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2 An Earth-Moon silicon isotope model

3 to track silicic magma origins

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15 **Abstract**

16 A comparison between lunar and terrestrial igneous rocks reveals that Si isotope
17 compositions become slightly, though significantly enriched in heavy isotopes from basalts to
18 granites as a function of the rock SiO_2 concentration and/or tectosilicate content. This is
19 interpreted as the result of a global igneous differentiation process that leads to an increased
20 amount of tectosilicates in the rocks. This relationship of increasing degree of melt
21 polymerization with increasing silicon isotope composition is particularly apparent in lunar
22 rocks. The terrestrial trend, however, is more scattered. Given the sensitivity of Si isotopes to
23 water-rock interactions, it is likely that the more erratic terrestrial trend reveals the
24 involvement of water that does not occur on the Moon. Hence, Si isotopes appear to reflect
25 the occurrence of low temperature water-rock interaction products, like clay minerals, in the
26 source of peraluminous leucogranites. Conversely, the heavy silicon isotope composition of
27 some andesites possibly trace the input of fluids involved in subduction zones and/or
28 interaction of the oceanic crust with isotopically heavy seawater before subduction.

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30 Keywords: Earth; Moon; igneous differentiation; silicon isotopes; granite; andesite

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32 **1. INTRODUCTION**

33 The origin of silicic rocks is an area of active research given their importance on the
34 enigmatic question regarding terrestrial continental crust formation and evolution. Radiogenic
35 and stable isotopes have been widely used to study granitoid sources, yet traditional isotopic
36 tracers rarely yield unambiguous information on magma sources or crustal contamination
37 (e.g., Renna et al., 2007; Taylor and Sheppard, 1986; Wei et al., 2008). Despite the limited
38 isotopic fractionations expected from metal stable isotope systems in high-temperature

contexts, recent works have shown that Li (e.g., Schuessler et al., 2009; Teng et al., 2009), Cu (Li et al., 2009), Fe (e.g., Heimann et al., 2008; Huang et al., 2009; Poitrasson and Freydier, 2005; Schuessler et al., 2009; Telus et al., 2012), Mg (e.g., Liu et al., 2010; Shen et al., 2009) and Zn (e.g., Telus et al., 2012; Chen et al., 2013) may give unique constraints on silicate rock petrogenesis. In this context, they provide a complementary approach alongside petrology, chemical compositions and radiogenic isotopes (e.g., Bonin, 2007; Litvinovsky et al., 2002; Martin, 2006; Tomascak et al., 2005).

Silicon is the second most abundant element in the silicate Earth after oxygen. As such, its stable isotope variations in geological materials may represent important information regarding mass transfer between terrestrial reservoirs. Despite early analytical limitations, Douthitt (1982) and later Ding et al. (1996) hinted that silicon isotope fractionation might occur among terrestrial igneous rocks. Specifically, they suggested that Si isotope compositions of granitoids are heavier than that of mafic igneous rocks. More recent data confirm the existence of a correlation between $\delta^{30}\text{Si}$ signatures and indices of magmatic differentiation on Earth (Savage et al., 2011a; Zambardi and Poitrasson, 2011b). However the exact mechanisms controlling Si isotope fractionation during petrogenesis and magmatic differentiation still remain an open question. Grant (1954) initially proposed on theoretical grounds that higher $\delta^{30}\text{Si}$ should be positively correlated to the degree of polymerization of silicate minerals. However, recent studies reveal that the mechanisms at play are more complicated and they also point to the influence of the nature of metals present in the crystalline structure (Méheut et al., 2009; Méheut and Schauble, 2014). Savage et al. (2011a) studied the well-characterized Hekla volcanic suite, Iceland, and they obtained a clear positive relationship between $\delta^{30}\text{Si}$ and the SiO_2 rock content. They could not distinguish magma mixing and fractional crystallization processes previously uncovered with Sr, O and Fe isotopes though (Schuessler et al., 2007; Sigmarsson et al., 1992). The same authors also

investigated the petrogenesis of the well known I- and S-type granites from SE Australia (Savage et al., 2011b, 2012). While some S-type granites show lighter $\delta^{30}\text{Si}$ than expected from the igneous trend they defined, the difference between these two granite types was not as clear cut as would have been expected from previous Sr, Nd and O isotope studies (e.g., McCulloch and Chappell, 1982; O'Neil and Chappell, 1977).

With the aim to clarify these issues, this study follows initial works (Savage et al., 2011a, 2012; Zambardi and Poitrasson, 2011a) and compares the Si isotopic signatures of a set of igneous terrestrial samples to bulk lunar rocks. We selected samples from various well-known key localities taken worldwide to see whether there is a general planetary trend. This approach proved to be useful in revealing a planetary-scale tendency of iron to become enriched in the heavier isotopes as the rock SiO_2 content increased (Poitrasson and Freydier, 2005). While remaining global, such an approach allows more general conclusions to be drawn than the study of a single igneous suite that may display a specific isotopic signatures, for example because of the local country rocks as in the case of the SE Australian granitoids (Savage et al., 2012) described above. The comparison of this terrestrial dataset with selected lunar samples spanning the petrologic range uncovered by the Apollo missions allows us to explore the possible contributions of different processes involved in fractionating Si stable isotopes through igneous petrogenesis at a planetary scale. In contrast to the Earth, lunar igneous processes do not involve water (Campbell and Taylor, 1983; Bonin et al., 2002; Day and Moynier, 2014), and this can serve as an interesting benchmark understanding the mechanism controlling the $\delta^{30}\text{Si}$ variations in terrestrial igneous rocks. This will also allows us to explore whether Si isotopes can be considered as a reliable sensor to track magmatic sources.

