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A baseline for the Sn isotopic composition of the upper continental crust

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Supplementary Information

The Supplementary Information includes:

- Analytical Method
- Geological Reference Material Analysis
- Tables S-1 and S-2
- Supplementary Information References

Analytical Method

Glacial diamictite powders obtained as described in Gaschnig *et al.* (2016) were carefully weighed. To pre-cleaned Teflon beakers, ca. 500 mg of powdered sample were double-spiked (using Sn abundance estimates from Gaschnig *et al*., 2016) and added 5 mL of concentrated nitric acid and 5 mL of concentrated HF, and left on a hotplate at 100ºC for 48 hours to digest. They were dried down and taken up in aqua regia at 150 °C for 24 hours to dissolve fluoride complexes. The samples were evaporated and added 5 mL of 10 N HCl and re-evaporated to dryness before finally making them into 2 mL of 0.5 N HCl solutions adequate for the anion-exchange chemistry protocol. The samples were loaded on 1 mL of Eichrom TRU resin contained in Biorad columns and conditioned with 4 mL of 0.5 N HCl. The matrix was eluted in 4 mL of 0.5 N HCl, 4 + 3 mL of 0.25 N HCl, and the Sn cuts were collected in 4 + 3 + 3 mL of 0.5 N HNO_3. One mL of 10 N HCl was added to the clean beakers prior to Sn collection to avoid the formation of insoluble compounds in the Sn-HNO_3 mixture.

Sample Sn stable isotope ratios were measured using a Thermo-Scientific Neptune Plus multi-collector inductively coupled plasma mass spectrometer operating in low-resolution mode. The sample solutions were introduced using an ESI Apex desolvation system and a PFA nebuliser with an uptake rate of 100 µL min^{-1}. In between sample measurements, three rinse cycles were performed using three different clean 0.5 N HCl solutions after which the on-peak zero was measured. Groups of two samples were bracketed by measurements of optimally double-spiked standards. The data reduction was carried out using Isospike (www.isospike.org; Creech and Paul, 2015; Creech *et al*., 2017) operated with the Iolite software. Tin isotopic ratios are reported with delta notation as $\delta^{122/118}$Sn relative to the NIST3161a standard and 2 standard deviations. Procedural blanks were measured and found insignificant compared to the Sn abundance in the measured samples (<1 ng). The external reproducibility of the protocol was ensured by processing two geological reference materials: BHVO-2 and BCR-2. The internal reproducibility of the method was tested by performing full replicates (double-spiking, dissolution and chemical separation): two replicates of BHVO-2 and four replicates of BCR-2.

Geological Reference Material Analysis

The $\delta^{122/118}$Sn value determined for BHVO-2 is 0.36 ± 0.01 ‰ and shows excellent reproducibility between the two replicates (0.37 ± 0.04 ‰ and 0.35 ± 0.06 ‰, with n = 4 and 3, respectively) and with literature data (0.33 ± 0.01 ‰; She *et al.*, 2023). Similar results are inferred from BCR-2 measurements which yield an average of 0.28 ± 0.01 ‰ over four full replicates and a total of 11 individual measurements. The yields of the purification process were estimated using the exact digested masses and the Sn concentration estimates from Gaschnig *et al*. (2016) and have typical values and dispersion for Sn purification (Creech *et al*., 2017): from 6.6 to 48.8 % with an average of 25.3 %. Although these values are arguably low, the four full replicates of BCR-2 with different yields (7.6, 29.5, 45.6 and 48.4 %) produced identical isotopic composition values within error (0.29 ± 0.01 ‰, 0.27 ± 0.04 ‰, 0.29 ± 0.03 ‰ and 0.27 ± 0.02 ‰ respectively), suggesting that the yield does not influence the accuracy of the isotopic measurements. The same is observed with both BHVO-2 full replicates (yields of 20.7 % and 40.3 % and $\delta^{122/118}$Sn of 0.37 ± 0.04 ‰ and 0.35 ± 0.06 ‰, respectively). Moreover, the BCR-2 and BHVO-2 full replicates were used to test the effect of HF addition in the collecting beaker and before each sample evaporation on the final yield. Both these HF additions significantly increase the yield by factors of 4 and 6 respectively, and the combination of both could increase the yields from 2 to 7 times (see Table S-2). Overall, this demonstrates the robustness of the double-spike method in correcting for possible fractionations associated to significant Sn loss occurring during the chemical processing and purification protocols necessary for Sn isotopic measurements.

