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

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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 and  
25 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 measurements  
30 are ca.  $\pm 0.02\text{‰}$  at 95% confidence). The Ti stable isotope compositions of  
31 differentiated terrestrial magmas define a well-defined positive correlation with  $\text{SiO}_2$   
32 content, which appears to result from the fractional crystallisation of Ti-bearing oxides  
33 with an inferred isotope fractionation factor of  $\Delta^{49}\text{Ti}_{\text{oxide-melt}} = -0.23\text{‰} \times 10^6/T^2$ .  
34 Primitive terrestrial basalts show no resolvable Ti isotope variations and display similar  
35 values to mantle-derived samples (peridotite and serpentinites), indicating that partial  
36 melting does not fractionate Ti stable isotopes and that the Earth's mantle has a  
37 homogeneous  $\delta^{49}\text{Ti}$  composition of  $+0.005 \pm 0.005$  (95% c.i.,  $n=30$ ). Eclogites also  
38 display similar Ti stable isotope compositions, suggesting that Ti is immobile during  
39 dehydration of subducted oceanic lithosphere. Lunar basalts have variable  $\delta^{49}\text{Ti}$   
40 values; low-Ti mare basalts have  $\delta^{49}\text{Ti}$  values similar to that of the bulk silicate Earth  
41 (BSE) while high-Ti lunar basalts display small enrichment in the heavy Ti isotopes.  
42 This is best interpreted in terms of source heterogeneity resulting from Ti stable isotope  
43 fractionation associated with ilmenite-melt equilibrium during the generation of the  
44 mantle source of high-Ti lunar mare basalts. The similarity in  $\delta^{49}\text{Ti}$  between terrestrial  
45 samples and low-Ti lunar basalts provides strong evidence that the Earth and Moon  
46 have identical stable Ti isotope compositions.

47 **1. Introduction**

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

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

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

77 Titanium has the advantage of being both lithophile and extremely refractory.  
78 It is therefore unlikely to have been affected by formation of the lunar and terrestrial  
79 cores, or volatile element depletion during the giant impact. It thus has the potential to  
80 provide unambiguous constraints on lunar magma ocean crystallization. Despite its  
81 abundance in igneous rocks and the extensive use of TiO<sub>2</sub> concentrations in high-  
82 temperature geochemistry, Ti stable isotopes have received very limited attention to  
83 date (Millet and Dauphas 2014; Zhang et al., 2014). Indeed, most of the studies so far  
84 focused on the detection of Ti isotopic anomalies to learn about nucleosynthetic  
85 processes, genetic relationships between planetary bodies, early solar system  
86 processes and/or cosmogenic effects (e.g.: Niederer et al., 1980; Niemeier, 1988;  
87 Trinquier et al., 2009; Zhang et al., 2011; 2012). Titanium exists in several  
88 coordinations in magmatic systems: it is predominantly present in 5-fold coordination  
89 in all silicate melts but is also present in 4- and 6-fold coordinations in silicic and mafic  
90 melts respectively (Farges et al., 1996; Farges and Brown, 1997). In addition, 5-fold  
91 coordinated titanium transitions to 6-fold coordination during crystallisation of Ti-  
92 bearing oxides (Farges and Brown, 1997). As stable isotope theory (Schauble, 2004)  
93 predicts that stable isotope fractionation will be driven by major contrasts in elemental  
94 bonding environment, the coordination behaviour of Ti raises the possibility that Ti  
95 stable isotopes may serve as a tracer of magmatic processes. Furthermore, as Ti is  
96 refractory and comparably immobile in fluids, Ti stable isotopes are also likely to be  
97 comparatively resistant to overprinting. A potential complexity however, lies with the  
98 presence of Ti<sup>3+</sup> in reduced magmas and planetary bodies such as the Moon.  $f_{O_2}$   
99 estimates for the lunar mantle range from the iron-wüstite buffer to 2 log units below it  
100 (i.e. IW-2), with a most likely value of ~IW-1 (Wadhwa, 2008). Experimental work has  
101 shown that in these conditions, the lunar mantle could contain up to 10% Ti<sup>3+</sup>

102 (Krawczynski et al., 2009). However, direct measurements of  $Ti^{3+}/\Sigma Ti$  (Simon et al.,  
103 2014) in pyroxenes and olivines from lunar basalts have not detected any  $Ti^{3+}$ .