2. SAMPLES AND METHODS

We analyzed the bulk rock silicon isotope compositions of selected terrestrial magmatic suites from key localities for which the igneous and hydrothermal evolution had been thoroughly studied in previous works, as detailed hereafter. These include andesites from the Merapi volcano (Indonesia) related to eruptive events between 1883 and 1994, monzonites from Mount Peloso (Corsica), as well as granites of Carboniferous to Jurassic ages from the French Massif Central, Corsica, Brittany, Cornwall and Iran. We also report silicon isotope data for 8 bulk lunar samples collected by the Apollo 11, 12, 14, 15 and 17 missions. These rocks were sampled from different locations on the Moon and they represent the main lithological units uncovered by the Apollo missions. They include low- and high-Ti mare basalts, along with anorthosites and the Mg-rich igneous suite from the highlands. We compare these new results to our previously reported silicon isotope signatures of mafic and ultramafic igneous samples and geostandard reference materials that also included differentiated magmatic rocks (Zambardi and Poitrasson, 2011b; Zambardi et al., 2013). As a result, our terrestrial sample selection covers a large variety of igneous rocks, with a continuous SiO₂ range going from 46.9 to 77.8 wt% (Table 1). The granitoid type range (or their effusive equivalent) is large, going from relatively mafic granodiorites to silica-rich peralkaline granites. All samples were unweathered. Some of them experienced various level of hydrothermal alteration, as determined from their mineralogy and geochemistry (Poitrasson et al. 1994, 1995b, 1998, 2000, 2002). These granitoid rocks also had contrasting petrogeneses, from the peraluminous leucogranites from the French Massif Central, Brittany or Cornwall, that are essentially crustal-derived, to the Corsican peralkaline granites that are dominantly mantle-derived (Cocherie et al., 1994; Darbyshire and Shepherd, 1994; Pin and Duthou, 1990; Poitrasson et al., 1995a). The full sample set is listed in Table 1.

Sample powders were prepared using quantities in excess of 100g as starting material for terrestrial samples, and 1g for lunar rocks due to limited sample availability. While this

may not be enough to have a powder representative of a coarse-grained bulk rock for trace element analysis (Potts, 1987), this seems sufficient for the isotope analysis of a major element like silicon, as further discussed below. Since a complete description of the analytical procedure is already given in Zambardi and Poitrasson (2011b), we present hereafter briefly the main steps of our approach. The sample solutions were prepared using an alkali fusion method adapted from Georg et al. (2006). Silicon purification was achieved by column chromatography using Biorad AG50-X12 cationic resins. Typical Si recovery was of at least 95% after the decomposition and purification steps. Procedural blanks for ^{28}Si were $\sim 30\text{ng}$, corresponding to less than 0.2% of the ^{28}Si isotope signal and were thus negligible. All the measurements were made using a Neptune (Thermo) MC-ICP-MS in medium or high-resolution mode, with wet plasma conditions and slightly acidic HCl solutions (0.05M for both samples and standards). Instrumental mass bias drift was corrected simultaneously using the sample standard bracketing technique and magnesium as internal standard. Measurements of $^{25}\text{Mg}/^{24}\text{Mg}$ ratios added in both standard and samples were performed using a dynamic measurement mode. Mass bias drift correction was then applied using Russell's exponential law (Russell et al., 1978). All the data are reported in Table 1 as $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ (‰) relative to the NBS-28 international standard (renamed SRM 8546 by NIST) following the relation:

$$\delta^{xx}\text{Si} = \left(\frac{\left(\frac{^{xx}\text{Si}}{^{28}\text{Si}} \right)_{\text{Sample}}}{\left(\frac{^{xx}\text{Si}}{^{28}\text{Si}} \right)_{\text{NBS-28}}} - 1 \right) \times 1000 \quad (1)$$

where the superscript xx denotes the Si isotope with either mass number 30 or 29.

Long-term external reproducibility for $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ was given by 46 measurements of BHVO-2 over three years. It yielded 2 standard deviations (2SD) of 0.07‰ and 0.05‰ for $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$, respectively. We found the composition of BHVO-2 to be $\delta^{30}\text{Si} = -0.27 \pm 0.07\text{‰}$, in agreement within uncertainties with previous measurements (e.g., Armytage et al., 2012; Fitoussi et al., 2009; Pringle et al., 2013; Savage et al., 2011a, 2014).

3. RESULTS

Mafic terrestrial magmatic rocks (komatiite, basalt, gabbro, dolerite and basaltic trachyandesite; see Table 1) show $\delta^{30}\text{Si}$ values similar to those of peridotites (Fig. 1), in agreement with previous mantle rock data (Savage et al., 2010). Altogether, these samples define a mean $\delta^{30}\text{Si}$ value of -0.27‰ (Zambardi et al., 2013). The Columbia River basalt BCR-1 has the highest SiO_2 content and also yields the heaviest Si isotope signature of all basalts (Fig. 1). Andesite samples have heavier Si isotope compositions, with an averaged $\delta^{30}\text{Si} = -0.19\text{‰}$. Andesites JA-2 and AGV-2 show the heaviest $\delta^{30}\text{Si}$ signatures of -0.13‰ and -0.15‰ , respectively, values only matched by some highly differentiated granites with $\text{SiO}_2 \geq 75\text{wt\%}$ (Fig. 1). Monzonites yield an average $\delta^{30}\text{Si} = -0.23\text{‰}$, in between basalt and andesite values. Granitoid samples show by far the largest variations in $\delta^{30}\text{Si}$, ranging from -0.37‰ to -0.10‰ , and yielding an average $\delta^{30}\text{Si} = -0.25\text{‰}$. Lastly, lunar samples range from -0.16 to -0.29‰ , with a mean of -0.24‰ . A clear positive relationship is found between $\delta^{30}\text{Si}$ and feldspar abundance (Table 1 and Fig. 2), the meaning of which will be discussed hereafter.

