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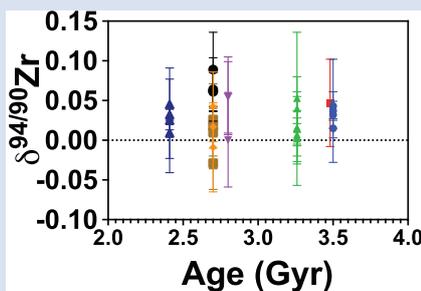
## Zirconium isotopic composition of the mantle through time

S.Y. Tian<sup>1</sup>, F. Moynier<sup>1\*</sup>, E.C. Inglis<sup>1</sup>, J. Creech<sup>1,2</sup>, M. Bizzarro<sup>1,3</sup>,  
J. Siebert<sup>1,4</sup>, J.M.D. Day<sup>1,5</sup>, I.S. Puchtel<sup>6</sup>



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### Abstract



Zirconium isotopes have the potential to trace both magmatic differentiation and crustal evolution, as well as deep Earth processes. Zirconium is compatible in bridgmanite where it has a higher coordination number than in silicate melt, implying that Zr isotopes could be fractionated during magma ocean crystallisation. We report the Zr isotopic composition of 31 komatiites from around the globe, ranging in age from 2.41 to 3.55 Ga. The  $\delta^{94/90}\text{Zr}$  (per mille deviation of  $^{94}\text{Zr}/^{90}\text{Zr}$  from IPGP-Zr standard) values for the komatiites are homogeneous at  $0.030 \pm 0.049$  ‰ (all errors are 2 s.d.), and consistent with associated basaltic rocks ( $0.048 \pm 0.032$  ‰). These results, identical within uncertainty of the bulk silicate Earth estimate from modern basalts, suggest that the mantle Zr isotope composition has been constant since at least 3.55 Ga. Combining the isotopic compositions of komatiites and basalts of all ages we suggest a conservative  $\delta^{94/90}\text{Zr} = 0.040 \pm 0.044$  ‰ ( $n = 72$ ) for the mantle composition. Several komatiite systems that we analysed in this study, including Schapenburg, Komati, and Weltevreden, have been previously argued to have isotope signatures consistent with magma ocean crystallisation processes. However, their Zr isotope compositions are indistinguishable from other komatiites, implying that bridgmanite crystallisation did not fractionate Zr isotopes to any measurable extent.

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### Introduction

Zirconium is a refractory element ( $T_c = 1741\text{K}$ ; Lodders, 2003), and its abundance and stable isotopic composition is, *a priori*, robust to evaporation processes that occurred during planetary formation. This makes Zr distinct from more volatile elements, like Zn (Moynier *et al.*, 2017) or even Si and Mg (Pringle *et al.*, 2014; Hin *et al.*, 2017). As with other high field strength elements, Zr is lithophile and incompatible (Woodhead *et al.*, 1993; Johnson, 1998) and is enriched in the continental crust (Rudnick and Gao, 2003). Zirconium isotopes fractionate during magmatic differentiation. For example, the most evolved lavas from Hekla volcano, Iceland, have a  $^{94}\text{Zr}/^{90}\text{Zr}$  ratio 0.5 ‰ higher than less evolved lavas. This is interpreted to reflect differences in coordination of zirconium between zircon and melt (Inglis *et al.*, 2019). Because of the resistance of zircons to physical and chemical abrasion and the availability of other isotope tracers (*e.g.*, O, Hf) and elements within them (*e.g.*, rare earth elements), they have found widespread application in the study of Earth's crust through time (Condie, 2005). The isotopic fractionation of Zr between granites and basalts (Inglis *et al.*, 2018) suggests that Zr isotopes could be used as tracers within zircons, and of crustal recycling in Earth's mantle, especially since Zr is a fluid immobile element and should be efficiently recycled into the mantle.

Presently, the Zr isotopic composition of the mantle is estimated by the analysis of relatively low degree basaltic partial melts (Inglis *et al.*, 2019).

Komatiites are ultramafic volcanic rocks with >18 wt. % MgO. They are formed by partial melting in hot mantle plumes, mostly during the Archean (*e.g.*, Arndt *et al.*, 2008). Since komatiites are mantle-derived high degree partial melts (>30 %) (Herzberg, 1992), and Zr is moderately incompatible, almost all Zr from the mantle source is efficiently extracted into komatiitic melts. As such, komatiitic melts must faithfully reflect the Zr isotopic composition of their mantle source. Similar logic has been used to estimate the composition of the mantle through time of several other elements, including Ca (Amsellem *et al.*, 2019), Ga (Kato *et al.*, 2017), and Ti (Greber *et al.*, 2017; Deng *et al.*, 2018).

