C (Barnicoat and Fry, 1986; Reinecke, 1991). Major and trace element data (Dale et  
149 al., 2007) show that all the samples selected suffered loss of volatile and fluid-mobile  
150 elements during metamorphic dehydration.

151

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

160

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

171

172 *Lunar samples.* Nine lunar mare basalts were analysed. Specifically, we selected 5  
173 high-Ti basalts (TiO<sub>2</sub> ranging from 12.2 to 13.4wt%) and 3 low-Ti basalts (TiO<sub>2</sub>  
174 ranging from 1.9 to 3.3wt%). A single green glass sample was also analysed (sample  
175 15426, TiO<sub>2</sub> = 0.5 wt%).

176

## 177 **2.2. Methods**

178 Samples were processed and measured using the double-spike method of  
179 Millet and Dauphas (2014), which is briefly outlined here. Between 10 to 50 mg of  
180 rock powder (for whole rock samples) or glass chips (for MORB glasses) were  
181 digested in a 1:1 mixture of concentrated HF and HNO<sub>3</sub> for 48 hours. After careful  
182 evaporation, samples were then taken up in nitric acid and dried down 3 times before  
183 being taken up in 6 M HCl and checked for residual solids. If samples were fully  
184 digested, approximately 30 mg of H<sub>3</sub>BO<sub>3</sub> was added to the solution in order to ensure  
185 that any potential fluorides (for which Ti has a strong affinity) having escaped visual  
186 inspection are re-dissolved and thus ensure that all the Ti contained in the sample is  
187 in solution. An aliquot containing 5 to 20 µg of Ti is then taken and mixed with a <sup>47</sup>Ti-



188 <sup>49</sup>Ti double spike in appropriate proportions (the Ti concentrations of the various  
189 rocks analysed were known from prior work). Purification of Ti was achieved  
190 following the procedure designed by Zhang et al. (2011) and using a two-step  
191 chemistry. Firstly, the samples were passed through a TODGA cartridge to remove  
192 almost all sample matrix. Samples were then further purified using AG1-X8 resin in  
193 order to separate Mo (thus limiting potential doubly charged interferences on Ti  
194 isotopes) and remaining Ca. It is notable that lunar samples and BHVO-2 rock  
195 standard were digested at the Origins Laboratory of the University of Chicago by flux  
196 fusion method using LiBO<sub>3</sub> as a fluxing agent. This was to ensure that potential  
197 refractory phases were fully digested. After fusion, samples are dissolved in 3M  
198 HNO<sub>3</sub> before an aliquot containing 20µg of Ti is taken and spiked in ideal  
199 proportions. Chemical purification of Ti was achieved using the procedure outlined  
200 above.

201 Isotope ratio measurements were carried out on Neptune Plus MC-ICP-MS  
202 installed in the Arthur Holmes laboratory at Durham University and at the Origins  
203 Laboratory of the University of Chicago. The samples were injected into the plasma  
204 torch using an Aridus II desolvating nebuliser and the isotope measurements were  
205 performed in medium resolution mode. Despite being double-spiked, all sample  
206 measurements were bracketed by measurements of double-spiked standards (OL-Ti)  
207 measured at the same concentration level in order to account for small unresolved  
208 polyatomic interferences on <sup>47</sup>Ti and <sup>48</sup>Ti produced in the mass spectrometer. Raw  
209 data is then processed offline using in-house double-spike deconvolution codes  
210 written in Mathematica<sup>®</sup>. All data is expressed as δ<sup>49</sup>Ti, which is the deviation of the  
211 <sup>49</sup>Ti/<sup>47</sup>Ti ratio of samples relative to that of the OL-Ti standard (Millet and Dauphas,  
212 2014). This standard is available from the corresponding author upon request.

213 Finally, it should be noted that double-spike measurements rely on the  
214 assumption that the 4 isotopes used in the double-spike deconvolution routine are  
215 related to by mass-dependent stable isotope fractionation only. Double-spike method

216 can provide inaccurate result if any of the isotopes involved is affected by mass-  
217 independent variation. To this day, no mass-independent variations have been found  
218 in terrestrial samples for Ti isotopes, but significant  $^{50}\text{Ti}$  anomalies have been  
219 detected in lunar samples related to cosmic ray exposure. These anomalies could  
220 lead to potentially inaccurate results if not accounted for. For this reason, our double-  
221 spike deconvolution procedure uses  $^{46}\text{Ti}$ ,  $^{47}\text{Ti}$ ,  $^{48}\text{Ti}$ , and  $^{49}\text{Ti}$  that are only related to  
222 each other by mass-dependent fractionation in both terrestrial and lunar rocks.

223

#### 224 **4. Results**

225 Data for all standards and samples analysed during the course of this study  
226 are given in Table 1. For samples measured once only, quoted errors are internal  
227 errors, whereas for samples measured multiple times, 95% confidence intervals were  
228 calculated using the Isoplot software (Ludwig, 2003). Repeated digestion and  
229 analysis of BCR-2, BHVO-2 (HF or flux fusion digestion) and JB-2 reference  
230 materials, previously analysed by Millet and Dauphas (2014) at the Origins  
231 Laboratory (University of Chicago), were conducted in order to certify data quality  
232 and the absence of inter-laboratory bias (Fig.1). The average Ti isotope compositions  
233 of standards analysed at Durham University is in excellent agreement with that of the  
234 Origins Laboratory data and demonstrates that the  $2\sigma$  reproducibility of our  $\delta^{49}\text{Ti}$   
235 measurements is *ca.*  $\pm 0.020\%$ . In addition, we have carried out replicate digestions  
236 and analysis of the RGM-1 rock standard (only in Durham) which all display values  
237 within analytical uncertainty ( $0.548 \pm 0.014\%$ , 95% c.i.,  $n=4$ ). Finally, for BHVO-2 rock  
238 standard, measurements of flux fusion digestions carried out in Chicago displays  
239 value within analytical uncertainty of HF-HNO<sub>3</sub> digestions performed in both Durham  
240 and Chicago (Greber et al., 2016; Fig. 1)

241 The  $\delta^{49}\text{Ti}$  values of all terrestrial samples ranges from -0.046 to +0.548‰.  
242 Samples of differentiated magmas display a large range in Ti isotope compositions

243 and an overall enrichment in isotopically heavy Ti isotopes (+0.054 to +0.548‰)  
244 relative to basalts and mantle-derived rocks (-0.046 to +0.049‰), which display more  
245 homogeneous compositions. In the MORB, OIB and IAB sample subsets, there  
246 appear to be no differences related to sampling localities.

247 Unlike primitive terrestrial samples, primitive lunar basalts display small but  
248 resolvable Ti stable isotope heterogeneity, which relates to their TiO<sub>2</sub> content. High-  
249 Ti basalts display overall heavier  $\delta^{49}\text{Ti}$  values (+0.011‰ to +0.033‰) relative to  
250 those of low-Ti lunar basalts and the single green glass sample analysed (-0.008 to  
251 +0.011‰).

252

## 253 **5. Discussion**

254 Significant variations exist in the Ti stable isotope compositions of terrestrial  
255 and lunar magmatic samples (Table 1). Below, we discuss the probable causes of Ti  
256 stable isotope fractionation and evaluate the degree of homogeneity of the Earth's  
257 mantle in terms of Ti stable isotopes. We then focus on the variability observed in the  
258 Ti stable isotope composition of primitive lunar mare basalts and discuss the  
259 implications of these data for the magmatic evolution of the Moon.

