Zirconium isotopic composition of the mantle through time

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Supplementary Information

The Supplementary Information includes:

Methods

Homogenous sample powders were aliquoted in order to obtain a minimum of 1 µg Zr per sample. This equated to a few 100s mg of powder in most cases. The aliquots were then spiked with a ^{91}Zr–^{96}Zr double-spike (51.4% ^{91}Zr and 48.6% ^{96}Zr) at an optimal spike to sample ratio of 43:57 prior to sample digestion (Inglis *et al.*, 2018). The sample powders were digested in Parr bombs using a mixture of concentrated HF and HNO_3 at a 3:1 (v/v) ratio to ensure full dissolution (see Inglis *et al.*, 2018). The samples were then dried down and dissolved in 2 mL of 6M HCl at 140 °C for one day, evaporated to dryness and further dissolved in 2 mL using a mixture of HCl (~6M) and HNO_3 (~16M) at a 3:1 (v/v) ratio at 120°C for one day. After this the solutions were visually checked to ensure that full dissolution was achieved. The protocol utilized for Zr stable isotope measurements here was adapted from Inglis *et al*. (2018) and is reported in Table S-2. We first had to increase the volume of the acid utilised in Inglis *et al*. (2018) for high Zr samples (*e.g.* basalts, zircons) to accommodate for the larger amount of sample loaded onto the columns. We also modified the protocol of chemical purification to take into account the high Ca/Zr ratio of komatiites compared to basalts, and the associated risk of Zr coprecipitation with Mg-Ca fluorides (Tanaka *et al.*, 2003). To do this we simply reverse the order of the two columns from Inglis *et al*. (2018) in order to remove Ca and Mg.

The full protocol included a first clean up of Fe using an AG1-X8 column with solutions as 6M HCl. The purified solutions were then dried down. Subsequently they were treated with 16M HNO_3 and evaporated to dryness before being loaded on 1 mL Eichrom DGA resin in 1 mL of 12M HNO_3. Elements including Ca, Fe, Ti and Mo were eluted with 12 mL of 12M HNO_3 and 12 mL 3M HNO_3 in sequence. Following this the Zr was eluted from the column in 10mL of a mixture HNO_3 (3M) and HF (0.2M). After evaporation of the Zr cut, the samples were loaded on a 2 mL anion exchange resin (Bio-Rad AG1-X8 200-400 mesh) in 4M HF. The matrix is eluted with 32 mL of 4M HF, apart

from Hf, Te and W which remain on the resin along with Zr (Schönbächler *et al.*, 2004). The remaining Zr were collected using 10 mL of a mixture of 6M HCl and 0.01M HF.

After purification, sample solutions were dried down and then treated with 16M HNO_3 at 100 °C for 2 hours to remove any potential organic residues eluted from the resin. Finally, the Zr cut was dried down and dissolved in a mixture of HNO_3 (0.5M) and HF (0.1M) for analysis.

The Zr isotopic composition was measured using a *Thermo Fisher* Neptune plus multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Institut de Physique du Globe de Paris, France, as described in Tian *et al.* (2020) and adapted from Inglis *et al.* (2018). The details of the instrumental operating parameters are given in Table S-3. Data acquisition consisted of 1 block of 50 cycles with integration time of 4.194 seconds. Washouts consisting of 7 minutes in 1M HNO_3 + 0.1M HF were conducted after every analysis, and baselines were measured on-peak prior to each analysis, comprising one block of 10 x 4.194 s integrations in 0.5M HNO3 + 0.1M HF. Ion beams from ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr, ^{95}Mo and ^{96}Zr were collected simultaneously in a static configuration using Faraday cups connected to 10^{11} Ω amplifiers. Three isotopic ratios are required in the double-spike equations to solve for the three unknowns: 1) mass-dependent fractionation factors of samples relative to the standard, 2) the instrumental fractionation factor and 3) the mass fraction of the Zr contributed from the double spike in the sample–double spike mixture. The Zr isotope ratios $^{91}Zr^+/^{90}Zr^+$, $^{94}Zr^+/^{90}Zr^+$ and $^{96}Zr^+/^{90}Zr^+$ were used for double spike data inversion calculation, which was achieved using the *IsoSpike* addon for the software package *Iolite* (Creech and Paul, 2015). The potential presence of Mo was monitored using mass $^{95}Mo^+$, and Mo interferences were corrected assuming the natural Mo isotope composition from Berglund and Wieser (2011) corrected for instrumental mass bias. Natural Mo isotope ratios were corrected using the instrumental mass bias determined from the double-spike calculations, and the calculated ^{92}Mo, ^{94}Mo and ^{96}Mo were subtracted from the signals of ^{92}Zr, ^{94}Zr and ^{96}Zr, respectively, prior to calculation of raw ratios; this procedure was repeated such that the mass bias (and, thus, corrected ratios) converged on a constant value.