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

111

## 112 **2. Samples and methods**

### 113 **2.1 Samples**

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

118

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

125

126 *Island Arc Basalts*. The island arc basalts studied here mainly comprise basalts  
127 sampled from oceanic arcs in order to limit the potential for crustal contamination and  
128 assimilation processes. In addition to the New Britain basalt data published by Millet  
129 and Dauphas (2014), 3 arc lavas from the Mariana arc were studied that were

130 previously analysed for major and trace elements by Yi et al. (2000). A single basalt  
131 from the Izu-Bonin arc, rock standard JB-2, was also analysed.

132

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

140

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

148

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

157

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

168

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

173

## 174 **2.2. Methods**

175 Samples were processed and measured using the double-spike method of  
176 Millet and Dauphas (2014), which is briefly outlined here. Between 10 to 50 mg of rock  
177 powder (for whole rock samples) or glass chips (for MORB glasses) were digested in  
178 a 1:1 mixture of concentrated HF and HNO<sub>3</sub> for 48 hours. After careful evaporation,  
179 samples were then taken up in nitric acid and dried down 3 times before being taken  
180 up in 6 M HCl and checked for residual solids. If samples were fully digested,  
181 approximately 30 mg of H<sub>3</sub>BO<sub>3</sub> was added to the solution in order to ensure that any  
182 potential fluorides (for which Ti has a strong affinity) having escaped visual inspection  
183 are re-dissolved and thus ensure that all the Ti contained in the sample is in solution.  
184 An aliquot containing 5 to 20 µg of Ti is then taken and mixed with a <sup>47</sup>Ti-<sup>49</sup>Ti double  
185 spike in appropriate proportions (the Ti concentrations of the various rocks analysed

186 were known from prior work). Purification of Ti was achieved following the procedure  
187 designed by Zhang et al. (2011) and using a two-step chemistry. Firstly, the samples  
188 were passed through a TODGA cartridge to remove almost all sample matrix. Samples  
189 were then further purified using AG1-X8 resin in order to separate Mo (thus limiting  
190 potential doubly charged interferences on Ti isotopes) and remaining Ca. It is notable  
191 that lunar samples and BHVO-2 rock standard were digested at the Origins Laboratory  
192 of the University of Chicago by flux fusion method using  $\text{LiBO}_3$  as a fluxing agent. This  
193 was to ensure that potential refractory phases were fully digested. After fusion,  
194 samples are dissolved in 3M  $\text{HNO}_3$  before an aliquot containing 20 $\mu\text{g}$  of Ti is taken  
195 and spiked in ideal proportions. Chemical purification of Ti was achieved using the  
196 procedure outlined above.

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

209 Finally, it should be noted that double-spike measurements rely on the  
210 assumption that the 4 isotopes used in the double-spike deconvolution routine are  
211 related to by mass-dependent stable isotope fractionation only. Double-spike method  
212 can provide inaccurate result if any of the isotopes involved is affected by mass-  
213 independent variation. To this day, no mass-independent variations have been found

214 in terrestrial samples for Ti isotopes, but significant  $^{50}\text{Ti}$  anomalies have been detected  
215 in lunar samples related to cosmic ray exposure. These anomalies could lead to  
216 potentially inaccurate results if not accounted for. For this reason, our double-spike  
217 deconvolution procedure uses  $^{46}\text{Ti}$ ,  $^{47}\text{Ti}$ ,  $^{48}\text{Ti}$ , and  $^{49}\text{Ti}$  that are only related to each other  
218 by mass-dependent fractionation in both terrestrial and lunar rocks.

