Supporting Information

Pons et al. 10.1073/pnas.1108061108

SI Materials and Methods

The chemical procedure is adapted from ref. 1.

Sample Digestion. After crushing in an agate mortar, 200 to 500 mg of powdered samples were digested for 48 hr in a 7:3 mL concentrated HF:HNO_3 mixture at about 130 °C and then evaporated to dryness. Concentrated HCl (5 mL) and a few drops of HClO4 were added to the dried sample to get rid of fluorides. Once evaporated again, samples were dissolved in 6N HNO3 and evaporated to dryness one last time to remove all traces of HClO4.

Zinc Chemical Separation. Teflon columns were filled with 500 µL AG1-X8 100–200 mesh anionic resin stored in 0.5N HNO_3. Resin was washed three times with Milli-Q water (18MΩ-grade) and 0.5N HNO_3 and then conditioned with 1.5N HBr. Sample is loaded onto the column in a 1.5N HBr medium (1). Zn^{2+} is strongly adsorbed on the resin whereas the matrix elements are eluted. Zinc is then recovered in 0.5N HNO_3. The protocol is then repeated to purify the zinc fraction. The process is summarized in Table S1.

Isotope Measurements. Zinc isotope ratios have been measured using the Nu 500 HR multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) at ENS Lyon following the procedure described in Maréchal et al. (2, 3). Isotope ratios are expressed in δ units, where δ is the deviation relative to the standard JMC 3-0749 L in permil:

$$\delta^{66}\mathrm{Zn}(\text{‰}) = \left[\frac{(^{66}\mathrm{Zn}/^{64}\mathrm{Zn})_{\mathrm{sample}}}{^{66}\mathrm{Zn}/^{64}\mathrm{Zn})_{\mathrm{standard}}} - 1\right] \times 1{,}000$$

The samples were introduced by free aspiration in 0.05 N subboiled distilled HNO_3 using a glass microconcentric nebulizer and a glass cyclonic spray chamber. Zinc istopes ($M = 64, 66, 67$, and 68) were measured together with copper (Cu: $M = 63, 65$). Nickel (Ni) was also monitored at mass 62 to correct the Ni contribution on mass 64. The instrumental mass fractionation was corrected using Cu-doping and [one standard]-[two samples] bracketing (4). We used Cu NIST-SRM 976 for doping and an exponential law to correct the instrumental mass bias.

1. Moynier F, Albarède F, Herzog G (2006) Isotopic composition of zinc, copper, and iron in lunar samples. *Geochim Cosmochim Acta* 70:6103–6117.
2. Maréchal CN, Télouk P, Albarède F (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem Geol* 156:251–273.
3. Maréchal CN, Nicolas E, Douchet C, Albarède F (2000) Abundance of zinc isotopes as a marine biogeochemical tracer. *Geochem Geophy Geosy* 1:1–15.
4. Albarède F (2004) Analytical methods for non-traditional isotopes. *Geochemistry of Non-Traditional Stable Isotopes*, eds Johnson CM, Beard BL, Albarède F. *Rev Mineral Geochem* 55:409–427.
5. Bentahila Y, Ben Othman D, Luck J (2008) Strontium, lead and zinc isotopes in marine cores as tracers of sedimentary provenance: A case study around Taiwan orogen. *Chem Geol* 248:62–82.
6. Pichat S, Douchet C, Albarède F (2003) Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka. *Earth Planet Sci Lett* 210:167–178.