4. DISCUSSION

4.1. Comparison with previous results

A compilation of the currently available silicon isotope data obtained so far by MC-ICP-MS on lunar samples reveals that whereas our measurements are in good agreement with Fitoussi and Bourdon (2012) results on mare basalts (Fig. 3), there are discrepancies with some of the analyses reported by Armytage et al. (2012). In contrast to our data, Armytage et al. (2012) found “no systematic $\delta^{30}\text{Si}$ differences [...] between any of the bulk [lunar] sample lithologies”. As noted by Savage et al. (2014), this is unexpected given the isotopic range associated with igneous differentiation on the Earth. While our data for those lunar samples

(Table 1) also measured by Armytage et al. (2012) are in agreement, (i.e., 14053, 15555 and 77215), these authors indicate that their three ferroan anorthosites were slightly, though not significantly heavier than other types of lunar samples they analyzed. Armytage et al. (2012) suggest that $\delta^{30}\text{Si}$ data from highland anorthosites may be contaminated by meteoritic materials. This is probably not the case for at least three of the highland samples (15415, 15455 and 76335) analyzed in the course of the present work since they yielded heavier $\delta^{30}\text{Si}$ than other lunar samples. Indeed, meteoritic contamination should cause a shift towards lighter isotope compositions given the more negative $\delta^{30}\text{Si}$ values measured in chondrites (e.g., Armytage et al., 2011; Fitoussi et al., 2009; Zambardi et al., 2013). Furthermore, we selected among the most pristine highland rock for this work according to the criteria of Warren (1993). However, Armytage et al. (2012) concluded on the basis of platinoid group elements contents that their anorthosite samples could not have undergone significant meteorite contamination. If so, then the remaining possible reason as to why two out of three highland anorthosites (60015 and 65035) they analyzed yielded significantly lighter Si isotope compositions than the $\delta^{30}\text{Si}$ we report for these rocks could be related to sample sizes. While we worked on powders made out of a minimum of 1 g of rock to minimize as far as possible the sample heterogeneity, Armytage et al. (2012) report that 65035 and 60015 powders were made out of a minimum of ~60 mg of sample material. This could be insufficient as powders produced from small aliquots of a coarse-grained anorthosite may show a nugget effect with ferromagnesian minerals that would lower the $\delta^{30}\text{Si}$ of the sample since they tend to show lighter silicon isotopic composition relative to felsic minerals (Grant, 1954; Méheut and Schauble, 2014; Savage et al., 2014). This explanation does not apply to the two mare basalts from Armytage et al. (2012) with lightest $\delta^{30}\text{Si}$, however, although a duplicate analysis of one of them, high-Ti basalt 70035, yielded $\delta^{30}\text{Si}$ values that are both within the trend or lower (Fig. 3). Whatever the precise explanation, this calls for new Si isotope measurements of at

least anorthosites 65035 and 60015. Finally, Fitoussi and Bourdon (2012) mention that they made their powders out of 1g of rock, as in the present work, which probably explains the better agreement with our results.

We have also compiled the available silicon isotope measurements of terrestrial igneous rocks obtained by MC-ICP-MS (Fig. 4). While there is not such a good linear trend for the Earth between $\delta^{30}\text{Si}$ and felsic mineral content compared to the Moon (Fig. 3), results obtained on silicate rock reference materials show that there is a good agreement between our data and those reported in previous studies of terrestrial rocks (see e.g., Zambardi and Poitrasson, 2011; Savage et al., 2011b; Zambardi et al., 2014).

4.2. The Moon as a reference for Si isotope variations during terrestrial igneous differentiation

With the exception of peraluminous granites, $\delta^{30}\text{Si}$ signatures correlate positively with increasing level of SiO_2 , although with some scatter (Fig. 1). Statistical tests confirm that the slope of this correlation (of 0.0034; See Table 2) is significantly different from 0. Such a correlation suggests both that high temperature processes significantly fractionates silicon stable isotopes and that igneous differentiation should control the Si isotope distribution in igneous rocks. However, no clear global correlations could be found between the $\delta^{30}\text{Si}$ and other indices of magmatic differentiation, such as major or trace element ratios. The link between $\delta^{30}\text{Si}$ and SiO_2 content of igneous rocks has been previously proposed in the literature (Ding et al., 1996; Douthitt, 1982). It is particularly clear in two recent studies using modern methods for Si isotope determination that focuses on co-genetic suites of volcanic rocks geodynamically restricted to rift zones and/or hot spots, with limited involvement of the continental crust in their petrogeneses (Savage et al., 2011a; Zambardi et al., 2014). This is not the case of the present study that involves genetically unrelated volcanic and plutonic

rocks, since our aim was to find a planetary scale trend, as previously uncovered for Fe isotopes (Poitrasson and Freydier, 2005). Our observation (Fig. 1) suggests that the mechanism(s) responsible for stable Si isotope fractionation along with magmatic differentiation tend to drive the rocks Si isotope compositions towards heavier $\delta^{30}\text{Si}$ values, regardless of their location on Earth and age. This inference was also recently made by Savage et al. (2014) in their compilation of available data. Inclusion of potentially partly cumulative rocks and granites that may have involved crustal rocks in their source material might explain the scattered trend of Figure 1.

In this context, it is interesting to compare the Earth with the Moon since the igneous history of the latter has been less protracted. Given that our satellite has neither atmosphere nor water, its surface is not affected by low temperature aqueous weathering and the lack of plate tectonics makes deep crustal recycling of weathered samples impossible. Similarly, there is no hydrothermal alteration on the Moon, again because of the lack of water. Given the limited variations of SiO_2 content among lunar samples, we report $\delta^{30}\text{Si}$ values as a function of the total amount of felsic minerals instead, taken from the Lunar Science Compendium (Meyer, 2008). This results in a very clear positive correlation with samples evenly distributed along the tectosilicate content range (Fig. 2). We assume in this case that the sum of felsic minerals represents an index of igneous differentiation as well, but at the planetary scale. This correlation for lunar rocks is much less scattered than the terrestrial samples in this Figure 2. It also appears better defined than the $\delta^{30}\text{Si}$ vs. SiO_2 relationship previously shown in the literature for terrestrial samples (Savage et al., 2011a; Zambardi et al., 2014) and expanded in the present study (Fig. 1 and 4). Hence, we take the more scattered terrestrial trend relative to the lunar one in Figure 2 as evidence for a more complex terrestrial petrogenetic processes and/or the involvement of components missing in the Moon, such as water. These contrasted relationships between $\delta^{30}\text{Si}$ and tectosilicate contents for the Moon and the Earth (Fig. 2) may

therefore be used to further constraint additional components and/or processes at work in the Earth's igneous evolution.