260

### 261 *5.1 Ti stable isotope fractionation during magma differentiation*

262 A striking feature of our terrestrial sample dataset is the significant enrichment  
263 of differentiated magmatic rocks in isotopically heavy Ti isotopes relative to more  
264 primitive magmatic rocks. This enrichment is correlated with SiO<sub>2</sub> content, suggesting  
265 a relationship with fractional crystallisation processes (Fig. 2). Titanium is highly to  
266 moderately incompatible in most of the silicate minerals typically involved in magma  
267 differentiation (pyroxenes, olivine, plagioclase, micas, quartz) regardless of the  
268 composition of the melt. Mass balance considerations therefore suggest that it is  
269 unlikely that the crystallisation of silicate mineral phases could have modified the Ti  
270 isotopic composition of the remaining melt.

271 Titanium behaviour during fractional crystallisation is mainly controlled by the  
272 crystallisation of Fe-Ti oxides that can occur at all stages of magma differentiation.  
273 The coordination of Ti in silicate melts and oxide minerals was investigated by  
274 Farges et al. (1996) and Farges and Brown (1997). In silicate melts, Ti is  
275 predominantly present in 4, 5, and 6-fold coordinations, whereas Fe-Ti oxides  
276 exclusively accommodate 6-folded Ti (Farges et al., 1996). As stable isotope theory  
277 (Schauble, 2004) predicts that isotopically heavy species will be preferentially  
278 concentrated in low-coordination, high-force constant (stronger and stiffer) bonding  
279 environments, at equilibrium Fe-Ti oxides might thus display enrichments in  
280 isotopically light Ti relative to the co-existing melt. The progressive crystallisation of  
281 Fe-Ti oxides during magmatic differentiation could potentially, therefore, drive the  
282 residual melt to heavy isotope compositions.

283 In order to test this hypothesis, we have modelled the evolution of a primitive  
284 basaltic melt to a silicic composition by fractional crystallisation using Rhyolite  
285 MELTS software (Gualda et al., 2012). The composition of the starting material is set  
286 to be similar to that of arc basalts (see Fig. 2 caption), crystallisation occurs at 1 kbar  
287 and the relative oxygen fugacity is assumed to be constant at the NNO buffer. At  
288 each calculation step, the compositions and respective mass of melt and minerals in  
289 equilibrium are calculated. Steps are defined by a 5°C incremental temperature  
290 decrease from the liquidus temperature (here 1118°C). The calculation stops when  
291 the temperature reaches 900°C, at which point *ca.* 70% of the liquid has crystallised  
292 and the SiO<sub>2</sub> content of the remaining liquid has reached 66 wt%. The Ti isotope  
293 evolution of the melt is calculated, at each step, using a Rayleigh distillation law and  
294 a bulk Ti stable isotope fractionation factor between the residual melt and the  
295 minerals removed. As silicate minerals have a negligible effect on the budget of Ti in  
296 differentiating magmas, their contribution to the Ti isotope evolution of the residual  
297 melt must also be negligible. Consequently, the bulk melt-residue Ti stable isotope  
298 fractionation factor is equal to that between Fe-Ti oxides and melt

299 ( $\Delta^{49}\text{Ti}_{\text{oxide-melt}}$ ) weighted according to the relative proportion of Ti sequestered by  
300 oxides at each temperature step. Assuming that the fractionation is equilibrium in  
301 nature, the model reproduces the observed trend in  $\delta^{49}\text{Ti}$  vs.  $\text{SiO}_2$  well for an  
302 empirical value of  $\Delta^{49}\text{Ti}_{\text{oxide-melt}} = -0.23\text{‰} \times 10^6/T^2$  (with T in K) indicating that  
303 fractional crystallisation of Fe-Ti oxides is a viable mechanism to explain the  
304 progressive enrichments of magmas in isotopically heavy Ti with increasing silica  
305 content. The predicted fractionation between oxide and melt at 900 °C is -0.167‰ for  
306  $\delta^{49}\text{Ti}$ . For comparison, Nuclear Resonant Inelastic X-ray Scattering (NRIXS) force  
307 constant measurements predict an equilibrium iron isotope fractionation between  
308 ilmenite (Krawczynski et al., 2014) and  $\text{Fe}^{2+}$ -bearing basaltic glasses (Dauphas et al.  
309 2014b) at the same temperature of -0.09‰ for  $\delta^{56}\text{Fe}$  (i.e., -0.05 ‰/amu). The  
310 equilibrium Ti isotope fractionation factor between oxide and melt that is needed to  
311 account for Ti isotope variations in silicic rocks is thus very reasonable. It should be  
312 noted that our preferred model does not account for any potential dependence of the  
313 Ti stable isotope fractionation factor on melt or Fe-Ti oxide chemical composition.  
314 Experimental work as well as measurements of oxide minerals in well-characterised  
315 sample suites will be needed to ascertain the oxide-melt isotopic fractionation factor  
316 inferred from measurements of differentiated terrestrial rocks.

317         The origin of the heavy Fe isotopic composition of silicic rocks with >70wt%  
318 has been the subject of some debate. The explanations proposed thus far include  
319 iron mobilization by exsolved fluids (Poitrasson and Freydier, 2005; Heimann et al.,  
320 2008; Telus et al., 2012), Soret migration (Lundstrom, 2009), and fractional  
321 crystallization (Telus et al. 2012; Sossi et al. 2012; Dauphas et al. 2014b). For most  
322 silicic rocks, fluid exsolution is unlikely to be the culprit because more fluid mobile Zn  
323 does not display correlated fractionation and iron isotope enrichments also affect  
324 anhydrous A-type granites (Telus et al., 2012; Sossi et al. 2012). The finding of  
325 significant isotope variations for a fluid-immobile element like Ti in silicic magmatic

326 rocks supports the view that fractional crystallization can drive stable isotope  
327 fractionations in transition metals. Iron and titanium stable isotope variations in  
328 magmatic rocks probably bear considerable insights into the processes governing  
329 magmatic evolution but equilibrium fractionation factors between minerals and melts  
330 need to be better known to reap the fruits of those studies.

331

## 332 *5.2 The Ti stable isotope composition of terrestrial basalts and the Bulk Silicate Earth*

333 Basaltic magmas display less variation in  $\delta^{49}\text{Ti}$  relative to differentiated  
334 magmas (ca. 0.1‰ compared to ca. 0.6‰; Fig. 3). The variation observed is  
335 statistically significant (relative to analytical precision) and may be related to  
336 heterogeneity of the terrestrial mantle or other processes. However, the full range of  
337 basalt  $\delta^{49}\text{Ti}$  variability is also observed in subduction zone basalts at the high end of  
338 the  $\text{SiO}_2$  range (52-54 wt%). Two of the basaltic lavas from the Marianas and one  
339 New Britain sample display the heaviest Ti stable isotope compositions of all the  
340 basalts analysed, whereas the JB-2 rock standard (Izu-Bonin arc) displays the  
341 lightest composition of the entire sample set. Other basalt samples from the New  
342 Britain and Mariana arcs, which have lower silica contents, all display  $\delta^{49}\text{Ti}$  values  
343 within analytical uncertainties, indicating that these three samples may have already  
344 been affected by the early onset of Fe-Ti oxide fractionation and are thus not  
345 representative of the Ti stable isotope composition of the sub arc mantle anymore.  
346 Fractional crystallisation cannot however explain the composition of the JB-2 rock  
347 standard, as no mineral phase typically involved during basaltic melt differentiation  
348 (e.g. olivine, pyroxenes, plagioclase, spinel, garnet) has been identified to  
349 preferentially incorporate the heavy isotopes of titanium relative to melt at  
350 equilibrium. As an arc basalt, JB-2 is expected to display anomalously low  
351 abundances of fluid immobile elements such as Ti and Nb relative to elements of  
352 similar incompatibility (Sm and Tb for Ti, Th and La for Nb;  $Ti/Ti^* = Ti_N / \sqrt{Sm_N \times Tb_N}$ )