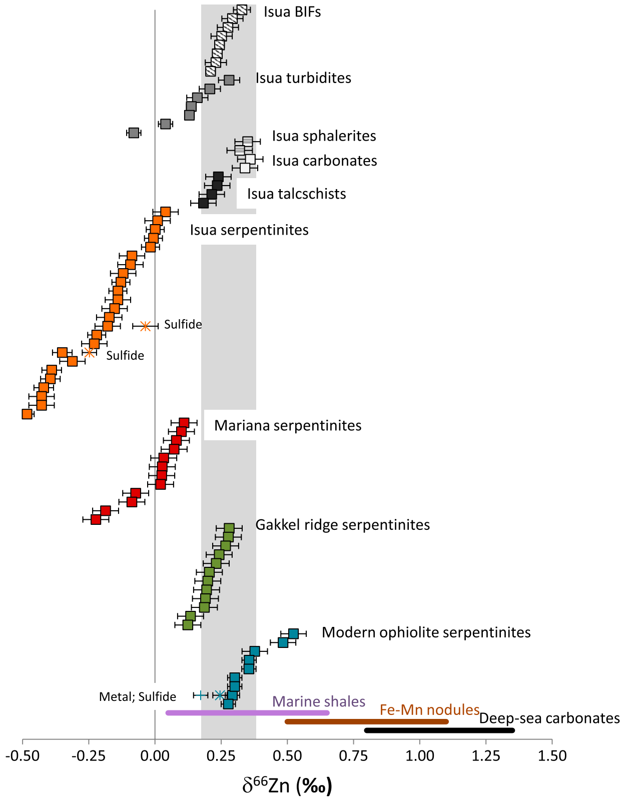

Fig. S1. Zinc isotope composition of Isua supracrustal rocks and serpentinites from Mariana forearc, Gakkel Ridge and ophiolites, compared to previous δ^{66}Zn data in marine shales (this study) (5), deep-sea carbonates (6) and FeMn nodules (3). The gray band represents the worldwide igneous average (4). Samples are plotted in the same order as presented in Table S2.

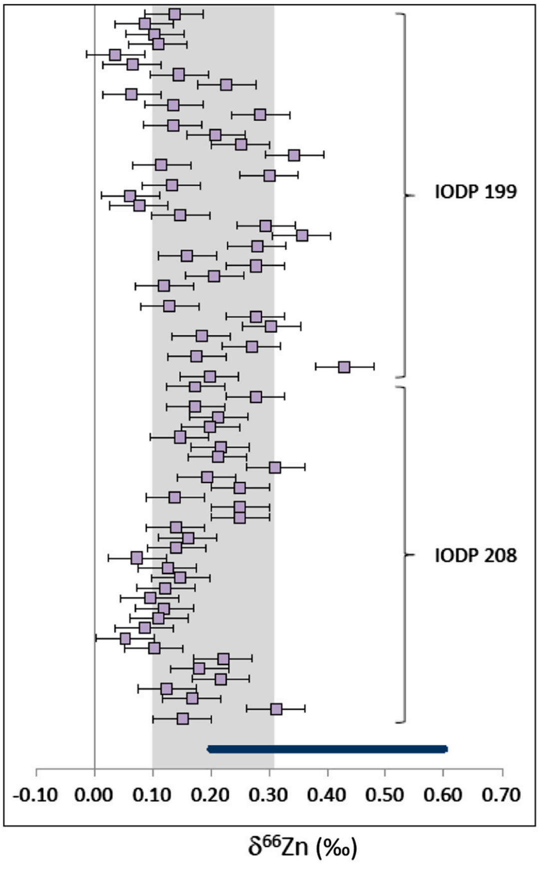

Fig. S2. δ^{66}Zn values of various marine shales from IODP cores 199 and 208 and literature (blue line) (5). Samples are plotted in the same order as presented in Table S3.

Table S1. Zinc column chromatography extraction and purification protocol (adapted from ref. 1)

Eluant	Volume (mL)	
1.5 N HBr	3	column conditioning
1.5 N HBr	0.5	sample loading on the resin
1.5 N HBr	3	elution of the matrix elements
0.5 N HNO_3	3	Zn elution

Resin type: AG1-X8, 100–200 mesh. Column material: teflon. Resin bed dimensions: height 1.5 cm, volume: 500 μL.

Table S2. Zinc isotope composition of Isua samples (serpentinites unless otherwise specified) and modern serpentinites