Supplementary Tables

Table S-1 Zirconium isotopic composition of 31 komatiites and of two geological reference materials. The data are reported as $\delta^{94/90}Zr$, the per mil deviation of the $^{94}Zr/^{90}Zr$ from the IPGP-Zr standard. "R" denotes full replicates of the sample measurements. Zr concentrations are calculated by isotope dilution. "n" are the number of replicates.

Sample name	Location	Age Ga	Texture	$\delta^{94/90}Zr$	2SD	Zr (ppm)	n
SCH1.6	Schapenburg, South Africa (SA)	3.55	Ol-spinifex	0.032	0.017	24.8	8
SCH2.1	Schapenburg, SA	3.55	Ol-spinifex	0.015	0.012	20.6	4
SCH2.6	Schapenburg, SA	3.55	Ol-spinifex	0.049	0.042	19.7	4
SCH2.6-R	Schapenburg, SA	3.55	Ol-spinifex	0.036	0.030	23.4	8
SCH2.6 average	Schapenburg, SA	3.55	Ol-spinifex	0.043	0.018	21.5	2
SCH3.6	Schapenburg, SA	3.55	Ol-spinifex	0.037	0.065	22.3	4
BV10	Komati, Barberton, SA	3.48	Ol-cumulate	0.047	0.055	19.2	4
12-2	Weltevreden, Barberton, SA	3.26	Ol-spinifex	0.004	0.024	9.2	2
12-6	Weltevreden, Barberton, SA	3.26	Ol-cumulate	0.007	0.014	3.1	4
12-8	Weltevreden, Barberton, SA	3.26	Ol-cumulate	0.016	0.028	4.5	4
12-8-R	Weltevreden, Barberton, SA	3.26	Ol-cumulate	0.014	0.01	4.3	6
12-8 average	Weltevreden, Barberton, SA	3.26	Ol-cumulate	0.015	0.003	4.4	2
501-1	Weltevreden, Barberton, SA	3.26	Ol-cumulate	0.016	0.021	3.6	6
564-2	Weltevreden, Barberton, SA	3.26	Ol-cumulate	0.040	0.040	3.6	4
564-4	Weltevreden, Barberton, SA	3.26	Ol-spinifex	0.016	0.037	9.1	2
564-4-R	Weltevreden, Barberton, SA	3.26	Ol-spinifex	-0.007	0.076	8.7	4
564-4-R	Weltevreden, Barberton, SA	3.26	Ol-spinifex	0.034	0.032	6.9	8
564-4 average	Weltevreden, Barberton, SA	3.26	Ol-spinifex	0.014	0.041	8.2	3
564-5	Weltevreden, Barberton, SA	3.26	Ol-spinifex	0.002	0.059	8.7	2
564-6	Weltevreden, Barberton, SA	3.26	Chilled margin	0.053	0.083	8.4	2
94100	Kostomuksha, Baltic Shield	2.8	Ol-cumulate	0.056	0.049	12.9	4
94126	Kostomuksha, Baltic Shield	2.8	Ol-cumulate	0.000	0.059	12.4	4
9497	Kostomuksha, Baltic Shield	2.8	Ol-spinifex	0.054	0.045	22.3	4
PH26	Pyke Hill, Canada	2.7	Ol-spinifex	0.042	0.044	14.0	2
PH27	Pyke Hill, Canada	2.7	Ol-spinifex	-0.009	0.056	15.6	4
PH28	Pyke Hill, Canada	2.7	Ol-spinifex	0.017	0.027	15.1	4
BC02	Boston Creek, Canada	2.7	Px-spinifex	0.064	0.040	57.2	4