The correlation between $\delta^{30}\text{Si}$ and tectosilicate content for lunar samples (Fig. 2) cannot be directly linked to a simple magmatic differentiation process related to fractional crystallization of a silicic melt restricted in space and time, as previously suggested in the case of the Hekla transitional alkaline suite (Savage et al., 2011a). This is because these lunar rocks were sampled over long distances on the Moon during the Apollo missions and they represent samples from petrogenetically distinct regions spanning different steps in the lunar igneous history. For instance, the anorthosites are thought to represent the products of the primitive lunar magma ocean crystallization, while the Mg-rich suite rocks (e.g., troctolite, norite) are remnants of the oldest post-magma ocean magmatism and mare high- and low-Ti basalts represent the most recent significant igneous activity on the Moon (e.g., Shearer et al., 2006). Besides their different petrographic nature and age, extended petrological studies led to the conclusion that the rocks making up the ferroan anorthositic crust, Mg-rich igneous suite and mare basalts had different petrogenetic histories, i.e., they cannot be linked through a common line of descent (Shearer et al., 2006). Hence, the trend depicted in Figure 2 could reveal the global positive correlation between $\delta^{30}\text{Si}$ and the degree of silicon polymerization in the rock-forming silicate phases, following the line of reasoning of Grant (1954). In this sense, whether the rock is representative of a silicic liquid or not is not essential for such a correlation. What matters is the mean degree of silicon polymerization of the bulk-rock, whether this element is locked in glass, minerals that crystallized in equilibrium with the melt or cumulative minerals. Therefore, the $\delta^{30}\text{Si}$ increase would simply accompany a global planetary differentiation that is characterized by an increasing content of felsic minerals in igneous rocks. This interpretation of Figure 2 can be assessed using the non-bridging oxygen/tetrahedral cations index ratio (NBO/T) that may be taken as a measure of the degree

of silicic melt polymerization (Mysen et al., 1985). When bulk lunar rock silicon isotope composition is plotted against their NBO/T index (Fig. 5), a trend shows that indeed, increasing $\delta^{30}\text{Si}$ correlates with decreasing NBO/T, and therefore increasing degree of polymerization of the silicic melt. It should be noted here that this trend is also apparent, though less well defined, if the data of Fitoussi and Bourdon (2012) and Armytage et al. (2012) are included, with the same outlying samples from the latter authors, as seen on Figure 3. While the trend of Figure 5 is not as clear as with mineral modes (Fig. 2), possibly because the NBO/T index is just a proxy, it is good enough to highlight the dominant role of silicic melt polymerization on silicon isotope composition in a water free planet like the Moon. The case for the Earth is more complicated given the occurrence of water, which is intrinsic to other processes also affecting $\delta^{30}\text{Si}$, as discussed below.

To compare terrestrial and lunar data, the amount of plagioclase, K-feldspar and quartz were computed for terrestrial intrusive and effusive rock samples based on their CIPW norm mineralogies (using the Microsoft Excel spread sheet from K. Hollocher available at: http://minerva.union.edu/hollochk/c_petrology/norms.htm). Mantle-derived peridotites were excluded since their lack of – or little – plagioclase content makes them unsuitable for this comparison based on felsic mineral modes. Furthermore, their isotopic signature may have been blurred by a protracted high-temperature geological history. According to Figure 2, most of the terrestrial samples fall on the Moon's trend within uncertainty, albeit more scattered. Interestingly, the most differentiated metaluminous and peralkaline granites and the lunar highland samples share a common Si isotopic signature for a similar amount of tectosilicates. This suggests that these terrestrial granites reflect the effect of magmatic differentiation on Si isotope compositions, whereas the other granite types have their $\delta^{30}\text{Si}$ affected by other processes/sources specific to the Earth. Taking the lunar trend on Figure 2 as reflecting the effect of igneous differentiation on Si isotope compositions, it becomes apparent that andesite

JA-2 shows a significantly heavier Si isotope signature than expected, whereas all peraluminous granites plot distinctly below the lunar trend. The deviance of andesites and peraluminous granite is also apparent on Figure 1 when compared to the igneous array for Si isotopes defined by Savage et al. (2011a). Therefore, additional processes/sources specifically occurring on the Earth should explain the enrichments or depletions in heavy or light isotopes relative to the general igneous differentiation trend.

4.3 Silicon isotopic evolution during terrestrial igneous differentiation

As mentioned earlier, the increase of $\delta^{30}\text{Si}$ with SiO_2 rock content was first predicted theoretically by Grant (1954). According to this model, elevated rock Si contents would result in high polymerization levels leading to enrichments in heavy Si isotopes. Predicted fractionation factors for $^{30}\text{Si}/^{28}\text{Si}$ between Si-poor and Si-rich silicic melts were expected to range from 4‰ to 2‰ for temperatures ranging from 1000°C to 1500°C, respectively. Considering all data now available on the Si isotope composition of terrestrial igneous materials (Ding et al., 1996; Douthitt, 1982; Savage et al., 2014; Savage et al., 2010; Savage et al., 2011a; Savage et al., 2012; Zambardi and Poitrasson, 2011b), such fractionation factors appear largely overestimated, yet the sense of fractionation was correctly predicted. Although this hypothesis may explain Si isotope fractionation during high temperature igneous processes at the bulk rock scale as suggested by Figure 5 for lunar samples, recent *ab initio* calculations (Méheut et al., 2009; Méheut and Schauble, 2014) do not fully confirm Grant's model at the mineral scale. Their computations indicate a deviation from the trend expected from Grant's predictions for some minerals, suggesting that the polymerization degree may not be the unique controlling factor of the Si isotope fractionations in igneous materials. The nature of the cations filling the silicate structure may be another important parameter to consider given that they will also impact the stiffness of the interatomic bonds of silicon

atoms with their neighbors in minerals, which in turn will directly affect isotopic fractionation factors. Besides, the temperature conditions during rock formation and the possible temperature gradients occurring during melt crystallization could also act as a fractionating mechanism for Si stable isotopes (Lundstrom, 2009; Richter et al., 2009; Zambardi et al., 2014). The detailed examination of such a process, however, requires the study of well characterized magmatic suites rather than genetically unrelated samples, which is not the purpose of this study. Given that the trend of increasing $\delta^{30}\text{Si}$ shown in Fig. 2 is observed at the bulk rock scale, one might predict a resulting reservoir of leftover material with light $\delta^{30}\text{Si}$ relative to the mantle starting sources for mass balance reasons, possibly in the lower crust. However, such a lighter lower crust could not be found within uncertainty (Savage et al., 2013b). This probably reflects the very small crustal proportion of the rocks having $\delta^{30}\text{Si}$ significantly above the mean Earth signature, that include strongly differentiated metaluminous and peralkaline granites and some andesites (Fig. 2).