353 and  $Nb/Nb^* = Nb_N / \sqrt{Th_N \times La_N}$ , concentrations are normalised to the primitive  
354 mantle composition of McDonough and Sun, 1995) in normalised trace element  
355 patterns. For example, compiled data for the Izu-Bonin arc eruptives (obtained from  
356 Georoc database) show that at similar SiO<sub>2</sub> contents to JB-2 (53.2wt%), Izu-Bonin  
357 magmas typically have Ti/Ti\* of 0.7 to 0.85 and Nb/Nb\* of 0.16 to 0.35. While JB-2  
358 displays the strong negative Nb anomaly (Nb/Nb\* = 0.21) expected for island arc  
359 lavas, it does not display a negative Ti anomaly (Ti/Ti\* = 1.02). This feature can be  
360 explained by oxide accumulation in this sample. In contrast to Ti, Nb does not  
361 partition into Fe-Ti oxides (Nielsen and Beard, 2000) and therefore the accumulation  
362 of Fe-Ti oxides would lead to decoupling of Ti and Nb concentrations as well as  
363 enrichment in light isotopes of titanium.

364         Once samples that are affected by Fe-Ti oxide crystallisation or accumulation  
365 are removed (i.e. most silicic lavas from the Mariana arc, the most silicic New Britain  
366 sample and JB-2 rock standard), the average  $\delta^{49}\text{Ti}$  values for island arc  
367 (+0.007±0.010‰, 95% c.i., n=8), intraplate (+0.009±0.019‰, 95% c.i., n=7) and mid-  
368 ocean ridge basalts (+0.001±0.008‰, 95% c.i., n=7) are all within statistical error of  
369 each other and within our analytical uncertainty (see Fig.1). Titanium behaves as a  
370 moderately incompatible element during melting of either spinel or garnet-bearing  
371 peridotite (Prytulak and Elliott, 2007) and is efficiently extracted from the mantle  
372 during basalt genesis. Mass-balance considerations thus dictate that basalts should  
373 record the Ti isotopic composition of their mantle source, unless melting occurs  
374 under Ti-oxide saturation. Our data on primitive basalts therefore indicates that the  
375 Earth's upper mantle has a homogeneous Ti stable isotope composition, within the  
376 precision of our measurements. In addition, the fact that the average value of our  
377 mantle samples (Beni Bousera Orogenic peridotite and Western Alps serpentinites)  
378 is indistinguishable from the average of all the primitive basalts analysed  
379 ( $\delta^{49}\text{Ti}_{\text{basalts}} = +0.006 \pm 0.006 \text{‰}$ , 95% c.i., n=22 vs.  $\delta^{49}\text{Ti}_{\text{mantle}} = +0.013 \pm 0.023 \text{‰}$ , 95% c.i.,

380 n=4) suggests that the partial melting of typical mantle lithologies (olivine +  
381 clinopyroxene + orthopyroxene + spinel and/or garnet) does not fractionate Ti stable  
382 isotopes.

383 In the bulk silicate Earth, Ti is mainly hosted in the mantle with only a minor  
384 proportion stored in the continental crust (McDonough, 1991). It is therefore possible to  
385 calculate the Ti stable isotope composition of the Bulk Silicate Earth as the variance-  
386 weighted mean of primitive basalts, eclogites and mantle-derived samples analysed  
387 in this study, which yields a  $\delta^{49}\text{Ti}$  value for the BSE (bulk silicate Earth) of  
388  $+0.005\pm 0.005\text{‰}$  (95% c.i., n=29). It is worth noting that measurement of a fully  
389 processed OL-Ti standard (digestion + chemical purification) shows that the  
390 analytical method used generates accurate results at the  $\sim\pm 0.012\text{‰}$  precision level  
391 (Millet and Dauphas, 2014), so it is unknown if the  $\delta^{49}\text{Ti}$  of the BSE value is accurate  
392 at the  $\pm 0.005\text{‰}$  level.

393 It is notable that primitive island arc basalts and MORBs display the same Ti  
394 stable isotope compositions. The mobility of Ti and other high-field-strength elements  
395 in subduction zone systems is a highly debated subject that mainly revolves around  
396 the stability of Ti-bearing phases during metamorphism of the down-going slab and  
397 the nature and composition of fluids in associated dehydration (e.g. Kessel et al.,  
398 2005). Experimental constraints have shown that rutile has low solubility in pure-H<sub>2</sub>O  
399 fluids (Audetat and Keppler, 2005) and that the rutile-aqueous fluid partition  
400 coefficients for Ti, Nb and Ta are very high (Brenan et al., 1994). However, the  
401 presence of rutile in fluid-related mineral veins of deep-subducted rocks (Gao et al.,  
402 2007) indicates potential mobility of Ti and other HFSE in subduction zone  
403 environments. This is corroborated by recent experimental work on fluorine and  
404 chlorine-rich fluids (Rapp et al., 2010) and albite-saturated fluids (Antignano and  
405 Manning, 2008) in which Ti and other HFSE appear to be orders of magnitude more  
406 soluble than in pure-H<sub>2</sub>O fluids. It is unclear in what speciation Ti is present in such



407 fluids and it is thus hard to predict the direction and magnitude of stable isotope  
408 fractionation between rutile and co-existing fluids. Nevertheless, the bonding  
409 environment of Ti in halogen or Na-bearing fluids will be different to that of rutile and  
410 it is expected that this process will generate stable isotope fractionation. The identical  
411 average Ti stable isotope composition of MORBs and island-arc basalts therefore  
412 indicates that, even if Ti is mobilised during dehydration in subduction zones, this  
413 process does not affect the budget of Ti across the whole mantle wedge. Moreover,  
414 the fact that the eclogites and subduction-related serpentinites measured during this  
415 study display the same Ti isotope composition as MORBs ( $\delta^{49}\text{Ti}_{\text{eclogites}} = -$   
416  $0.014 \pm 0.015\text{‰}$ , 95% c.i.,  $n=3$  and  $\delta^{49}\text{Ti}_{\text{serpentinites}} = +0.016 \pm 0.043\text{‰}$ , 95% c.i.,  $n=3$ )  
417 despite having been extensively dehydrated argues against significant mobility of Ti  
418 in subduction zones and hints that recycling of oceanic lithosphere may not generate  
419 detectable Ti stable isotope variation within Earth's mantle.

420

### 421 *5.3 Titanium stable isotope heterogeneity of the lunar mantle as a consequence of* 422 *the LMO crystallisation*

423 Although limited in range, it appears that lunar mare basalts display slightly  
424 variable Ti stable isotope composition (Fig. 3). This variability is due to the heavier  
425 isotope composition of the high-Ti lunar basalts (Fig. 3). Titanium is an extremely  
426 refractory element that only partitions into gaseous phases at extremely high  
427 temperatures (Zhang et al., 2014). It is therefore extremely unlikely that the  
428 difference between the two classes of lunar basalts is a consequence of evaporation  
429 during eruptive processes, neither can it be due to silicate-metal segregation as core  
430 formation in both the Earth and Moon took place under conditions that were too  
431 oxidizing for titanium to partition into the core (Wade and Wood, 2001). The titanium  
432 stable isotope variability observed in lunar basalts must therefore be related to  
433 processes that took place during the magmatic evolution of the Moon.