219

#### 220 **4. Results**

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

237 The  $\delta^{49}\text{Ti}$  values of all terrestrial samples ranges from -0.046 to +0.548‰.  
238 Samples of differentiated magmas display a large range in Ti isotope compositions  
239 and an overall enrichment in isotopically heavy Ti isotopes (+0.054 to +0.548‰)  
240 relative to basalts and mantle-derived rocks (-0.046 to +0.049‰), which display more

241 homogeneous compositions. In the MORB, OIB and IAB sample subsets, there appear  
242 to be no differences related to sampling localities.

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

247

## 248 **5. Discussion**

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

255

### 256 *5.1 Ti stable isotope fractionation during magma differentiation*

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

266 Titanium behaviour during fractional crystallisation is mainly controlled by the  
267 crystallisation of Fe-Ti oxides that can occur at all stages of magma differentiation. The  
268 coordination of Ti in silicate melts and oxide minerals was investigated by Farges et

269 al. (1996) and Farges and Brown (1997). In silicate melts, Ti is predominantly present  
270 in 4, 5, and 6-fold coordinations, whereas Fe-Ti oxides exclusively accommodate 6-  
271 folded Ti (Farges et al., 1996). As stable isotope theory (Schauble, 2004) predicts that  
272 isotopically heavy species will be preferentially concentrated in low-coordination, high-  
273 force constant (stronger and stiffer) bonding environments, at equilibrium Fe-Ti oxides  
274 might thus display enrichments in isotopically light Ti relative to the co-existing melt.  
275 The progressive crystallisation of Fe-Ti oxides during magmatic differentiation could  
276 potentially, therefore, drive the residual melt to heavy isotope compositions.

277 In order to test this hypothesis, we have modelled the evolution of a primitive  
278 basaltic melt to a silicic composition by fractional crystallisation using Rhyolite MELTS  
279 software (Gualda et al., 2012). The composition of the starting material is set to be  
280 similar to that of arc basalts (see Fig. 2 caption), crystallisation occurs at 1 kbar and  
281 the relative oxygen fugacity is assumed to be constant at the NNO buffer. At each  
282 calculation step, the compositions and respective mass of melt and minerals in  
283 equilibrium are calculated. Steps are defined by a 5°C incremental temperature  
284 decrease from the liquidus temperature (here 1118°C). The calculation stops when the  
285 temperature reaches 900°C, at which point *ca.* 70% of the liquid has crystallised and  
286 the SiO<sub>2</sub> content of the remaining liquid has reached 66 wt%. The Ti isotope evolution  
287 of the melt is calculated, at each step, using a Rayleigh distillation law and a bulk Ti  
288 stable isotope fractionation factor between the residual melt and the minerals removed.  
289 As silicate minerals have a negligible effect on the budget of Ti in differentiating  
290 magmas, their contribution to the Ti isotope evolution of the residual melt must also be  
291 negligible. Consequently, the bulk melt-residue Ti stable isotope fractionation factor is  
292 equal to that between Fe-Ti oxides and melt ( $\Delta^{49}\text{Ti}_{\text{oxide-melt}}$ ) weighted according to  
293 the relative proportion of Ti sequestered by oxides at each temperature step. Assuming  
294 that the fractionation is equilibrium in nature, the model reproduces the observed trend  
295 in  $\delta^{49}\text{Ti}$  vs. SiO<sub>2</sub> well for an empirical value of  $\Delta^{49}\text{Ti}_{\text{oxide-melt}} = -0.23\text{‰} \times$