Komatiites span a range of ages and, thus, provide the potential to investigate initial mantle composition and, in particular, the processes of crystallisation of an early terrestrial magma ocean (Puchtel *et al.*, 2013, 2016b; Byerly *et al.*, 2017). For example, some komatiites from the Weltevreden formation in the Barberton Greenstone Belt, South Africa, have unusual Ca isotopic compositions compared with other komatiites and are interpreted as a record of mantle source heterogeneities induced

1. Université de Paris, Institut de Physique du Globe de Paris, CNRS, Paris, France  
 2. Department of Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia  
 3. Centre for Star and Planet Formation, Globe Institute, University of Copenhagen, Copenhagen, Denmark  
 4. Institut Universitaire de France, Paris, France  
 5. Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA 92093, USA  
 6. Department of Geology, University of Maryland, 8000 Regents Drive, College Park, MD 20742, USA  
 \* Corresponding author (email: moynier@ipgp.fr)



by magma ocean crystallisation (Amsellem *et al.*, 2019). Zirconium is useful to search for traces of magma ocean crystallisation processes because it is compatible in bridgmanite ( $D_{\text{bridgmanite-melt}} > 1$ ; Corgne *et al.*, 2005) and has different coordination numbers (CN) between bridgmanite (CN = 8, where it substitutes for Mg; Smyth and Bish, 1988), and silicate melt (CN = 6; Farges *et al.*, 1991). Since heavier isotopes tend to concentrate in the phases where it makes tighter bonds it is likely that crystallisation of bridgmanite from a melt would leave the residual liquid enriched in the heavier isotopes compared to bulk mantle.

## Samples and Methods

Thirty one komatiite samples (olivine- and pyroxene-spinifex-textured and olivine cumulates) were studied (Table S-1). The komatiite samples are from Fennoscandia (Victoria's Lava Lake, Vetryny Belt; Kostomuksha Greenstone Belt), South Africa (Komati, Weltevreden, and Schapenburg Formations of the Barberton Greenstone Belt), Zimbabwe (Belingwe Greenstone Belt) and Canada (Boston Creek Flow, Abitibi Greenstone Belt and Munro Township). All samples have previously been studied for trace and highly siderophile element abundances,  $^{186,187}\text{Os}$ ,  $^{142,143}\text{Nd}$ ,  $^{182}\text{W}$  isotope systematics (Puchtel *et al.*, 1998, 2001, 2005, 2009, 2013, 2016a,b), and for Ca stable isotopes (Amsellem *et al.*, 2019). Two widely available reference materials (BHVO-2 and AGV-2) for which Zr isotopic compositions have been reported previously (Inglis *et al.*, 2018; Tian *et al.*, 2020) were also analysed.

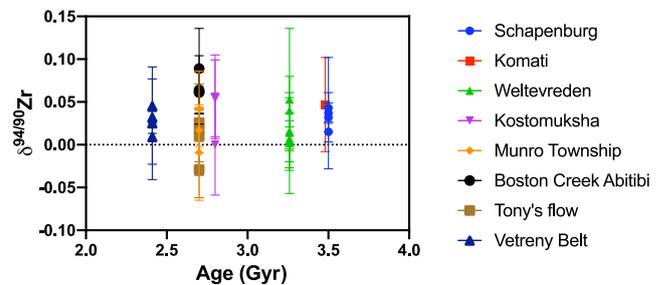
Given that komatiites have much lower Zr content than any previously analysed samples, we performed several full replicates (weighing, spike addition, dissolution, chemical separation, mass spectrometry analyses) (see Table S-1). These samples are noted "R" in Table S-1. The Zr isotopic composition was measured using a ThermoFischer Neptune plus MC-ICP-MS at the IGP as described in Tian *et al.* (2020). The protocol utilised for Zr stable isotope measurements was adapted from Inglis *et al.* (2018) and is reported in Table S-2. The size of columns utilised had to be scaled up and the chemical purification method modified due to the high Ca/Zr of komatiites, and the associated risk of Zr coprecipitation with Mg, Ca fluorides (Tanaka *et al.*, 2003). To do this, the column procedure from Inglis *et al.* (2018) was reversed. The details of the analytical methods can be found in the Supplementary Information.