434           The source of High-Ti basalts are thought to be genetically linked to ilmenite-  
435 bearing cumulates formed between 95% and 99.5% solidification of the LMO (e.g.  
436 Snyder et al., 1992) as opposed to the sources of Low-Ti basalts that are formed  
437 earlier (<85% solidification) in the solidification sequence of the LMO before the  
438 onset of ilmenite crystallization (e.g. Hallis et al., 2014). Other minerals present in  
439 lunar mantle sources are olivine and pyroxenes, in which Ti is highly to moderately  
440 incompatible. Low-Ti lunar basalts display  $\delta^{49}\text{Ti}$  values that are indistinguishable from  
441 that of the Earth's mantle. Results on terrestrial basalts undersaturated in Fe-Ti  
442 oxides ( $\text{SiO}_2 < 52\text{wt}\%$  in fig. 2) as well as mantle samples shows that olivine and  
443 pyroxenes do not fractionate Ti stable isotopes during fractional crystallisation or  
444 partial melting (Farges et al., 1996). Thus, low-Ti lunar basalts provide the best  
445 estimate of the Ti stable isotope composition of the lunar mantle, which is  $\delta^{49}\text{Ti}=-$   
446  $0.003\pm 0.014\text{‰}$  ( $n=4$ ) which is within statistical error to that of the Earth's mantle.  
447 Importantly, preliminary data for ordinary, enstatite and carbonaceous chondrites  
448 (Williams et al., 2015; Greber et al., 2016) also show uniform  $\delta^{49}\text{Ti}$  within error of the  
449 Earth's mantle ( $\delta^{49}\text{Ti}=+0.004\pm 0.010\text{‰}$ ; Greber et al., 2016). Taken overall, the data  
450 for terrestrial, lunar and meteoritic samples available to date is consistent with recent  
451 models arguing for an Earth-like composition of the Moon-forming impactor (Dauphas  
452 et al., 2014a; Mastrobuono-Battisti et al., 2015).

453           As a Fe-Ti oxide, ilmenite hosts six-fold Ti in its structure and is thus expected  
454 to preferentially incorporate light isotopes relative to melts at equilibrium as can be  
455 inferred from measurements of terrestrial silicic rocks. This behaviour provides an  
456 opportunity to test the models proposed for the generation of high-Ti lunar basalts. If  
457 all models agree on the involvement of an ilmenite-pyroxene cumulate layer in the  
458 late stages of LMO solidification, the details of the signatures of those cumulates  
459 were incorporated in high-Ti mare basalts is still a matter of debate. One view argues  
460 that high-Ti lunar basalts are derived from low-Ti lunar basalts through assimilation of

461 ilmenite and pyroxene during magma ascent to the surface (Wagner and Grove,  
462 1997). However, experimental work regarding the kinetics of assimilation of pyroxene  
463 and ilmenite suggests that ilmenite does not dissolve fast enough relative to  
464 pyroxene to generate compositions similar to high-Ti basalts (Van Orman and Grove,  
465 2000) and would instead generate melt composition too rich in calcium. The other  
466 view involves the fertilisation of deep-seated ilmenite-free cumulates (i.e. formed  
467 earlier during the solidification of the LMO) by sinking ilmenite-bearing cumulates  
468 (Hess and Parmentier, 1995; Hallis et al., 2014). Concerns regarding the buoyancy of  
469 magmas generated by such sources as well as the elevated viscosity of the ilmenite-  
470 rich layer have lead to the formulation of a third model. Instead of solid-state mixing,  
471 this last model argues for fertilisation of the ilmenite-free cumulates by negatively  
472 buoyant partial melts of the ilmenite-rich layer formed as a result of the late heavy  
473 bombardment (Van Orman and Grove, 2000; Elkins-Tanton et al., 2002, 2004).

474         In order to test the solid-state mixing and the partial-melt fertilisation models,  
475 we modelled the evolution of the LMO during the crystallisation of the ilmenite-rich  
476 layer and examined its impact on the Ti stable isotope composition of high-Ti lunar  
477 melts. We assume a Ti concentration of 3wt% at 95% PCS and mineral proportions  
478 similar to Snyder et al. (1992). At all steps of calculations, we calculate the Ti  
479 concentrations as well as the  $\delta^{49}\text{Ti}$  of the residual melt, instantaneous cumulates as  
480 well as the bulk cumulate. We use the oxide-melt Ti isotope fractionation factor  
481 calculated in section 5.1 as a proxy for the ilmenite-melt fractionation factor. A simple  
482 Rayleigh distillation model ( $T=1125^\circ\text{C}$ ; Van Orman and Grove, 2000) allows us to  
483 estimate the Ti stable isotope composition of the ilmenite-rich layer and evolving  
484 magma (Fig. 4). Calculations are stopped at 99.5% solidification, at which point  
485 0.25wt% Ti remains in the liquid. Overall, modelled ilmenite-bearing cumulates vary  
486 from -0.107‰ to +0.175‰. The remaining liquid at the end of ilmenite crystallisation  
487 is strongly enriched in heavy isotopes ( $\delta^{49}\text{Ti}=+0.288\text{‰}$ ).

488 For the solid-state mixing model, we followed calculations by Hallis et al.  
489 (2014) who argued that high-Ti lunar basalt sources formed by mixing ilmenite-free  
490 cumulate made at 80% PCS with cumulates formed at 95%PCS (earliest ilmenite  
491 cumulates) in 80:20 proportions, this mixture is then topped up with 1% of trapped  
492 instantaneous residual liquid (TIRL at 95%PCS). Assuming Ti concentrations of  
493 0.5wt% and 6wt% for the respective cumulates and 2.6wt% for the liquid (based on  
494 our LMO solidification model), it is possible to estimate a  $\delta^{49}\text{Ti}$  of the high-Ti lunar  
495 basalts mantle sources of -0.068‰. Interestingly, solid-state mixing models for the  
496 generation of high-Ti lunar basalts imply that ilmenite is exhausted during the  
497 generation of high-Ti melts (Ringwood and Kesson, 1976; Elkins-Tanton et al., 2002).  
498 Mass balance suggests that melts generated this way should display a  $\delta^{49}\text{Ti}$  identical  
499 to that of their source and therefore lighter than low-Ti lunar basalts, contrary to our  
500 measurements. However, if ilmenite was not exhausted during partial melting, high-Ti  
501 lunar basalts should display heavier isotope composition than this modelled source.  
502 Uncertainty on the kinetics of ilmenite dissolution during lunar mantle melting to make  
503 high-Ti mare basalts makes further modelling difficult. Nevertheless, if ilmenite was a  
504 residual phase during generation of high-Ti magma, one may expect a negative  
505 relationship between Ti content and  $\delta^{49}\text{Ti}$  of high-Ti lunar basalts. Such relationship  
506 does not appear in our data but this may be due to the relatively homogeneous  $\text{TiO}_2$   
507 content of the samples measured here (12.2 to 13.4wt%) compared to the full range  
508 shown by high-Ti lunar basalts.

509 An alternative to direct mixing of isotopically light ilmenite-bearing cumulates  
510 into the sources of low-Ti lunar basalts is the fertilisation of these sources by  
511 negatively buoyant partial melts of these cumulates. This partial melting may have  
512 occurred as a result of the late heavy bombardment, directly through shock melting  
513 but also by adiabatic melting cause by the incurred mantle convection. Regardless of  
514 the process involved, our results predict that these partial melts should be enriched in

515 heavy isotopes of Ti relative to the residue. Quantitative constraints on the  
516 composition of these melts is currently lacking but as such, this model may provide a  
517 straightforward way to generate lunar mantle source with both elevated Ti content  
518 and heavy Ti stable isotope composition

519

## 520 **6. Conclusion**

521 This study presents the first investigation of the stable Ti isotope compositions of  
522 terrestrial and lunar igneous rocks. The main conclusions of this study are:

523 • The Ti stable isotope composition of terrestrial magmas shows a large  
524 variability that appears to be positively correlated with SiO<sub>2</sub> content. This is most  
525 likely the result of crystallisation of isotopically light Ti-oxides during magmatic  
526 differentiation with  $\Delta^{49}\text{Ti}_{\text{oxide-melt}} = -0.23\text{‰} \times 10^6/T^2$ ; -0.106‰ at 1,200 °C). This  
527 observed fractionation is in agreement with the relative coordination of Ti between  
528 oxide minerals and silicate melts but further experimental data is needed to ascertain  
529 this value and assess whether it is equilibrium or kinetic in nature.