296  $10^6/T^2$  (with T in K) indicating that fractional crystallisation of Fe-Ti oxides is a viable  
297 mechanism to explain the progressive enrichments of magmas in isotopically heavy Ti  
298 with increasing silica content. The predicted fractionation between oxide and melt at  
299 900 °C is -0.167‰ for  $\delta^{49}\text{Ti}$ . For comparison, Nuclear Resonant Inelastic X-ray  
300 Scattering (NRXS) force constant measurements predict an equilibrium iron isotope  
301 fractionation between ilmenite (Krawczynski et al., 2014) and  $\text{Fe}^{2+}$ -bearing basaltic  
302 glasses (Dauphas et al. 2014b) at the same temperature of -0.09‰ for  $\delta^{56}\text{Fe}$  (i.e., -  
303 0.05 ‰/amu). The equilibrium Ti isotope fractionation factor between oxide and melt  
304 that is needed to account for Ti isotope variations in silicic rocks is thus very  
305 reasonable. It should be noted that our preferred model does not account for any  
306 potential dependence of the Ti stable isotope fractionation factor on melt or Fe-Ti oxide  
307 chemical composition. Experimental work as well as measurements of oxide minerals  
308 in well-characterised sample suites will be needed to ascertain the oxide-melt isotopic  
309 fractionation factor inferred from measurements of differentiated terrestrial rocks.

310         The origin of the heavy Fe isotopic composition of silicic rocks with >70wt%  
311 has been the subject of some debate. The explanations proposed thus far include iron  
312 mobilization by exsolved fluids (Poitrasson and Freydier, 2005; Heimann et al., 2008;  
313 Telus et al., 2012), Soret migration (Lundstrom, 2009), and fractional crystallization  
314 (Telus et al. 2012; Sossi et al. 2012; Dauphas et al. 2014b). For most silicic rocks, fluid  
315 exsolution is unlikely to be the culprit because more fluid mobile Zn does not display  
316 correlated fractionation and iron isotope enrichments also affect anhydrous A-type  
317 granites (Telus et al., 2012; Sossi et al. 2012). The finding of significant isotope  
318 variations for a fluid-immobile element like Ti in silicic magmatic rocks supports the  
319 view that fractional crystallization can drive stable isotope fractionations in transition  
320 metals. Iron and titanium stable isotope variations in magmatic rocks probably bear  
321 considerable insights into the processes governing magmatic evolution but equilibrium

322 fractionation factors between minerals and melts need to be better know to reap the  
323 fruits of those studies.

324

## 325 *5.2 The Ti stable isotope composition of terrestrial basalts and the Bulk Silicate Earth*

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

345  $Ti/Ti^* = Ti_N / \sqrt{Sm_N \times Tb_N}$  and  $Nb/Nb^* = Nb_N / \sqrt{Th_N \times La_N}$ , concentrations are

346 normalised to the primitive mantle composition of McDonough and Sun, 1995) in  
347 normalised trace element patterns. For example, compiled data for the Izu-Bonin arc  
348 eruptives (obtained from Georoc database) show that at similar  $\text{SiO}_2$  contents to JB-2

349 (53.2wt%), Izu-Bonin magmas typically have  $Ti/Ti^*$  of 0.7 to 0.85 and  $Nb/Nb^*$  of 0.16  
350 to 0.35. While JB-2 displays the strong negative Nb anomaly ( $Nb/Nb^* = 0.21$ ) expected  
351 for island arc lavas, it does not display a negative Ti anomaly ( $Ti/Ti^* = 1.02$ ). This  
352 feature can be explained by oxide accumulation in this sample. In contrast to Ti, Nb  
353 does not partition into Fe-Ti oxides (Nielsen and Beard, 2000) and therefore the  
354 accumulation of Fe-Ti oxides would lead to decoupling of Ti and Nb concentrations as  
355 well as enrichment in light isotopes of titanium.