Supplementary Tables

Table S-1 Tin isotopic compositions of twenty-four glacial diamictites and two geological reference materials.

Stratigraphic unit	Location	Depositional age (Ga)	Reference	Sn (ppm)	$\delta^{122/118}Sn_{NIST3161a}$ (‰)	2 s.d.	*n*
Archean							
Afrikander	South Africa	2.96	Guy *et al.* (2010)	0.39	0.19	0.01	1
Coronation	South Africa	2.96	Guy *et al.* (2010)	1.58	0.20	0.01	1
Mozaan	South Africa	2.97	Young *et al.* (1998)	0.95	0.38	0.01	1
Promise	South Africa	2.96	Guy *et al.* (2010)	0.89	0.20	0.01	1
Palaeoproterozoic							
Bottle Creek	USA	2.28	Houston *et al.* (1992)	1.05	0.26	0.04	3
Bruce	Canada	2.38	Melezhik *et al.* (2013)	1.72	0.00	0.02	3
Duitschland	South Africa	2.38	Melezhik *et al.* (2013)	3.56	0.19	0.01	1
Gowganda	Canada	2.40	Melezhik *et al.* (2013)	1.33	0.15	0.03	2
Makganyene	South Africa	2.44	Melezhik *et al.* (2013)	2.08	0.15	0.01	2
Ramsay Lake	Canada	2.44	Melezhik *et al.* (2013)	1.36	0.28	0.01	1
Timeball Hill	South Africa	2.25	Melezhik *et al.* (2013)	2.67	0.17	0.00	2
Neoproterozoic							
Blaubeker	Namibia	0.69	Prave *et al.* (2011)	1.89	0.25	0.01	3
Chuos	Namibia	0.69	Le Heron *et al.* (2013)	1.60	0.22	0.01	4
Gaskiers	Canada	0.58	Carto and Eyles (2011)	1.87	0.24	0.00	2
Ghaub	Namibia	0.64	Hoffman (2011)	1.54	0.21	0.01	3
Gucheng	China	0.68	Liu *et al.* (2008)	2.24	0.25	0.01	1
Kaigas	Namibia	0.76	Frimmel (2011)	3.93	0.24	0.01	3
Konnarock	USA	0.67	Rankin (1993)	2.63	0.32	0.02	2
Nantuo	China	0.65	Zhou *et al.* (2004)	2.49	0.21	0.01	1
Numees	Namibia	0.65	Frimmel (2011)	2.38	0.24	0.01	3
Pocatello	USA	0.69	Keeley *et al.* (2013)	3.03	0.23	0.02	2
Palaeozoic							
Bolivia	South America	0.32	Starck and del Papa (2006)	2.68	0.23	0.01	1
Dwyka East	South Africa	0.30	Visser (1982)	2.31	0.26	0.03	3
Dwyka West	South Africa	0.30	Visser (1982)	1.38	0.21	0.01	1
Reference materials							
BHVO-2					0.36	0.03	7
BCR-2					0.28	0.03	11

Table S-2 Results testing the chemical protocol on six full replicates of reference materials. The addition of concentrated HF in the beaker before evaporation and in the collecting beaker is tested as a potential factor influencing the separation yield and isotopic ratios. Although the yield is positively affected by these additional steps in the protocol, the measured isotopic compositions are identical within error.

Sample	Conc. HF in beaker before evaporation	Conc. HF in collecting beaker	*n*	Yield (%)	$\delta^{122/118}$Sn	2 s.d.
BHVO-2			4	20.7	0.37	0.04
BHVO-2	X	X	3	40.3	0.35	0.06
BCR-2			2	7.6	0.29	0.01
BCR-2	X		3	45.6	0.29	0.03
BCR-2		X	3	29.5	0.27	0.04
BCR-2	X	X	3	48.4	0.27	0.02

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