In an earlier study, Ding (1996) measured the Si isotope compositions of mineral separates from three different granites. Although with different $\delta^{30}\text{Si}$ compositions depending on the host granite, mineral types displayed the same relative difference. Biotites and muscovites were found to be isotopically lighter than feldspars and quartz by about 0.3‰. Such results imply that a given mineral has a specific Si isotope fractionation factor during its crystallisation, which means that the bulk rock isotopic signature should result from its specific mineral assemblage arising from its igneous history, as well as the isotopic composition of the source rock from which the original magma has formed. Those early results were recently confirmed using more precise measurements (Savage et al., 2011a; Savage et al., 2012), thereby supporting the view that increasing bulk rock $\delta^{30}\text{Si}$ reflects a global igneous differentiation at the planetary scale that leads to rocks with increased amounts of tectosilicates as depicted in Figure 2. Savage et al. (2011a) could not model easily their

data from the Hekla transitional alkaline volcano by a simple fractional crystallization process though. They also showed that Si isotopes could not reproduce in detail the trends previously observed with Fe isotopes (Schuessler et al., 2009). Interestingly, Schuessler et al. (2009) also found that bulk rock Li isotopes did not show similar variations in the Hekla suite as a function of the degree of magmatic differentiation, strengthening the view that each stable isotope system will trace specific processes. In the case of silicon, the bulk rock isotopic signature would simply reflect the mean degree of silicon polymerization, whether it is occurring in glass or minerals that may be cumulative or not, as detailed above. Instead, iron isotopes were interpreted to fit well the magma mixing and fractional crystallization models inferred for the Hekla volcanism (Schuessler et al., 2009) on the basis of trace element concentrations, radiogenic and oxygen isotopes (Sigmarsson et al., 1992). Hence, we conclude that the global positive trend between $\delta^{30}\text{Si}$ with SiO_2 (Fig. 1), or felsic mineral contents (Fig. 2), should be interpreted in terms of the mean degree of silicon polymerization of the studied igneous rocks, as particularly apparent in lunar rocks (Fig. 3), whatever their precise mineral assemblage, rather than resulting from a specific magmatic process that may have a variable importance depending of the igneous suite considered (See also Telus et al., 2012, for Fe, Zn, Mg and U isotopes).

4.4 Influence of the rock protolith on their Si isotope composition

Outside the global planetary trend stand the peraluminous granites that display significantly more negative values, given their high SiO_2 contents (Table 1; Fig. 2). Such peculiar light isotope compositions could be attributed to the specific source of these granites that are thought to derive from relatively shallow crustal partial melts of (meta-)sediments (Vidal et al., 1984). It has been shown that rocks weathered by surface waters will tend to acquire an isotopically light Si isotope signature (e.g., Opfergelt et al., 2012; Savage et al.,

2013a; Ziegler et al., 2005). Hence, if sediments incorporating such weathered rock residues subsequently melt to form granitoids, it is expected that the latter will thereby acquire this light $\delta^{30}\text{Si}$ value. Therefore, Si isotope compositions of leucogranites would be a direct evidence for the involvement of clay-rich material in their source (Zambardi and Poitrasson, 2011a), as it has been inferred on the basis of the major element chemistry of these rocks, interpreted in the light of melting experiments of pelitic rocks (see, e.g., Sylvester, 1998).

This hypothesis was also recently proposed in a study of S-type granites from SE Australia (Savage et al., 2012), but the shift towards light $\delta^{30}\text{Si}$ in such granites was not as always as strong as for the leucogranites of this study (Fig. 4), presumably because their metapelitic source involved less clay minerals. Also, at least one of the putative metasedimentary sources involved in SE Australian S-type granites was found to have $\delta^{30}\text{Si}$ values similar to that of I-type granitoids (Savage et al., 2012).

A subsequent study of shale samples from various world locations by Savage et al. (2013a) has shown their great diversity in $\delta^{30}\text{Si}$ compositions, ranging from -0.8 to 0‰. As noted by these authors, this range could have been even greater given the permil fractionation level observed among soil clay minerals during weathering (e.g., Opfergelt et al., 2012; Ziegler et al., 2005). It is thus difficult to assign with a good degree of certainty a putative sedimentary protolith end-member $\delta^{30}\text{Si}$ composition in the present study for the peraluminous leucogranites from Iran, Cornwall (UK) and the French Massif Central values reported in Table 1 and Fig. 1 and 2. It is interesting to note, however, that the $\sim -0.35\text{‰}$ $\delta^{30}\text{Si}$ composition found for most of these granites is close to the $\sim -0.37\text{‰}$ mean shale value reported by Savage et al. (2013a). This would imply that the studied leucogranites protoliths are nearly exclusively made of such clay-rich sediments, in good agreement with the canonical petrogenetic model of these peraluminous leucogranites (e.g., Pin and Duthou, 1990; Vidal et al., 1984).

However, while the $\delta^{30}\text{Si}$ range of clay-rich shales is large worldwide, Savage et al. (2013) noted that each basin show a much narrower variation. This means that future analyses of some representative inferred protoliths of the peraluminous leucogranites from Iran, Cornwall (UK) and the French Massif Central should easily provide a more precise estimate of their proportion involved in the petrogenesis of these rocks.

Shen et al. (2009) also inferred the importance of clay-rich minerals in the source of peraluminous leucogranites using Mg isotopes, although the fractionation factor was opposite because weathering produce clay-rich material with high $\delta^{26}\text{Mg}$. However, Savage et al. (2013) could not find clear relationships between stable Si and Mg (and Li) isotopes, presumably because these elements are differently affected by weathering, given the lower mobility of silicon relative to Mg and Li. It is therefore difficult to make further inferences for the granite suites studied in the absence of Mg and Li isotope measurements on the same samples.