356         Once samples that are affected by Fe-Ti oxide crystallisation or accumulation  
357 are removed (i.e. most silicic lavas from the Mariana arc, the most silicic New Britain  
358 sample and JB-2 rock standard), the average  $\delta^{49}Ti$  values for island arc  
359 ( $+0.007 \pm 0.010\text{‰}$ , 95% c.i.,  $n=8$ ), intraplate ( $+0.009 \pm 0.019\text{‰}$ , 95% c.i.,  $n=7$ ) and mid-  
360 ocean ridge basalts ( $+0.001 \pm 0.008\text{‰}$ , 95% c.i.,  $n=7$ ) are all within statistical error of  
361 each other and within our analytical uncertainty (see Fig.1). Titanium behaves as a  
362 moderately incompatible element during melting of either spinel or garnet-bearing  
363 peridotite (Prytulak and Elliott, 2007) and is efficiently extracted from the mantle during  
364 basalt genesis. Mass-balance considerations thus dictate that basalts should record  
365 the Ti isotopic composition of their mantle source, unless melting occurs under Ti-oxide  
366 saturation. Our data on primitive basalts therefore indicates that the Earth's upper  
367 mantle has a homogeneous Ti stable isotope composition, within the precision of our  
368 measurements. In addition, the fact that the average value of our mantle samples (Beni  
369 Bousera Orogenic peridotite and Western Alps serpentinites) is indistinguishable from  
370 the average of all the primitive basalts analysed ( $\delta^{49}Ti_{\text{basalts}} = +0.006 \pm 0.006\text{‰}$ , 95% c.i.,  
371  $n=22$  vs.  $\delta^{49}Ti_{\text{mantle}} = +0.013 \pm 0.023\text{‰}$ , 95% c.i.,  $n=4$ ) suggests that the partial melting of  
372 typical mantle lithologies (olivine + clinopyroxene + orthopyroxene + spinel and/or  
373 garnet) does not fractionate Ti stable isotopes.

374         In the bulk silicate Earth, Ti is mainly hosted in the mantle with only a minor  
375 proportion stored the continental crust (McDonough, 1991). It is therefore possible to

376 calculate the Ti stable isotope composition of the Bulk Silicate Earth as the variance-  
377 weighted mean of primitive basalts, eclogites and mantle-derived samples analysed in  
378 this study, which yields a  $\delta^{49}\text{Ti}$  value for the BSE (bulk silicate Earth) of  
379  $+0.005\pm 0.005\%$  (95% c.i.,  $n=29$ ). It is worth noting that measurement of a fully  
380 processed OL-Ti standard (digestion + chemical purification) shows that the analytical  
381 method used generates accurate results at the  $\sim\pm 0.012\%$  precision level (Millet and  
382 Dauphas, 2014), so it is unknown if the  $\delta^{49}\text{Ti}$  of the BSE value is accurate at the  
383  $\pm 0.005\%$  level.

384 It is notable that primitive island arc basalts and MORBs display the same Ti  
385 stable isotope compositions. The mobility of Ti and other high-field-strength elements  
386 in subduction zone systems is a highly debated subject that mainly revolves around  
387 the stability of Ti-bearing phases during metamorphism of the down-going slab and the  
388 nature and composition of fluids in associated dehydration (e.g. Kessel et al., 2005).  
389 Experimental constraints have shown that rutile has low solubility in pure- $\text{H}_2\text{O}$  fluids  
390 (Audetat and Keppler, 2005) and that the rutile-aqueous fluid partition coefficients for  
391 Ti, Nb and Ta are very high (Brenan et al., 1994). However, the presence of rutile in  
392 fluid-related mineral veins of deep-subducted rocks (Gao et al., 2007) indicates  
393 potential mobility of Ti and other HFSE in subduction zone environments. This is  
394 corroborated by recent experimental work on fluorine and chlorine-rich fluids (Rapp et  
395 al., 2010) and albite-saturated fluids (Antignano and Manning, 2008) in which Ti and  
396 other HFSE appear to be orders of magnitude more soluble than in pure- $\text{H}_2\text{O}$  fluids. It  
397 is unclear in what speciation Ti is present in such fluids and it is thus hard to predict  
398 the direction and magnitude of stable isotope fractionation between rutile and co-  
399 existing fluids. Nevertheless, the bonding environment of Ti in halogen or Na-bearing  
400 fluids will be different to that of rutile and it is expected that this process will generate  
401 stable isotope fractionation. The identical average Ti stable isotope composition of  
402 MORBs and island-arc basalts therefore indicates that, even if Ti is mobilised during