BC03	Boston Creek, Canada	2.7	Px-spinifex	0.089	0.047	62.9	4
BC06	Boston Creek, Canada	2.7	Ol-cumulate	0.061	0.024	53.2	4
BC08	Boston Creek, Canada	2.7	Ol-cumulate	0.062	0.026	14.2	4
ZV10	Tony's flow, Zimbabwe	2.7	Ol cumulate	-0.029	0.033	12.7	4
ZV10-R	Tony's flow, Zimbabwe	2.7	Ol cumulate	-0.006	0.078	11.4	4
ZV10 average	Tony's flow, Zimbabwe	2.7	Ol cumulate	-0.018	0.033	12.0	2
TN17	Tony's flow, Zimbabwe	2.7	Ol cumulate	0.010	0.030	10.0	4
TN18	Tony's flow, Zimbabwe	2.7	Ol cumulate	0.018	0.053	9.3	4
TN19	Tony's flow, Zimbabwe	2.7	Ol cumulate	0.026	0.062	11.2	4
01001	Vetreny Belt, Baltic Shield	2.41	Ol-cumulate	0.035	0.050	34.1	4
01001-R	Vetreny Belt, Baltic Shield	2.41	Ol-cumulate	0.030	0.013	34.0	4
01001 average	Vetreny Belt, Baltic Shield	2.41	Ol-cumulate	0.032	0.007	34.0	2
01104	Vetreny Belt, Baltic Shield	2.41	Ol-cumulate	0.009	0.032	35.4	4
01104-R	Vetreny Belt, Baltic Shield	2.41	Ol-cumulate	0.035	0.039	36.0	4
01104 average	Vetreny Belt, Baltic Shield	2.41	Ol-cumulate	0.022	0.037	35.7	2
01105	Vetreny Belt, Baltic Shield	2.41	Ol-cumulate	0.025	0.066	29.5	4
01106	Vetreny Belt, Baltic Shield	2.41	Ol-cumulate	0.045	0.032	35.8	4
BHVO-2	USGS GRM			0.033	0.025	155.6	4
AGV-2	USGS GRM			0.017	0.065	238.7	4

Table S-2 Zirconium chemical purification protocol.

First stage. AG1-X8 (2 mL, 200–400 mesh)		
Step	Reagent	Volume(mL)
Resin cleaning	2M HNO_3	8
	MQ H_2O	8
Conditioning	6 M HCl	8 (4*2)
Sample load and Zr collection	6 M HCl	8 (2+6)
Second stage. DGA (1.4 mL, 200–400 mesh)		
Step	Reagent	Volume(mL)
Resin cleaning	MQ H_2O	6
	12 M HNO_3	6
	3 M HNO_3 + 0.2 M HF	6
Conditioning	12 M HNO_3	8 (4*2)
Sample load	12 M HNO_3	1
Matrix elution	12 M HNO_3	12 (6*2)
	3 M HNO_3	12 (6*2)
Zr collection	3 M HNO_3 + 0.2 M HF	10 (5*2)
Third stage. AG1-X8 (2 mL, 200–400 mesh)		
Step	Reagent	Volume(mL)
Resin cleaning	2M HNO_3	6
	MQ H_2O	6
	6M HCl + 0.01M HF	6
	MQ H_2O	2
Conditioning	4 M HF	8 (4*2)
Sample load	4 M HF	2
Matrix elution	4 M HF	32 (8*4)
Zr collection	6M HCl +0.01M HF	10 (5*2)

Table S-3 MC-ICP-MS operation parameters for Zr isotope measurements.

Neptune Plus MC-ICP-MS	
RF power	1200 W
Cool gas flow	16 L min^{-1}
Auxiliary gas flow	~ 1 L min^{-1}
Sample gas flow	~ 1 L min^{-1}
Argon make-up gas flow (only CSC Mode)	0.29 ~ 0.34 L min^{-1}
Cones	Ni Jet cone, Ni 'H' cone
Mass resolution mode	Low (M/ΔM $\approx$ 1700)
Acceleration voltage	10 kV
Mass analyzer pressure	~ 8 x 10^{-9} mbar
Introduction System	PFA cyclonic spray chamber
Sample uptake rate	~ 50 mL min^{-1}
Solution running concentration	200 ng mL^{-1}
Typical sensitivity	~ 9 V
Integration time	4.194 s
Cycle numbers per analysis	50
Washout time	7 min
Faraday cup Configuration	
L2	^{90}Zr
L1	^{91}Zr
C	^{92}Zr
H2	^{94}Zr
H3	^{95}Mo
H4	^{96}Zr

Supplementary Information References

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