530 • The average  $\delta^{49}\text{Ti}$  values of primitive mid-ocean ridge, island-arc and  
531 intraplate basalts are identical within our analytical uncertainties (ca.  $\pm 0.020\text{‰}$ ). In  
532 addition, a preliminary set of mantle-derived samples also show  $\delta^{49}\text{Ti}$  values within  
533 error of primitive terrestrial basalts. This demonstrates that little Ti stable isotope  
534 fractionation occurs during partial melting, and suggests that Earth's mantle (and the  
535 by extension the bulk Earth because no Ti is in the core) has a homogeneous Ti  
536 stable isotope composition of  $\delta^{49}\text{Ti}_{\text{BSE}} = +0.005 \pm 0.005\text{‰}$  (95% c.i., n=29).

537 • The lack of any significant fractionation of Ti stable isotopes between  
538 MORBs, and island-arc basalts, as well as eclogites and serpentinites from  
539 subduction zones argues against a significant mobility of Ti in fluorine or chlorine  
540 bearing fluids across the mantle wedge during dehydration of downgoing slabs.

541 • Finally, primitive lunar basalts possess Ti stable isotope compositions  
542 ranging from terrestrial values to slightly enriched in heavy isotopes ( $\delta^{49}\text{Ti}$  up to  
543  $+0.033\pm 0.015\%$ ). Low-Ti lunar basalts all display  $\delta^{49}\text{Ti}$  values within error of the  
544 terrestrial mantle value whereas high-Ti lunar basalts display small but distinct  
545 enrichment in isotopically heavy Ti. The heavy  $\delta^{49}\text{Ti}$  values recorded in high-Ti mare  
546 basalts indicate that their mantle source regions may have been fertilised either by  
547 ilmenite cumulates formed in the latest stages of the LMO or by negatively buoyant  
548 partial melts of ilmenite-bearing cumulates during the Late Heavy Bombardment.

549

### 550 **Acknowledgements**

551 MAM acknowledges financial support from Durham University and a Marie Curie  
552 COFUND International Junior Fellowship held at Durham University. ND was  
553 supported by grants from NSF (EAR 1144429, 1444951, 1502591) and NASA  
554 (NNX12AH60G, NNX14AK09G, NNX15AJ25G). NDG was supported by the Swiss  
555 National Science Foundation (grant P2BEP2-158983). HMW acknowledges support  
556 from NERC Advanced Fellowship NE/F014295/2 and the ERC (Consolidator Grant  
557 “HabitablePlanet” 306655).

558

559 **References**

560 Antignano, A., and Manning, C. E., 2008, Rutile solubility in H<sub>2</sub>O, H<sub>2</sub>O-SiO<sub>2</sub>, and  
561 H<sub>2</sub>O-NaAlSi<sub>3</sub>O<sub>8</sub> fluids at 0.7-2.0 GPa and 700-1000 °C: implications for mobility of  
562 nominally insoluble elements. *Chemical Geology*, v. 255, p. 283-293.

563

564 Audetat A., Keppler H., 2005, Solubility of rutile in subduction zone fluids, as  
565 determined by experiments in the hydrothermal diamond anvil cell: *Earth and*  
566 *Planetary Science Letters*, v. 232, p. 393–402.

567

568 Baker P.E., Buckley F., Holland J.G., 1974, Petrology and geochemistry of Easter  
569 Island, *Contrib. Min. Petrol.*, 44, 2, 85-100.

570

571 Batiza, R., Niu, Y., 1992. Petrology and magma chamber processes at the East  
572 Pacific Rise 9°30'N. *J. Geophys. Res.* 97, 6779–6797.

573

574 Barnicoat A.C, Fry N., 1986, High-pressure metamorphism of the Zermatt-Saas  
575 ophiolite zone, Switzerland, *J. Geol. Soc.*, 143 (1986), pp. 607–618

576

577 Bonnand P., Parkinson I.J., Annand M., 2016, Mass dependent fractionation of stable  
578 chromium isotopes in mare basalts: Implications for the formation and the  
579 differentiation of the Moon, *Geochimica et Cosmochimica Acta*, 175 , pp. 208-221.

580 Brenan J.M., Shaw H.F., Phinney D.L., Ryerson F.J., 1994, Rutile-fluid partitioning of  
581 Nb, Ta, Zr, U and Th: Implications for high-field-strength element depletions in island-  
582 arc basalts, *Earth Planet. Sci. Lett.*, 128, pp. 327–339

583

584 Canup R.M., 2012, Forming a Moon with an Earth-like composition via a giant impact.  
585 *Science* 338, 1052–1055.

586

587 Clayton R.N., 1993, Oxygen isotopes in meteorites, *Annu. Rev. Earth Planet. Sci.*,  
588 21, 115-149  
589

590 Clayton R. N., Hurd J. M. and Mayeda T. K., 1973, Oxygen isotopic compositions of  
591 Apollo 15, 16, and 17 samples, and their bearing on lunar origin and petrogenesis.  
592 *Proc. 4th Lunar Sci. Conf.* 1535–1542.  
593

594 Cúk M, Stewart ST., 2012, Making the Moon from a fast-spinning Earth: a giant  
595 impact followed by resonant despinning. *Science*, 338, 1047–1052.  
596

597 Dale C.W., Gannoun A., Burton K.W., Argles T.W., Parkinson I.J., 2007, Rhenium–  
598 osmium isotope and elemental behaviour during subduction of oceanic crust and the  
599 implications for mantle recycling, *Earth Planet. Sci. Lett.*, 177, pp. 211–225  
600

601 Dauphas N., Marty B., Resiberg L., 2002, Molybdenum Nucleosynthetic Dichotomy  
602 Revealed in Primitive Meteorites, *ApJ*, 569:L139-L142.  
603

604 Dauphas N., Burkhardt C., Warren P.H., Teng F.-Z., 2014a, Geochemical arguments  
605 for an Earth-like Moon-forming impactor, *Phil. Trans. R. Soc. A* 372: 20130244.  
606 <http://dx.doi.org/10.1098/rsta.2013.0244>  
607

608 Dauphas N., Roskosz M., Alp E.E., Neuville D.R., Hu M.Y., Sio C.K., Tissot F.L.H.,  
609 Zhao J., Tissandier L., Médard E., Cordier C., 2014b, Magma redox and structural  
610 controls on iron isotope variations in Earth's mantle and crust, *Earth Planet. Sci.*  
611 *Lett.*, 398, pp. 127–140  
612