403 dehydration in subduction zones, this process does not affect the budget of Ti across  
404 the whole mantle wedge. Moreover, the fact that the eclogites and subduction-related  
405 serpentinites measured during this study display the same Ti isotope composition as  
406 MORBs ( $\delta^{49}\text{Ti}_{\text{eclogites}}=-0.014\pm 0.015\text{‰}$ , 95% c.i., n=3 and  
407  $\delta^{49}\text{Ti}_{\text{serpentinites}}=+0.016\pm 0.043\text{‰}$ , 95% c.i., n=3) despite having been extensively  
408 dehydrated argues against significant mobility of Ti in subduction zones and hints that  
409 recycling of oceanic lithosphere may not generate detectable Ti stable isotope  
410 variation within Earth's mantle.

411

### 412 *5.3 Titanium stable isotope heterogeneity of the lunar mantle as a consequence of the* 413 *LMO crystallisation*

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

425 The source of High-Ti basalts are thought to be genetically linked to ilmenite-  
426 bearing cumulates formed between 95% and 99.5% solidification of the LMO (e.g.  
427 Snyder et al., 1992) as opposed to the sources of Low-Ti basalts that are formed earlier  
428 (<85% solidification) in the solidification sequence of the LMO before the onset of  
429 ilmenite crystallization (e.g. Hallis et al., 2014). Other minerals present in lunar mantle

430 sources are olivine and pyroxenes, in which Ti is highly to moderately incompatible.  
431 Low-Ti lunar basalts display  $\delta^{49}\text{Ti}$  values that are indistinguishable from that of the  
432 Earth's mantle. Results on terrestrial basalts undersaturated in Fe-Ti oxides ( $\text{SiO}_2 <$   
433  $52\text{wt\%}$  in fig. 2) as well as mantle samples shows that olivine and pyroxenes do not  
434 fractionate Ti stable isotopes during fractional crystallisation or partial melting (Farges  
435 et al., 1996). Thus, low-Ti lunar basalts provide the best estimate of the Ti stable  
436 isotope composition of the lunar mantle, which is  $\delta^{49}\text{Ti} = -0.003 \pm 0.014\text{‰}$  ( $n=4$ ) which is  
437 within statistical error to that of the Earth's mantle. Importantly, preliminary data for  
438 ordinary, enstatite and carbonaceous chondrites (Williams et al., 2015; Greber et al.,  
439 2016) also show uniform  $\delta^{49}\text{Ti}$  within error of the Earth's mantle  
440 ( $\delta^{49}\text{Ti} = +0.004 \pm 0.010\text{‰}$ ; Greber et al., 2016). Taken overall, the data for terrestrial,  
441 lunar and meteoritic samples available to date is consistent with recent models arguing  
442 for an Earth-like composition of the Moon-forming impactor (Dauphas et al., 2014a;  
443 Mastrobuono-Battisti et al., 2015).

444 As a Fe-Ti oxide, ilmenite hosts six-fold Ti in its structure and is thus expected  
445 to preferentially incorporate light isotopes relative to melts at equilibrium as can be  
446 inferred from measurements of terrestrial silicic rocks. This behaviour provides an  
447 opportunity to test the models proposed for the generation of high-Ti lunar basalts. If  
448 all models agree on the involvement of an ilmenite-pyroxene cumulate layer in the late  
449 stages of LMO solidification, the details of the signatures of those cumulates were  
450 incorporated in high-Ti mare basalts is still a matter of debate. One view argues that  
451 high-Ti lunar basalts are derived from low-Ti lunar basalts through assimilation of  
452 ilmenite and pyroxene during magma ascent to the surface (Wagner and Grove, 1997).  
453 However, experimental work regarding the kinetics of assimilation of pyroxene and  
454 ilmenite suggests that ilmenite does not dissolve fast enough relative to pyroxene to  
455 generate compositions similar to high-Ti basalts (Van Orman and Grove, 2000) and  
456 would instead generate melt composition too rich in calcium. The other view involves