At the other end of the silicon isotope composition spectra is the red granite of Porto, sample 9108, and particularly andesite JA-2 (Fig. 2). The high $\delta^{30}\text{Si}$ andesite values relative to their SiO_2 content is especially apparent in Figure 1 when compared to the igneous array of Savage et al. (2011a), since AGV-2 and one Merapi volcano Andesite are also outside the array, besides JA-2. Although we do not have a simple explanation for this, the Porto red granite complex, in Corsica, shows evidence for extreme hydrothermal alteration at the end of the intrusion emplacement (Poitrasson et al., 1995b). Similarly, the fluids released from a subducting slab play a key role in andesite petrogenesis (e.g., Schmidt and Poli, 1998). Both low and high temperature fluid-rock interactions produce water or hydrothermal fluids enriched in heavy silicon isotopes (Abraham et al., 2011; Ziegler et al., 2005). Seawater itself is isotopically heavy, with an estimated mean $\delta^{30}\text{Si}$ of $1.1 \pm 0.3\text{‰}$, with Si outputs, for example in the form of diatomite deposits, having an isotopic composition close to this value (De La

Rocha et al., 2000). It is thus feasible that in some cases, the interaction of such fluids with extremely hydrothermally altered granites, or with the mantle wedge involved in andesite petrogenesis via the incorporation of silicon from the subducted slab, may leave a slightly heavy $\delta^{30}\text{Si}$ imprint on these rocks, or their protolith, that can be subsequently inherited in the case of andesites. Although speculative at this stage, a rough mass balance calculation using the marine Si output $\delta^{30}\text{Si}$ of 1.1‰ (De La Rocha et al., 2000) and the maximum deviation from the igneous trend in Fig. 1 displayed by sample JA-2 would imply up to ~9% of marine derived silicon being involved into the petrogenesis of andesites. Subduction-derived fluids may not display Si isotope signatures as heavy as those of seawater because of the elevated temperature of hydrothermal systems that may limit the extent of stable isotope fractionation. In this case, a higher proportion of hydrothermally-derived silicon would be incorporated into the protoliths of the andesites. Further detailed work is required on such examples for a better understanding and quantification of the mechanisms involved.

6. CONCLUSIONS

Silicon isotopes are slightly but significantly fractionated through igneous differentiation at the planetary scale, starting from light Si isotope compositions in basalts to heavier Si isotope compositions in peralkaline and metaluminous granites. Silicon isotope signatures appear to be controlled by modal mineralogy, and especially the amount of felsic tectosilicate minerals (i.e., feldspar and quartz) in the rocks. The particularly good lunar trend that can also be related to an index of polymerization (NBO/T) suggest that this is the main factor driving the bulk rock silicon isotope composition in a water-free planet.

The comparison of Earth and Moon data in this study reveals that most rocks follow the same isotopic trend, but it is more scattered for the Earth relatively to the Moon. Lunar highlands have $\delta^{30}\text{Si}$ similar to those of terrestrial peralkaline and metaluminous granites,

suggesting the latter essentially reflect Si isotope compositions attributable to igneous differentiation on Earth.

Using lunar data as a reference for the terrestrial igneous differentiation allows the identification of terrestrial magmatic rocks with lighter or heavier Si isotope signatures relative to the lunar trend for a given level of igneous differentiation. Light $\delta^{30}\text{Si}$ values relative to the igneous differentiation trend may be attributed to an isotopically light sediment/metapelitic source component of peraluminous leucogranites, whereas heavy Si isotope enrichments may be attributed to the assimilation of silicon from aqueous fluids by the protoliths of andesites in subduction zones or towards the end of the emplacement of strongly hydrothermalized granites.

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Figure captions

Fig. 1: $\delta^{30}\text{Si}$ (‰) relative to NBS-28 as a function of SiO_2 (wt.%) for terrestrial igneous bulk rock samples. Uncertainties are expressed as 2 standard errors (2SE). Note the positive trend that is scattered by peraluminous leucogranite and andesite values. Data are from Table 1, except for the peridotites data that are from Zambardi et al. (2013). The igneous array (solid line) and its 2 standard error envelope (dashed lines) defined by Savage et al. (2011a) are reported for comparison. It is: $\delta^{30}\text{Si}$ (‰) = $0.0056 \times \text{SiO}_2$ (wt.%) – 0.567 according to Savage et al. (2014).

Fig. 2: $\delta^{30}\text{Si}$ bulk-rock signatures (‰) relative to NBS-28 expressed as a function of the total amount of felsic minerals (quartz (Qtz), alkali feldspar (Kfs) and plagioclase (Plg)) in igneous rocks from the Earth (blue circles) and the Moon (orange squares) in wt. %. Uncertainties are expressed as 2SE. The black line and yellow path represents the average and 2SE uncertainty mean for lunar samples, respectively. The Lunar array is: $\delta^{30}\text{Si}$ (‰) = $0.0018 \times \text{tectosilicates}$ (wt.%) – 0.333, with $R^2 = 0.97$. Note the more scattered trend for the Earth relative to the Moon that denotes a more complex petrogenetic history for terrestrial rocks due to the involvement of water.

Fig. 3: Compilation of the available silicon isotope data obtained by MC-ICP-MS on lunar samples plotted against their felsic mineral modal compositions (abundances in vol. % of mostly plagioclase and K-feldspar, compiled by Meyer, 2008). While the agreement between

Fitoussi and Bourdon (2012) data (white triangles) and our own results (orange squares) is generally good, some data from Armitage et al., (2012) (white diamonds) deviate markedly from the relationship uncovered. As discussed in the text, this could be interpreted as an issue with aliquot size. With modal contents expressed as vol.%, the Lunar array (black line) is: $\delta^{30}\text{Si} (\text{‰}) = 0.0017 \times \text{tectosilicates (wt.\%)} - 0.331$, with $R^2 = 0.96$. The dashed lines represent the 2SE uncertainty mean for lunar samples.

Fig. 4: Compilation of the available silicon isotope data obtained by MC-ICP-MS on terrestrial igneous rocks plotted against their SiO_2 contents. Our results (orange squares) are compared to those of Zambardi et al. (2014) (white circles) and those of Savage et al. (2011a; 2012; 2014) (white triangles) that seem to show a broad general agreement. This is confirmed by comparable results of analyses made by the different groups on silicate rock reference material. The igneous array (see details in Fig. 1 caption) of Savage et al. (2014) is reported for comparison.