613 Debret, B., Andreani, M., Muñoz, M., Bolfan-Casanova, N., Carlut, J., Nicollet, C.,  
614 Schwartz, S., Trcera, N., 2014, Evolution of Fe redox state in serpentine during  
615 subduction. *Earth and Planetary Science Letters* 400, 206–218.  
616  
617 Dempsey S.R., 2012, *Geochemistry of the volcanic rocks from the Sunda arc*, PhD  
618 Thesis, Durham University.  
619  
620 Escrig S., Capmas F., Dupré B., Allégre C.J., 2004, Osmium isotopic constraints on  
621 the nature of the DUPAL anomaly from Indian mid-ocean-ridge basalts, *Nature*, 431,  
622 pp. 59–63  
623  
624 Elkins-Tanton L.T., Van Orman J.A., Hager B.H., Grove T.L., 2002, Re-examination  
625 of the lunar magma ocean cumulate overturn hypothesis: melting or mixing is  
626 required, *Earth Planet. Sci. Lett.*, 196, pp. 239-249  
627  
628 Elkins-Tanton L.T., Burgess S., Yin Q-Z., 2011, The lunar magma ocean: Reconciling  
629 the solidification process with lunar petrology and geochronology, *Earth Planet. Sci.*  
630 *Lett.*, 304, pp. 326-336  
631  
632 Elkins-Tanton L.T., Hager B.H., Grove T.L., 2004, Magmatic effects of the lunar late  
633 heavy bombardment, *Earth Planet. Sci. Lett.*, 222, pp. 17-27  
634  
635 Farges F., Brown Jr. G.E., Rehr J.J., 1996, Coordination chemistry of Ti (IV) in  
636 silicate glasses and melts: I. XAFS study of titanium coordination in oxide model  
637 compounds, *Geochimica et Cosmochimica Acta*, 60 (16) (1996), pp. 3023–3038  
638  
639 Farges F., Brown Jr. G.E., 1997, Coordination chemistry of titanium (IV) in silicate  
640 glasses and melts: IV. XANES studies of synthetic and natural volcanic glasses and

641 tektites at ambient temperature and pressure, *Geochim. Cosmochim. Acta*, 61 (9)  
642 (1997), pp. 1863–1870

643

644 Gao J., John T., Klemd R., Xiong X.M., 2007, Mobilization of Ti–Nb–Ta during  
645 subduction: evidence from rutile-bearing dehydration segregations and veins hosted  
646 in eclogite, Tianshan, NW China, *Geochim. Cosmochim. Acta*, 71, pp. 4974–4996

647

648 Greber N.D., Dauphas N., Millet M.-A., Puchel I.S., 2016, The titanium isotope  
649 composition of chondrites and Earth, *Lunar and Planetary Science XL*, Abstract  
650 #1448.

651

652 Gualda G.A.R., Ghiorso M.S., Lemons R.V., Carley T.L., 2012, Rhyolite-MELTS: a  
653 modified calibration of MELTS optimized for silica-rich, fluid-bearing magmatic  
654 systems, *J. Petrol.*, 53, pp. 875–890.

655

656 Heimann A., Beard B.L., Johnson C.M., 2008, The role of volatile exsolution and sub-  
657 solidus fluid/rock interactions in producing high  $^{56}\text{Fe}/^{54}\text{Fe}$  ratios in siliceous igneous  
658 rocks, *Geochimica et Cosmochimica Acta*, 72, 4379-4396.

659

660 Hallis L.J., Annand, M., Strekopytov S., 2014, Trace-element modeling of mare  
661 basalt parental melts: Implications for a heterogeneous lunar mantle, *Geochimica et*  
662 *Cosmochimica Acta*, 134, 289-316.

663

664 Hess P.C. and Parmentier E.M., 1995, A model for the thermal and chemical  
665 evolution of the Moon's interior: implications for the onset of mare volcanism, *Earth*  
666 *Planet. Sci. Lett.* 134, 501–514

667

668 Kessel R., Schmidt M.W., Ulmer P., Pettke T., 2005, Trace element signature of  
669 subduction-zone fluids, melts and supercritical liquids at 120–180 km depth, *Nature*,  
670 437, 724-727.

671

672 Krawczynski, M.J., Sutton, S.R., Grove. T.L., Newville, M., 2009, Titanium oxidation  
673 state and coordination in the lunar high-titanium glass source mantle. *Lunar and*  
674 *Planetary Science XL*, Abstract #2164.

675

676 Krawczynski, M.J., Millet M.-A., Dauphas N., Van Orman J.A., The mare basalt Fe-  
677 isotope dichotomy: a preliminary exploration into the role of ilmenite fractionation,  
678 *Lunar and Planetary Science XLIV*, Abstract #2620.

679

680 Liu Y, Spicuzza MJ, Craddock PR, Day J, Valley JW, Dauphas N, Taylor LA. 2010  
681 Oxygen and iron isotope constraints on near-surface fractionation effects and the  
682 composition of lunar mare basalt source regions. *Geochim. Cosmochim. Acta* 74,  
683 6249–6262.

684

685 Longhi J., 1992, Experimental petrology and petrogenesis of mare volcanics,  
686 *Geochim. Cosmochim. Acta*, 56, 2235-2251

687

688 Ludwig K. (2003) ISOPLOT: a geochronological toolkit for Microsoft Excel 3.00.  
689 Berkeley Geochronology Center Special Publication No. 4, Berkeley, CA 94709.

690

691 Lugmair G, Shukolyukov A. 1998 Early Solar System timescales according to <sup>53</sup>Mn-  
692 <sup>53</sup>Cr systematics. *Geochim. Cosmochim. Acta* 62, 2863–2886.

693

694 Lundstrom C.L., 2009, Hypothesis for the origin of convergent margin granitoids and  
695 Earth's continental crust by thermal migration zone refining, *Geochim. Cosmochim.*  
696 *Acta*, 73, 5709-5729  
697

698 Mastrobuono-Battisti A., Perets H.B., Raymond S., 2015, A primordial origin for the  
699 compositional similarity between the Earth and the Moon, *Nature*, 520, 212-215.  
700

701 McDonough W.F., 1991, Partial melting of subducted oceanic crust and its residual  
702 eclogitic lithology, *Philos. Trans. R. Soc. Lond. Ser. A: Math. Phys. Sci.*, 335 (1991),  
703 pp. 407–418  
704

705 McDonough W.F., Sun S.-S., 1995, The composition of the Earth, *Chem. Geol.*, 120  
706 (1995), pp. 223–253  
707

708 Millet, M.-A., Doucelance, R., Schiano, P., David, K. and Bosq, C., 2008, Mantle  
709 plume heterogeneity versus shallow-level interactions: A case study, the São Nicolau  
710 Island, Cape Verde archipelago. *Jour. Volc. Geo. Res.*, 176(2), 265-276  
711

712 Millet M.-A. and Dauphas N., 2014, Ultra-precise titanium stable isotope  
713 measurements by double-spike high resolution MC-ICP-MS *J. Anal. At. Spectrom.*,  
714 2014,29, 1444-1458  
715

716 Niederer F.R., Papanastassiou D.A., Wasserburg G.J. (1980) Endemic isotopic  
717 anomalies in titanium. *The Astrophysical Journal* 240, L73-L77.  
718

719 Nielsen, R.L. and Beard, J.S., 2000, Magnetite-melt HFSE partitioning, *Chemical*  
720 *Geology* 164: 21-34

721

722 Niemeyer S., 1988, Isotopic diversity in nebular dust: The distribution of Ti isotopic  
723 anomalies in carbonaceous chondrites. *Geochim. Cosmochim. Acta* 52, 2941-2954.

724

725 Pahlevan K, Stevenson DJ. 2007 Equilibration in the aftermath of the lunar-forming  
726 giant impact. *Earth Planet. Sci. Lett.* 262, 438–449

727

728 Paniello RC, Day JM, Moynier F., 2012, Zinc isotopic evidence for the origin of the  
729 Moon. *Nature* 490, 376–379.

730

731 Pearson D.G., Irvine G.J., Ionov D.A., Boyd F.R., Dreibus G.E., 2004, Re–Os isotope  
732 systematics and platinum group element fractionation during mantle melt extraction:  
733 a study of massif and xenolith peridotite suites, *Chem. Geol.*, 208, pp. 29–59

734

735 Poitrasson F., Halliday A.N., Lee D-C., Levasseur S., Teutsch N., 2004, Iron isotope  
736 differences between Earth, Moon, Mars and Vesta as possible records of contrasted  
737 accretion mechanisms, *Earth. Planet. Sci. Lett.*, 223, pp. 253-266

738

739 Poitrasson F., Freydier R., 2005, Heavy iron isotope composition of granites  
740 determined by high resolution MC-ICP-MS, *Chem. Geol.* 222, 132-147.