457 the fertilisation of deep-seated ilmenite-free cumulates (i.e. formed earlier during the  
458 solidification of the LMO) by sinking ilmenite-bearing cumulates (Hess and Parmentier,  
459 1995; Hallis et al., 2014). Concerns regarding the buoyancy of magmas generated by  
460 such sources as well as the elevated viscosity of the ilmenite-rich layer have lead to  
461 the formulation of a third model. Instead of solid-state mixing, this last model argues  
462 for fertilisation of the ilmenite-free cumulates by negatively buoyant partial melts of the  
463 ilmenite-rich layer formed as a result of the late heavy bombardment (Van Orman and  
464 Grove, 2000; Elkins-Tanton et al., 2002, 2004).

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

479 For the solid-state mixing model, we followed calculations by Hallis et al. (2014)  
480 who argued that high-Ti lunar basalt sources formed by mixing ilmenite-free cumulate  
481 made at 80% PCS with cumulates formed at 95%PCS (earliest ilmenite cumulates) in  
482 80:20 proportions, this mixture is then topped up with 1% of trapped instantaneous  
483 residual liquid (TIRL at 95%PCS). Assuming Ti concentrations of 0.5wt% and 6wt%

484 for the respective cumulates and 2.6wt% for the liquid (based on our LMO solidification  
485 model), it is possible to estimate a  $\delta^{49}\text{Ti}$  of the high-Ti lunar basalts mantle sources of  
486 -0.068‰. Interestingly, solid-state mixing models for the generation of high-Ti lunar  
487 basalts imply that ilmenite is exhausted during the generation of high-Ti melts  
488 (Ringwood and Kesson, 1976; Elkins-Tanton et al., 2002). Mass balance suggests that  
489 melts generated this way should display a  $\delta^{49}\text{Ti}$  identical to that of their source and  
490 therefore lighter than low-Ti lunar basalts, contrary to our measurements. However, if  
491 ilmenite was not exhausted during partial melting, high-Ti lunar basalts should display  
492 heavier isotope composition than this modelled source. Uncertainty on the kinetics of  
493 ilmenite dissolution during lunar mantle melting to make high-Ti mare basalts makes  
494 further modelling difficult. Nevertheless, if ilmenite was a residual phase during  
495 generation of high-Ti magma, one may expect a negative relationship between Ti  
496 content and  $\delta^{49}\text{Ti}$  of high-Ti lunar basalts. Such relationship does not appear in our  
497 data but this may be due to the relatively homogeneous  $\text{TiO}_2$  content of the samples  
498 measured here (12.2 to 13.4wt%) compared to the full range shown by high-Ti lunar  
499 basalts.

500 An alternative to direct mixing of isotopically light ilmenite-bearing cumulates  
501 into the sources of low-Ti lunar basalts is the fertilisation of these sources by negatively  
502 buoyant partial melts of these cumulates. This partial melting may have occurred as a  
503 result of the late heavy bombardment, directly through shock melting but also by  
504 adiabatic melting cause by the incurred mantle convection. Regardless of the process  
505 involved, our results predict that these partial melts should be enriched in heavy  
506 isotopes of Ti relative to the residue. Quantitative constraints on the composition of  
507 these melts is currently lacking but as such, this model may provide a straightforward  
508 way to generate lunar mantle source with both elevated Ti content and heavy Ti stable  
509 isotope composition

510

511 **6. Conclusion**

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

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

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

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

532 • Finally, primitive lunar basalts possess Ti stable isotope compositions ranging  
533 from terrestrial values to slightly enriched in heavy isotopes ( $\delta^{49}\text{Ti}$  up to  
534  $+0.033 \pm 0.015\text{‰}$ ). Low-Ti lunar basalts all display  $\delta^{49}\text{Ti}$  values within error of the  
535 terrestrial mantle value whereas high-Ti lunar basalts display small but distinct  
536 enrichment in isotopically heavy Ti. The heavy  $\delta^{49}\text{Ti}$  values recorded in high-Ti mare  
537 basalts indicate that their mantle source regions may have been fertilised either by

538 ilmenite cumulates formed in the latest stages of the LMO or by negatively buoyant  
539 partial melts of ilmenite-bearing cumulates during the Late Heavy Bombardment.