Sample location and nature	Sample reference	δ^{66}Zn ‰	±2 s.d
Isua			
BIF	111	0.33	0.018
BIF	110	0.29	0.040
BIF	116	0.28	0.018
BIF	128	0.25	0.018
BIF	126	0.24	0.040
BIF	122	0.24	0.040
BIF	IM	0.23	0.040
BIF	BIF 460037	0.21	0.032
turbidite	30078 bouma	0.28	0.018
turbidite	K	0.21	0.040
turbidite	BOUMA 06018	0.16	0.018
turbidite	L	0.14	0.040
turbidite	H	0.13	0.040
turbidite	bouma 60024	0.04	0.027
turbidite	bouma 60026	−0.08	0.027
sphalerite vein	B1	0.35	0.048
sphalerite vein	B2	0.32	0.048
carbonate	carbo1	0.36	0.048
carbonate	carbo2	0.34	0.048
talcschist	talc 1	0.24	0.048
talcschist	talc 2	0.24	0.048
talcschist	talc 3	0.21	0.048
talcschist	talc 4	0.18	0.048
	70024	0.04	0.048
	isua 4	0.01	0.037
	13	0.00	0.034
	940093	−0.01	0.048
	isua 3	−0.02	0.037
	isua 1	−0.09	0.048
	isua 2	−0.09	0.048
	17b	−0.12	0.048
	8a	−0.13	0.034
	20	−0.14	0.048
	22a	−0.14	0.048
	70006	−0.15	0.034
	940094 bulk rock	−0.17	0.027
sulfide	940094 sulfides	−0.04	0.027
	70019	−0.18	0.034
	22b	−0.22	0.048
	17a	−0.23	0.048
	8c	−0.31	0.048
	8c bulk rock	−0.35	0.048
sulfide	8c sulfides	−0.25	0.048
	isua 6	−0.39	0.037
	70009	−0.39	0.034
	19a	−0.42	0.034
	70019	−0.43	0.048
	isua 5	−0.43	0.037
	70014	−0.48	0.048
Mariana—IODP leg 195			
	U1200A 00006R 01 WW - 2	0.11	0.049
	U1200A 00006R 01 WW - 1	0.10	0.049
	U1200A 00016R 01 WW - 2	0.08	0.049
	U1200A 00016R 01 WW - 1	0.07	0.049
	U1200A 00010R 01 WW - 1	0.03	0.049

Sample location and nature	Sample reference	δ^{66}Zn ‰	±2 s.d
	U1200A 00007R 02 WW - 2	0.03	0.049
	U1200A 00007R 02 WW - 1	0.03	0.049
	U1200A 00010R 01 WW - 2	0.02	0.049
	U1200A 00013R 01 WW - 1	−0.07	0.049
	U1200A 00013R 01 WW - 2	−0.09	0.049
	U1200A 00017G 01 WW - 2	−0.19	0.049
	U1200A 00017G 01 WW - 1	−0.22	0.049
Gakkel ridge			
	HLY 0102 85 45 - 2	0.28	0.049
	HLY 0102 70 99 - 1	0.28	0.049
	HLY 0102 70 99 - 2	0.27	0.049
	HLY 0102 87 8 - 1	0.24	0.049
	HLY 0102 246 19 - 2	0.23	0.049
	HLY 0102 246 19 - 1	0.21	0.049
	HLY 0102 257 46 - 1	0.20	0.049
	HLY 0102 87 8 - 2	0.19	0.049
	HLY 0102 85 45 - 1	0.19	0.049
	HLY 0102 257 46 - 2	0.19	0.049
	HLY 0102 70 73 - 1	0.13	0.049
	HLY 0102 70 73 - 2	0.12	0.049
Baja California			
	M5	0.48	0.027
	M6	0.52	0.027
	M2	0.35	0.048
	M4	0.30	0.048
	M1 bulk rock	0.29	0.027
sufide	M1 sulfide	0.25	0.027
metal	M1 metal	0.17	0.027
	M3	0.28	0.048
Alps			
	A1	0.38	0.027
	A2	0.36	0.027
	A3	0.30	0.027

Measured on Nu 500 HR MC-ICPMS (ENS de Lyon).