## Results

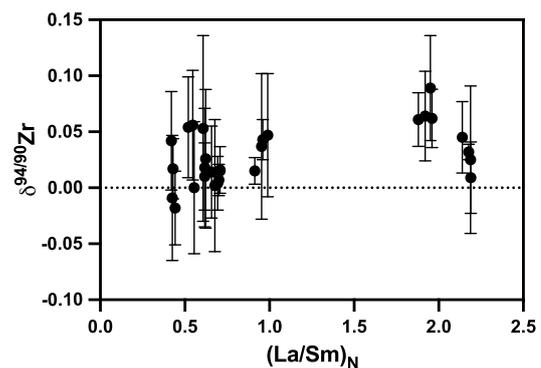
The Zr isotopic compositions are reported in Table S-1 as:

$$\delta^{94/90}\text{Zr} = \left[ \frac{\left( \frac{^{94}\text{Zr}}{^{90}\text{Zr}} \right)_{\text{sample}}}{\left( \frac{^{94}\text{Zr}}{^{90}\text{Zr}} \right)_{\text{IPGP-Zr}}} - 1 \right] \times 1000 \quad \text{Eq. 1}$$

There is presently no international Zr isotopic standard commercially available and the majority of the Zr isotopic data for rock samples have been reported against the IPGP-Zr standard (calibrated against a variety of geostandards; Inglis *et al.*, 2018; Feng *et al.*, 2020; Guo *et al.*, 2020; Tian *et al.*, 2020). Alternatively, three other standards have been used: zircon GJ-1 for *in situ* analyses (Zhang *et al.*, 2019), an elemental Zr standard, NIST SRM3169 (Feng *et al.*, 2020) and a standard in development by NIST (Ibañez-Mejía and Tissot, 2019; Tompkins *et al.*, 2020) for bulk measurements. These three standards have been calibrated against the IPGP-Zr standard (Tian *et al.*, 2020).



**Figure 1** Zirconium isotopic composition of komatiites as a function of their crystallisation ages. The  $\delta^{94/90}\text{Zr}$  values are constant through 1 Ga and in various locations indicating that the terrestrial mantle had a constant  $\delta^{94/90}\text{Zr}$  value through time. The Weltevreden komatiites have unusual Ca isotope signatures consistent with magma ocean crystallisation processes. They do not have a different Zr isotopic composition from other komatiites. Errors as 2 s.d. of replicated measurements (typically 4).



**Figure 2** Zirconium isotopic composition of the komatiites as a function of the La/Sm ratio normalised to primitive mantle composition  $[(\text{La}/\text{Sm})_N]$ . Variations in  $(\text{La}/\text{Sm})_N$  are interpreted to reflect prior melt extraction from komatiite source mantles. The absence of variation suggests that prior melt extraction did not fractionate Zr isotopes and that the source of the komatiites reflects the composition of the Archean mantle. Errors as 2 s.d. of the replicated measurements (typically 4).

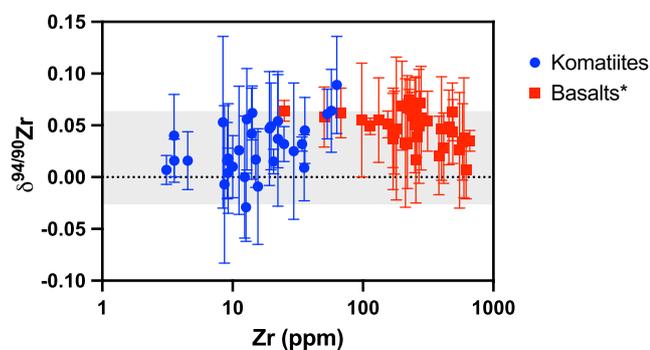
The  $\delta^{94/90}\text{Zr}$  values of BHVO-2 ( $0.033 \pm 0.025$  ‰) and AGV-2 ( $0.017 \pm 0.065$  ‰) are consistent with the previous measurements obtained using a different chemical protocol ( $\delta^{94/90}\text{Zr} = 0.044 \pm 0.044$  ‰ and  $0.044 \pm 0.050$  ‰, respectively), (Inglis *et al.*, 2018) and the values reported in Tian *et al.* (2020) ( $0.045 \pm 0.025$  ‰ and  $0.035 \pm 0.037$  ‰, respectively). Reproducibility of replicate analyses is consistent within the internal error defined by multiple replicate measurements of the same sample solutions. For example, the two replicates of SCH2.6 return a value of  $\delta^{94/90}\text{Zr} = 0.043 \pm 0.018$  ‰ (2 s.d.). In general, the Zr isotopic compositions of komatiites are relatively invariant, and show no correlation with age (Fig. 1) or the degree of prior melt removal (Fig. 2). The  $\delta^{94/90}\text{Zr}$  values of all the komatiites range from  $-0.018$  to  $+0.089$ , with an average value of  $0.030 \pm 0.04$  ‰ (2 s.d.,  $n = 31$ ).