540

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825 **Captions**

826

827 Table 1: Ti stable isotope composition of samples measured during the course of this  
828 study. Data presented for samples replicated multiple times are weighted means and  
829 95% c.i. calculated using Isoplot (Ludwig, 2003). For rock standards BHVO-2, BCR-2  
830 and JB2, averages represent the combination of data obtained by Millet and Dauphas  
831 (2014) and this study. For BHVO-2, measurement made after flux fusion digestion  
832 carried out in Chicago is represented as a filled diamond.

833

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

839

840 **Figure 2:** Evolution of  $\delta^{49}\text{Ti}$  values with  $\text{SiO}_2$  concentration (wt%) of magmatic rocks.  
841 Arc basalts are in black squares whereas samples from the Agung volcano  
842 differentiation suite are in white squares. Other differentiated magmatic rocks are in  
843 grey circles. The budget of titanium during magma differentiation is controlled by the  
844 ongoing fractional crystallisation of isotopically light Ti oxides. Black curve represents  
845 the fractional crystallisation model generated using Rhyolite-Melts (see full text for  
846 details) and designed to fit the Agung Volcano cogenetic sample set. Starting melt  
847 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;  $\text{MgO}$ :  
848 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 obtained  
849 using a Ti stable isotope fractionation factor between oxides and melts of  
850  $\Delta^{49}\text{Ti}_{\text{oxide-melt}} = -0.23 \times 10^6 / T^2$ .

851

852 **Figure 3:** Ti stable isotope compositions ( $\delta^{49}\text{Ti}$  relative to OL-Ti) of terrestrial basalts,  
853 mantle-derived samples and eclogites as well as lunar mare basalts. Weighted means  
854 and 95% c.i. are calculated using Isoplot (Ludwig, 2003). Data for New Britain samples  
855 are from Millet and Dauphas (2014). Samples represented with open symbols show  
856 signs of fractionation or accumulation of Ti oxides based on  $\text{TiO}_2$  concentrations and  
857 are removed from the calculation of the  $^{49}\text{Ti}$  value of the BSE. Once these samples are  
858 removed, the  $\delta^{49}\text{Ti}$  terrestrial igneous rocks show no resolvable variation between  
859 sampling location or geological context or petrographic type, indicating that the BSE  
860 has homogeneous Ti stable isotope composition of  $+0.005\pm 0.005$  ‰ relative to OL-Ti  
861 (95% c.i.). Low-Ti lunar basalts (red) show  $\delta^{49}\text{Ti}$  values within error of the BSE whereas  
862 High-Ti mare basalts (green) show values ranging from BSE to enriched in heavy  
863 isotopes.

864

865 **Figure 4:** Rayleigh distillation model showing the effect of ilmenite crystallisation during  
866 the late stages of solidification of the Lunar Magma Ocean. The ilmenite-melt Ti stable  
867 isotope fractionation factor is assumed to be equal to the oxide-melt fractionation factor  
868 calculated from the Agung volcano differentiation suite. Temperature is set at  $1125^\circ\text{C}$   
869 and mineral proportions are taken from Snyder et al. (1992). Kds for Ti for the mineral  
870 phases are set as follows: Ilmenite: 20; Clinopyroxene: 0.15; Pigeonite: 0.15 and  
871 Plagioclase: 0.

872

873 **Table 1**

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>								
<i>Japan</i>	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	SO284viiix	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

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