Fig. 5: $\delta^{30}\text{Si} (\text{‰})$ relative to NBS-28 as a function of the ratio of non-bridging oxygens over tetrahedral cations (NBO/T) for lunar rocks. This dimensionless molar ratio is a measure of the degree of polymerization of silicate melts (Mysen, 1985), with increasing NBO/T values corresponding to a decreasing degree of melt polymerization. This relationship supports the view that silicic melt polymerization is the dominant factor that determine bulk-rock silicon isotope compositions in a water-free planet. The equation for the line is $\delta^{30}\text{Si} (\text{‰}) = -0.08 \times \text{NBO/T} - 0.15$, with $R^2 = 0.88$.

Table 1: Mineral content, silicon abundance and isotopic composition for magmatic lunar and terrestrial rocks.

Samples	Nature	Location	SiO ₂ ³ (wt.%)	Quartz (wt.%)	Orthoclase (wt.%)	Plagioclase (wt.%)	Sum felsic Minerals ⁴ (wt.%)	δ ³⁰ Si (‰)	2SE	δ ²⁹ Si (‰)	2SE	# of analyses
Lunar samples :												
10049,99 ¹	High-Ti Mare basalt	Mare Tranquillitatis	42.0				19	-0.28	0.03	-0.13	0.02	7
12045,3 ¹	Ilmenite Mare basalt	Oceanus Procellarum	42.2				19	-0.29	0.05	-0.13	0.01	9
14053,246 ¹	Low-Ti Mare basalt	Fra Mauro	46.3				39	-0.27	0.07	-0.10	0.02	6
15415,143	Ferroan anorthosite	Hadley Apennines	44.9				99	-0.16	0.03	-0.05	0.02	6
15455,9	Cataclastic Anorthositic Norite	Hadley Apennines	47.7				70	-0.21	0.02	-0.10	0.02	8
15555,922 ¹	Olivine normative Mare basalt	Hadley Apennines	44.6				28	-0.28	0.04	-0.13	0.02	8
76335,36	Troctolite	Taurus Littrow	43.4				85	-0.17	0.04	-0.07	0.02	6
77215,234 ¹	Norite	Taurus Littrow	51.2				50	-0.24	0.04	-0.10	0.03	6
Terrestrial samples :												
PMS ²	Microgabbro	Pitscurrie, UK	46.9	0	0	55	55	-0.29	0.03	-0.14	0.02	6
BCR-1 ²	Basalt	Columbia river, USA	54.1	4	10	45	59	-0.19	0.03	-0.11	0.03	6
BHVO-2 ²	Basalt	Hawaii, USA	49.9	0	3	45	48	-0.27	0.01	-0.14	0.01	46
BIR-1 ²	Basalt	Reikjavik, Iceland	48.0	0	0	50	50	-0.27	0.04	-0.12	0.02	6
ES-9104 ²	Basaltic	Esterel massif, France	52.3	0	22	42	64	-0.25	0.02	-0.11	0.02	12
DR-N ²	Trachyandesite Diorite	Neuntelstein, France	52.9	3	10	55	68	-0.26	0.02	-0.12	0.03	6
JA-2 ²	Andesite	Goshikidai Plateau, Japan	56.4	5	11	49	65	-0.13	0.02	-0.06	0.01	6
AGV-2 ²	Andesite	Lake County, USA	59.4	8	17	55	79	-0.15	0.03	-0.07	0.03	6
MA-1883	Andesite	Merapi Volcano, Indonesia	54.6	2	12	62	75	-0.18	0.03	-0.07	0.09	3
MA-1940	Andesite	Merapi Volcano, Indonesia	55.3	3	13	58	74	-0.22	0.03	-0.10	0.03	3
MA-1956	Andesite	Merapi Volcano, Indonesia	55.3	2	11	60	73	-0.22	0.06	-0.10	0.01	3
MA-1994	Andesite	Merapi Volcano, Indonesia	56.6	5	12	59	76	-0.23	0.03	-0.10	0.02	3
84027	Monzonite	Mount Peloso, France	61.9	8	35	45	88	-0.25	0.04	-0.11	0.03	6
84028	Monzonite	Mount Peloso, France	65.6	9	39	45	93	-0.24	0.04	-0.10	0.02	6
84087	Monzonite	Mount Peloso, France	72.0	22	33	42	97	-0.21	0.02	-0.10	0.02	6
TA-9105	Aluminous and peralkaline granite	Tana, France	75.6	34	28	34	96	-0.15	0.04	-0.06	0.02	6
CB-9202	Aluminous and peralkaline granite	Mantelluccio, France	76.9	33	30	32	95	-0.16	0.05	-0.07	0.03	6
PO-9207	Aluminous and peralkaline granite	Porto, France	76.1	30	33	34	98	-0.15	0.06	-0.06	0.03	6
9108	Aluminous and peralkaline granite	Porto, France	77.8	38	27	32	97	-0.10	0.04	-0.03	0.04	6
EV-9101	Aluminous and peralkaline granite	Evisa, France	76.7	35	27	33	94	-0.20	0.02	-0.08	0.02	6
PC-9401	Monzogranite/gra nodiorite	Urbalacone, France	64.9	16	23	49	89	-0.17	0.04	-0.05	0.02	6
SN-9402	Monzogranite/gra nodiorite	Saint Nectaire, France	65.0	18	30	39	86	-0.22	0.06	-0.10	0.03	6
GA ²	Monzogranite/gra nodiorite	Andlau, France	69.9	26	24	42	92	-0.25	0.03	-0.12	0.01	16
CA-9404	Peraluminous leucrogranite	Carnmenellis, UK	70.1	26	36	30	92	-0.36	0.07	-0.16	0.05	3
CA-9414	Peraluminous leucrogranite	Carnmenellis, UK	73.2	29	36	30	95	-0.34	0.08	-0.16	0.02	3
CA-9415	Peraluminous leucrogranite	Carnmenellis, UK	71.3	29	36	28	92	-0.34	0.07	-0.16	0.03	9
MLA46B2	Peraluminous leucrogranite	Millevache, France	75.2	33	27	35	95	-0.28	0.02	-0.13	0.03	3
AA	Peraluminous leucrogranite	Bodmin, UK	73.5	35	30	28	92	-0.36	0.03	-0.18	0.03	3
C70	Peraluminous leucrogranite	Dumet Island, France	74.8	36	30	28	93	-0.37	0.04	-0.18	0.02	3
B39	Peraluminous leucrogranite	Shir-Kuh, Iran	77.4	40	30	26	96	-0.28	0.04	-0.13	0.04	3