Table S3. Zinc isotope composition of marine shale samples

sample location and nature	sample reference	δ^{66}Zn ‰	±2 s.d
IODP leg 199 - Equatorial Pacific Ocean			
	199 1218A 001H 01W 3 4	0.14	0.050
	199 1218A 001H 01W 9 10	0.09	0.050
	199 1218A 001H 01W 12 13	0.10	0.050
	199 1218A 001H 01W 30 31	0.11	0.050
	199 1218A 001H 01W 50 51	0.04	0.050
	199 1218A 001H 01W 80 81	0.07	0.050
	199 1218A 001H 01W 120 121	0.15	0.050
	199 1218A 001H 01W 137 138	0.23	0.050
	199 1218 A 001H 02W 40 41	0.06	0.050
	199 1218A 001H 02W 80 81	0.14	0.050
	199 1218A 001H 02W 140 141	0.29	0.050
	199 1218A 001H 03W 50 51	0.13	0.050
	199 1218A 001H 04W 50 51	0.21	0.050
	199 1218A 001H 05W 50 51	0.25	0.050
	199 1218A 001H 06W 40 41	0.34	0.050
	199 1218A 002H 01W 50 51	0.12	0.050
	199 1218A 002H 02W 50 51	0.30	0.050
	199 1218A 002H 02W 90 91	0.13	0.050
	199 1218A 002H 03W 50 51	0.06	0.050
	199 1218A 002H 06W 50 51	0.08	0.050
	199 1218A 003H 01W 50 51	0.15	0.050
	199 1218A 003H 03W 90 91	0.29	0.050
	199 1218A 003H 05W 50 51	0.36	0.050
	199 1218A 004H 01W 50 51	0.28	0.050
	199 1218A 004H 03W 90-91	0.16	0.050
	199 1218A 004H 04W 130-131	0.28	0.050
	199 1218A 005H 02W 50-51	0.21	0.050
	199 1218A 005H 04W 28-29	0.12	0.050

sample location and nature	sample reference	$\delta^{66}Zn$ ‰	±2 s.d
	199 1218A 005H 06W 100-101	0.13	0.050
	199 1218A 006H 02W 50-51	0.28	0.050
	199 1218A 006H 06W 80-81	0.30	0.050
	199 1218A 006H 06W 80-81	0.18	0.050
	199 1218A 006H 07W 50 51	0.27	0.050
	199 1218A 007H 01W 50-51 1	0.18	0.050
	199 1218A 007H 01W 50-51 2	0.43	0.050
IODP leg 208 - Walvis Ridge			
	208 1262 B1 1W 5-6	0.20	0.050
	208 1262 B1 1W 55-56	0.17	0.050
	208 1262 B1 1W 140-141	0.28	0.050
	208 1262 B1 2W 50-51	0.17	0.050
	208 1262 B1 3W 55-56	0.21	0.050
	208 1262 B1 3W 120-121	0.20	0.050
	208 1262 B1 4W 90-91	0.15	0.050
	208 1262 B1 5W 40-41	0.22	0.050
	208 1262 B2 1W 55-56	0.21	0.050
	208 1262 B2 3W 75-76	0.31	0.050
	208 1262 B3 1W 55-56	0.19	0.050
	208 1262 B2 5W 56-57	0.25	0.050
	208 1262 B3 3W 60-61	0.14	0.050
	208 1262 B3 5W 85-86	0.25	0.050
	208 1262 B4 1W 110-111	0.25	0.050
	208 1262 B4 3W 60-61	0.14	0.050
	208 1262 B4 5W 35-36	0.16	0.050
	208 1262 B5 1W 135-136	0.14	0.050
	208 1262 B5 3W 45-46	0.07	0.050
	208 1262 B5 5W 35-36	0.13	0.050
	208 1262 B5 7W 30-31	0.15	0.050
	208 1262 B6 2W 70-71	0.12	0.050
	208 1262 B6 3W 120-121	0.10	0.050
	208 1262 B6 4W 115-116	0.12	0.050
	208 1262 B6 5W 115-116	0.11	0.050
	208 1262 B6 6W 115-116	0.09	0.050
	208 1262 B7 1W 115-116	0.05	0.050
	208 1262 B7 2W 75-76	0.10	0.050
	208 1262 B7 4W 75-76	0.22	0.050
	208 1262 B7 6W 75-76	0.18	0.050
	208 1262 B7 8W 15-16	0.22	0.050
	208 1262 B8 1W 75-76	0.12	0.050
	208 1262 B8 2W 75-76	0.17	0.050
	208 1262 B8 4W 90-91	0.31	0.050
	208 1262 B8 6W 135-136	0.15	0.050

Measured on Nu 500 HR MC-ICPMS (ENS de Lyon).