741

742 Prytulak J., Elliott T., 2007, TiO<sub>2</sub> enrichment in ocean island basalts, *Earth. Planet.*  
743 *Sci. Lett.*, 263, pp. 388–403

744

745 Puchelt H., Emmermann R., 1983, Petrogenetic implications of tholeiitic basalt  
746 glasses from the East Pacific rise and the Galapagos spreading center, *Chem. Geol.*,  
747 38 , pp. 39–56

748

749 Rapp J.F., Klemme S., Butler I.B., Harley S.L., 2010, Extremely high solubility of  
750 rutile in chloride and fluoride-bearing metamorphic fluids: an experimental  
751 investigation, *Geology*, 38, pp. 323–326  
752

753 Reinecke T, 1991, Very-high-pressure metamorphism and uplift of coesite bearing  
754 metasediments from the Zermatt-Saas zone, Western Alps, *Eur. J. Mineral.*, 3 (1),  
755 pp. 7–17  
756

757 Reufer A, Meier MM, Benz W, Wieler R. 2012 A hit-and-run giant impact scenario,  
758 *Icarus* 221, 296–299.  
759

760 Ringwood A.E., Kesson S.E., 1976, A dynamic model for mare basalt petrogenesis,  
761 *Proc. Lunar Planet. Sci. Conf.*, 7, pp. 1697–1722  
762

763 Schauble E. A., 2004, Applying stable isotope fractionation theory to new systems. In  
764 *Geochemistry of Non-traditional Stable Isotopes*, vol. 55 (eds. C. M. Johnson, B. L.  
765 Beard and F. Albarede). pp. 65–111  
766

767 Sedaghatpour F, Teng F-Z, Liu Y, Sears DW, Taylor LA. 2013 Magnesium isotopic  
768 composition of the Moon. *Geochim. Cosmochim. Acta* 120, 1–16.  
769

770 Seitz H-M, Brey GP, Weyer S, Durali S, Ott U, Münker C, Mezger K. 2006 Lithium  
771 isotope compositions of Martian and lunar reservoirs. *Earth Planet. Sci. Lett.* 245, 6–  
772 18.  
773

774 Simon S.B., Sutton S.R., Grossman L., 2008, Valence of Ti in lunar igneous rocks:  
775 The first direct measurements, *Lunar and Planetary Science XLV*, abstr. #1063.  
776

777 Simon S.B., Sutton S.R., Grossman L., 2014, Valence of Ti in lunar igneous rocks:  
778 The first direct measurements, *Lunar and Planetary Science XLV*, abstr. #1063.  
779

780 Sharp Z, Shearer C, McKeegan K, Barnes J, Wang Y. 2010 The chlorine isotope  
781 composition of the Moon and implications for an anhydrous mantle. *Science* 329,  
782 1050–1053.  
783

784 Snyder G.A., Taylor L.A., Neal C.R., 1992, A chemical model for generating the  
785 sources of mare basalts: combined equilibrium and fractional crystallization of the  
786 lunar magmasphere, *Geochim. Cosmochim. Acta* 56, 3809–3823.  
787

788 Sossi P.A., Foden J.D., Halverson G.P., 2012, Redox-controlled iron isotope  
789 fractionation during magmatic differentiation: an example from the Red Hill intrusion,  
790 S. Tasmania, *Contrib. Min. Petrol.*, 164, 757-772.  
791

792 Telus M., Dauphas N., Moynier F., Tissot F.L.H., Teng F-Z., Nabelek P.I., Craddock  
793 P.R., Groat L.A., 2012, Iron, zinc, magnesium and uranium isotopic fractionation  
794 during continental crust differentiation: The tale from migmatites, granitoids, and  
795 pegmatites, *Geochim. Cosmochim. Acta* 97, 247–26.5  
796

797 Trinquier A., Elliott T., Ulfbeck D., Coath C., Krot A.N., Bizzarro M, 2009, Origin of  
798 Nucleosynthetic Isotope Heterogeneity in the Solar Protoplanetary Disk, *Science*,  
799 324, 374-376  
800

801 Turner, S., Hawkesworth, C., Rogers, N. and King, P., 1997. U---Th isotope  
802 disequilibria and ocean island basalt generation in the Azores. *Chem. Geol.*, 139(1-  
803 4): 145-164  
804

805 Van Orman J.A., Grove T.L., 2000, Origin of lunar high-titanium ultramafic glasses:  
806 Constraints from phase relations and dissolution kinetics of clinopyroxene-ilmenite  
807 cumulates, *Meteoritics & Planetary Science*, 35, 783-794.  
808

809 Wade J., Wood B.J., 2001, The Earth's 'missing' Niobium may be in the core, *Nature*,  
810 409, pp. 75–78  
811

812 Weyer S, Anbar AD, Brey GP, Munker C, Mezger K, Woodland AB. 2005, Iron  
813 isotope fractionation during planetary differentiation. *Earth Planet. Sci. Lett.* 240,  
814 251–264  
815

816 Williams N.H., Schönbächler M., Fehr M.A., Akram W.M., Parkinson I.J., 2014,  
817 Different heterogeneously distributed Titanium isotope components in solar system  
818 materials and mass-dependent titanium isotope variations, *Lunar and Planetary*  
819 *Science XL*, Abstract #2183.  
820

821 Yi W., Halliday A.N., Alt J.C., Lee D.C., Reckhamper M., Garcia M.O., Su Y.J., 2000,  
822 Cadmium, indium, tin, tellurium, and sulfur in oceanic basalts: implications for  
823 chalcophile element fractionation in the Earth, *J. Geophys. Res.*, 105, pp. 18927–  
824 18948  
825

826 Zhang J., Dauphas N., Davis A. M. and Pourmand A., 2011, A new method for MC-  
827 ICPMS measurement of titanium isotopic composition: Identification of correlated  
828 isotope anomalies in meteorites. *J. Anal. At. Spectrom.* **26**, 2197–2205.  
829

830 Zhang J., Dauphas N., Davis A. M., Leya I. and Fedkin A., 2012, The proto-Earth as  
831 a significant source of lunar material. *Nature Geosci.* 5, 251–255.  
832



833 Zhang J., Huang S., Davis A.M., Dauphas N., Hashimoto A., Jacobsen S.B., 2014,  
834 Calcium and titanium isotopic fractionations during evaporation. *Geochim.*  
835 *Cosmochim. Acta* 140, 365-380.

836 **Captions**

837

838 Table 1: Ti stable isotope composition of samples measured during the course of this  
839 study. Data presented for samples replicated multiple times are weighted means and  
840 95% c.i. calculated using Isoplot (Ludwig, 2003). For rock standards BHVO-2, BCR-2  
841 and JB2, averages represent the combination of data obtained by Millet and  
842 Dauphas (2014) and this study. For BHVO-2, measurement made after flux fusion  
843 digestion carried out in Chicago is represented as a filled diamond.

844

845 **Figure 1:**  $\delta^{49}\text{Ti}$  values of BHVO-2, BCR-2 and JB2 basaltic rock standards measured  
846 during the course of this study. Filled symbols represent data generated at the  
847 Origins Laboratory and published in Millet and Dauphas (2014), while open symbols  
848 represent data obtained at Durham University. Data for all rock standards are in  
849 excellent agreement between the two laboratories.