## Discussion

*No measurable effects on Zr during magma ocean crystallisation.* Based on Os, Nd, Hf, O and Ca isotopic compositions of some komatiites like Weltevreden it has been suggested that they

recorded the fractionation of minerals stable under magma ocean conditions (Puchtel *et al.*, 2013; Byerly *et al.*, 2017; Amsellem *et al.*, 2019). The source of these komatiites is enriched in the heavier isotopes of Ca, consistent with the extraction of light Ca in Ca perovskite into the lower mantle and the preservation of mantle heterogeneity until at least the extraction of the komatiites at 3.26 Ga (Amsellem *et al.*, 2019). Given the compatibility of Zr in bridgmanite and the CN differences between bridgmanite and silicate melt outlined previously, crystallisation of bridgmanite could fractionate Zr isotopes. The Weltevreden komatiites do not have anomalous Zr isotopic compositions (average  $\delta^{94/90}\text{Zr}$  value for Weltevreden is  $0.019 \pm 0.036$  ‰, compared to  $0.032 \pm 0.054$  ‰ for other komatiites; *t* test, *p* value = 0.19) and, therefore, cannot validate the hypothesis. Assuming magma ocean fractionation effects in the source of Weltevreden komatiites, the absence of Zr isotopic variations likely reflects limited bridgmanite-melt fractionation, because the difference in CN at high temperatures was insufficient to induce isotopic fractionation resolvable within analytical uncertainty.

**Evolution of the Zr isotopic composition of Earth's mantle.** The similarity (*t* test, *p* value = 0.56) of Zr isotope composition between spinifex-textured and chilled margin komatiites ( $\delta^{94/90}\text{Zr} = 0.027 \pm 0.044$  ‰, *n* = 14) and olivine cumulates ( $\delta^{94/90}\text{Zr} = 0.033 \pm 0.054$  ‰, *n* = 17; Table S-1) indicates that there was limited isotopic fractionation during komatiite crystallisation. This is illustrated by the absence of correlation between  $\delta^{94/90}\text{Zr}$  and Zr content (Fig. 3,  $R^2 = 0.2$ ). Since komatiites are formed at temperatures >2000 K (Arndt *et al.*, 2008), isotopic fractionation during partial melting is minimised, and, therefore, they must represent the composition of their source. The sources of komatiites had been variably depleted by prior melt extractions, as evidenced from variations in the ratios of the light and heavy REE. This is exemplified by the normalised La/Sm ratio to the primitive mantle composition,  $(\text{La}/\text{Sm})_N$ , that deviates from one. Prior melt extraction would also have extracted Zr from the source and, potentially, fractionated Zr isotopes. The komatiites analysed here encompass a large range of  $(\text{La}/\text{Sm})_N$  values, from 0.44 to 2.2 (Puchtel *et al.*, 1998, 2001, 2005; 2009, 2013, 2016a,b). The absence of correlation ( $R^2 = 0.2$ ) between the  $\delta^{94/90}\text{Zr}$  values and  $(\text{La}/\text{Sm})_N$  (Fig. 2) indicates that the mantle sources of komatiites were not isotopically fractionated by prior melt extractions. The absence of temporal  $\delta^{94/90}\text{Zr}$  variations from 3.5 to 2.41 Ga (Fig. 1,  $R^2 = 0.004$ ) provides further evidence that prior melt extraction did not change the Zr isotopic composition of the komatiite mantle sources.



**Figure 3** Zirconium isotopic composition of komatiites (this study) and basalts (literature) as a function of the Zr content of the samples. While Zr content varies over two orders of magnitude, the  $\delta^{94/90}\text{Zr}$  are consistent with an average value of  $0.040 \pm 0.044$  (2 s.d., *n* = 72), which best reflects the composition of Earth's mantle (grey band). Errors as 2 s.d. of replicate measurements (typically 4). Data from Inglis *et al.* (2019).

Therefore, the average  $\delta^{94/90}\text{Zr}$  value of komatiites should reflect the composition of their mantle source. The average Zr isotopic composition of komatiites ( $\delta^{94/90}\text{Zr} = 0.030 \pm 0.049$  ‰) overlaps with the mantle's estimate based on young basaltic rocks ( $\delta^{94/90}\text{Zr} = 0.048 \pm 0.032$  ‰, Inglis *et al.*, 2019). When averaged together with the previously analysed basalts (Inglis *et al.*, 2019), a conservative estimate for the  $\delta^{94/90}\text{Zr}$  for the Earth's mantle of  $0.040 \pm 0.044$  ‰ (2 s.d., *n* = 72) is calculated (grey band in Fig. 3). However, it should be noted that basalts are slightly lighter than komatiites (*t* test, *p* value = 0.001), which may indicate that low degree partial melt could be enriched in the heavier isotopes of Zr as previously suggested to explain the enrichments in light Zr isotopes in the mantle source of N-MORBs (Inglis *et al.*, 2019). Future analyses of mantle peridotites would allow further assessment of this issue.

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Editor: Anat Shahar

## Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2033>.



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