Isotopic data are reported relative to NBS-28 standard. Uncertainties for isotope data are given as 2 standard errors using the Student *t*-correcting factor. ¹: Isotope data from Zambardi et al. (2013) and ² from Zambardi and Poitrasson (2011). ³: Lunar sample SiO₂ concentrations come from the Lunar sample Compendium (Meyer, 2008). ⁴: Mostly plagioclases for lunar sample modes. Lunar data were recalculated as wt. % modes considering vol. % abundances (data from Meyer, 2008) and minerals densities to compare with Quartz, Orthose and Plagioclase norms computed using the CIPW method for terrestrial samples.

Table 1

Table 1: Mineral content, silicon abundance and isotopic composition for magmatic lunar and terrestrial rocks.

Samples	Nature	Location	SiO ₂ ³ (wt.%)	Quartz (wt.%)	Orthoclase (wt.%)	Plagioclase (wt.%)	Sum felsic Minerals ⁴ (wt.%)	δ ³⁰ Si (‰)	2SE	δ ²⁹ Si (‰)	2SE	# of analyses
Lunar samples :												
10049,99 ¹	High-Ti Mare basalt	Mare Tranquillitatis	42.0				19	-0.28	0.03	-0.13	0.02	7
12045,3 ¹	Ilmenite Mare basalt	Oceanus Procellarum	42.2				19	-0.29	0.05	-0.13	0.01	9
14053,246 ¹	Low-Ti Mare basalt	Fra Mauro	46.3				39	-0.27	0.07	-0.10	0.02	6
15415,143	Ferroan anorthosite	Hadley Apennines	44.9				99	-0.16	0.03	-0.05	0.02	6
15455,9	Cataclastic Anorthositic Norite	Hadley Apennines	47.7				70	-0.21	0.02	-0.10	0.02	8
15555,922 ¹	Olivine normative Mare basalt	Hadley Apennines	44.6				28	-0.28	0.04	-0.13	0.02	8
76335,36	Troctolite	Taurus Littrow	43.4				85	-0.17	0.04	-0.07	0.02	6
77215,234 ¹	Norite	Taurus Littrow	51.2				50	-0.24	0.04	-0.10	0.03	6
Terrestrial samples :												
PMS ²	Microgabbro	Pitscurrie, UK	46.9	0	0	55	55	-0.29	0.03	-0.14	0.02	6
BCR-1 ²	Basalt	Columbia river, USA	54.1	4	10	45	59	-0.19	0.03	-0.11	0.03	6
BHVO-2 ²	Basalt	Hawaii, USA	49.9	0	3	45	48	-0.27	0.01	-0.14	0.01	46
BIR-1 ²	Basalt	Reikjavik, Iceland	48.0	0	0	50	50	-0.27	0.04	-0.12	0.02	6
ES-9104 ²	Basaltic	Esterel massif, France	52.3	0	22	42	64	-0.25	0.02	-0.11	0.02	12
DR-N ²	Trachyandesite Diorite	Neuntelstein, France	52.9	3	10	55	68	-0.26	0.02	-0.12	0.03	6
JA-2 ²	Andesite	Goshikidai Plateau, Japan	56.4	5	11	49	65	-0.13	0.02	-0.06	0.01	6
AGV-2 ²	Andesite	Lake County, USA	59.4	8	17	55	79	-0.15	0.03	-0.07	0.03	6
MA-1883	Andesite	Merapi Volcano, Indonesia	54.6	2	12	62	75	-0.18	0.03	-0.07	0.09	3
MA-1940	Andesite	Merapi Volcano, Indonesia	55.3	3	13	58	74	-0.22	0.03	-0.10	0.03	3
MA-1956	Andesite	Merapi Volcano, Indonesia	55.3	2	11	60	73	-0.22	0.06	-0.10	0.01	3
MA-1994	Andesite	Merapi Volcano, Indonesia	56.6	5	12	59	76	-0.23	0.03	-0.10	0.02	3
84027	Monzonite	Mount Peloso, France	61.9	8	35	45	88	-0.25	0.04	-0.11	0.03	6
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GA ²	Monzogranite/gra nodiorite	Andlau, France	69.9	26	24	42	92	-0.25	0.03	-0.12	0.01	16
CA-9404	Peraluminous leucrogranite	Carnmenellis, UK	70.1	26	36	30	92	-0.36	0.07	-0.16	0.05	3
CA-9414	Peraluminous leucrogranite	Carnmenellis, UK	73.2	29	36	30	95	-0.34	0.08	-0.16	0.02	3
CA-9415	Peraluminous leucrogranite	Carnmenellis, UK	71.3	29	36	28	92	-0.34	0.07	-0.16	0.03	9
MLA46B2	Peraluminous leucrogranite	Millevache, France	75.2	33	27	35	95	-0.28	0.02	-0.13	0.03	3
AA	Peraluminous leucrogranite	Bodmin, UK	73.5	35	30	28	92	-0.36	0.03	-0.18	0.03	3
C70	Peraluminous leucrogranite	Dumet Island, France	74.8	36	30	28	93	-0.37	0.04	-0.18	0.02	3
B39	Peraluminous leucrogranite	Shir-Kuh, Iran	77.4	40	30	26	96	-0.28	0.04	-0.13	0.04	3

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Table 2

Table 2: Statistical significance F-test for the correlations between bulk-rock $\delta^{30}\text{Si}$ and SiO_2 for terrestrial samples, excluding leucogranites, using an inverse F-law. Two variables are statistically correlated when $F\text{-test} > F\text{-critical}$. The test is performed at a 95% confidence level. The slope range was computed using a student law.

Slope	0.0034
R^2	0.57
Slope min.	0.0024
Slope max.	0.0045
F-test	45.30
F-critical	4.13
Degree of freedom	34
α	0.05

Figure 1

Figure 2

Figure 3

New Figure 4

Figure 4

Figure 5