850

851 **Figure 2:** Evolution of  $\delta^{49}\text{Ti}$  values with  $\text{SiO}_2$  concentration (wt%) of magmatic rocks.  
852 Arc basalts are in black squares whereas samples from the Agung volcano  
853 differentiation suite are in white squares. Other differentiated magmatic rocks are in  
854 grey circles. The budget of titanium during magma differentiation is controlled by the  
855 ongoing fractional crystallisation of isotopically light Ti oxides. Black curve represents  
856 the fractional crystallisation model generated using Rhyolite-Melts (see full text for  
857 details) and designed to fit the Agung Volcano cogenetic sample set. Starting melt  
858 composition (in wt%) is set at  $\text{SiO}_2$ : 50;  $\text{TiO}_2$ : 1;  $\text{Al}_2\text{O}_3$ : 18.5;  $\text{FeO}_{\text{tot}}$ : 11;  $\text{MnO}$ : 0.2;  
859  $\text{MgO}$ : 5.5;  $\text{CaO}$ : 9;  $\text{Na}_2\text{O}$ : 2.5;  $\text{K}_2\text{O}$ : 0.7;  $\text{P}_2\text{O}_5$ : 0.2;  $\text{H}_2\text{O}$ : 1.8. Best fit for the data is  
860 obtained using a Ti stable isotope fractionation factor between oxides and melts of

861 
$$\Delta^{49}\text{Ti}_{\text{oxide-melt}} = -0.23 \times 10^6 / T^2.$$

862

863 **Figure 3:** Ti stable isotope compositions ( $\delta^{49}\text{Ti}$  relative to OL-Ti) of terrestrial basalts,  
864 mantle-derived samples and eclogites as well as lunar mare basalts. Weighted  
865 means and 95% c.i. are calculated using Isoplot (Ludwig, 2003). Data for New Britain  
866 samples are from Millet and Dauphas (2014). Samples represented with open  
867 symbols show signs of fractionation or accumulation of Ti oxides based on  $\text{TiO}_2$   
868 concentrations and are removed from the calculation of the  $^{49}\text{Ti}$  value of the BSE.  
869 Once these samples are removed, the  $\delta^{49}\text{Ti}$  terrestrial igneous rocks show no  
870 resolvable variation between sampling location or geological context or petrographic  
871 type, indicating that the BSE has homogeneous Ti stable isotope composition of  
872  $+0.005\pm 0.005$  ‰ relative to OL-Ti (95% c.i.). Low-Ti lunar basalts (red) show  $\delta^{49}\text{Ti}$   
873 values within error of the BSE whereas High-Ti mare basalts (green) show values  
874 ranging from BSE to enriched in heavy isotopes.

875

876 **Figure 4:** Rayleigh distillation model showing the effect of ilmenite crystallisation  
877 during the late stages of solidification of the Lunar Magma Ocean. The ilmenite-melt  
878 Ti stable isotope fractionation factor is assumed to be equal to the oxide-melt  
879 fractionation factor calculated from the Agung volcano differentiation suite.  
880 Temperature is set at 1125°C and mineral proportions are taken from Snyder et al.  
881 (1992). Kds for Ti for the mineral phases are set as follows: Ilmenite: 20;  
882 Clinopyroxene: 0.15; Pigeonite: 0.15 and Plagioclase: 0.

883

Type/Locality	Sample	Lab	SiO <sub>2</sub>	TiO <sub>2</sub>	MgO	δ <sup>49</sup> Ti	95% c.i.	n
<i>MORB</i>								
North Atlantic	A127D8-2	Dur	50.08	0.81	9.43	-0.003	0.020	1
North Atlantic	A127D11-1	Dur	51.1	1.17	8.55	0.006	0.020	1
EPR	R94-2	Dur	51.0	1.33	7.59	0.002	0.028	1
EPR	R82-1	Dur	49.3	1.06	9.17	0.002	0.014	1
Pacific	Sonne12 42a	Dur	49.93	1.5	8.23	0.005	0.021	1
Indian	MD57 9-1	Dur	51.87	0.98	8.88	-0.010	0.025	1
Indian	MD57 10-1	Dur	50.69	1.68	6.84	0.011	0.040	1
<i>Island Arc Basalts</i>								
Japan	JB-2	Dur/OL	53.2	1.19	4.66	-0.046	0.009	3
Marianas	ALV1846-9	Dur	49.67	0.57	6.95	0.008	0.017	1
Marianas	1883-5	Dur	52.26	0.77	5.46	0.049	0.013	1
Marianas	1885-6	Dur	54.6	0.79	5.8	0.036	0.018	1
<i>Intraplate</i>								
Columbia River	BCR-2	Dur/OL	54.1	2.26	3.59	-0.015	0.005	12
Easter	17678	Dur	47.79	2.97	7.79	-0.004	0.020	1
Hawaii	BHVO-2	Dur/OL	49.9	2.73	7.23	0.020	0.006	12
Cape Verde	SN01	Dur	41.01	2.88	15.09	0.005	0.022	1
Cape Verde	SN10	Dur	39.88	2.90	12.50	0.008	0.022	1
Azores	S1	Dur	45.31	4.09	7.76	0.026	0.027	1
Azores	S3	Dur	46.43	3.59	8.34	0.037	0.018	1
Azores	SJ52	Dur	44.35	3.78	8.20	0.017	0.018	1
<i>Eclogites</i>								
Zermatt-Saas	SO241ii	Dur	47.14	2.75	5.20	-0.015	0.025	1
Zermatt-Saas	SO241v 2	Dur	49.04	2.72	5.51	0.004	0.031	1
Zermatt-Saas	SO284viix	Dur	49.9	0.7	8.8	-0.025	0.025	1
<i>Mantle-derived</i>								
Alpine Serpentinite	Bch9	Dur	40.21	0.09	36.04	0.012	0.031	1
Alpine Serpentinite	MM15	Dur	39.53	0.06	36.34	-0.003	0.028	1
Alpine Serpentinite	LZ14b	Dur	39.03	0.07	38.13	0.030	0.023	1
Beni Bousera Peridotite	GP13	Dur	44.91	0.14	39.79	0.007	0.022	1
<i>Differentiated magmas</i>								
Basaltic andesite	S19	Dur	54.49	2.11	6.38	0.103	0.022	2
Andesite	AGV1	Dur	58.84	1.05	1.53	0.084	0.029	2
Granite	G2	Dur	69.14	0.48	0.75	0.459	0.027	2
Rhyolite	RGM1	Dur	73.4	0.27	0.275	0.548	0.014	4
Agung	AGU03	Dur	58.01	0.76	2.92	0.120	0.027	1
Agung	AGU16	Dur	59.93	0.7	2.3	0.179	0.029	1
Agung	AGU20	Dur	62.69	0.6	1.77	0.248	0.032	1
Agung	AGU21	Dur	54.08	0.92	4.13	0.054	0.026	1
Agung	AGU23	Dur	56.42	0.76	2.95	0.108	0.029	1
Agung	AGU25	Dur	65.16	0.55	1.46	0.259	0.019	1
<i>Moon</i>								
High-Ti	70017	OL	--	13.3	--	0.015	0.011	5
High-Ti	70215	OL	--	13.0	--	0.033	0.015	5
High-Ti	71055	OL	--	13.4	--	0.011	0.017	5
High-Ti	72155	OL	--	12.2	--	0.023	0.009	5
High-Ti	75075	OL	--	13.4	--	0.018	0.014	5
Low-Ti	15597	OL	--	1.85	--	-0.008	0.010	5
Low-Ti	12009	OL	--	3.30	--	-0.008	0.013	5
Low-Ti	15016	OL	--	2.30	--	-0.008	0.019	4
Green Glass	15426	OL	--	0.50	--	0.011	0.017	4

