

Supporting Information (Tables S1~S4, Figures S1~S4) of Shen et al. “Rapid and precise measurements of natural carbonate rare earth elements in femtogram quantities by inductive coupled plasma sector field mass spectrometry”

Table S1. REE/Ca ratios (nmol/mol) in CarbREE-I standard

Elemental ratio	CarbREE-I	CarbREE-II
La/Ca	527.7	125.4
Ce/Ca	624.0	225.2
Pr/Ca	457.9	61.38
Nd/Ca	447.3	59.96
Sm/Ca	429.1	57.52
Eu/Ca	424.6	56.92
Gd/Ca	410.3	55.00
Tb/Ca	406.0	54.42
Dy/Ca	397.0	53.22
Ho/Ca	391.2	52.44
Er/Ca	385.7	51.71
Tm/Ca	381.9	51.20
Yb/Ca	372.9	49.98
Lu/Ca	368.8	49.43

Table S2. Instrumental settings**ICP-SF-MS: Element II**

RF power	1200 W
Skimmer cone	H
Cooling Ar flow (L/min)	16
Auxiliary Ar flow (L/min)	0.8-1.2
Sample Ar flow (L/min)	0.8-1.0
Sample solution uptake rate ($\mu\text{L}/\text{min}$)	80 (ESI-100 nebulizer)

Introduction system: Aridus

Spray Chamber temperature	110 °C
Desolvator temperature	160 °C
Ar sweep flux (L/min)	4-6 (daily optimum)
N ₂ flux (mL/min)	0.05-0.15 (daily optimum)

Table S3. Data acquisition methods

	Detection mode	Peak-hopping mode with B-scan and E-scan	
	Resolution	Low resolution	$M/\Delta M = 300$
	Point per peak	1	
	Data acquisition time (s)	190	
	Washout time (s)	70	
	Sample volume (μL)	240	
Isotopes	Idle time (s)	Integration time (s)	Detection mode
^{46}Ca	0.120	0.030	Analog
^{138}Ba	0.080	0.020	Analog
^{139}La	0.001	0.030	Counting
^{140}Ce	0.001	0.030	Counting
^{141}Pr	0.001	0.040	Counting
^{146}Nd	0.001	0.035	Counting
^{147}Sm	0.001	0.040	Counting
^{153}Eu	0.001	0.040	Counting
^{159}Tb	0.028	0.060	Counting
^{160}Gd	0.001	0.060	Counting
^{163}Dy	0.001	0.060	Counting
^{165}Ho	0.001	0.060	Counting
^{166}Er	0.001	0.080	Counting
^{169}Tm	0.001	0.080	Counting
^{172}Yb	0.001	0.080	Counting
^{175}Lu	0.001	0.080	Counting

Table S4. Reproducibility of REE/Ca ratios for two natural carbonates, coral and foraminifer[#].

	Coral ST0506		Foraminifer FORAM-GM	
	nmol/mol	2 RSD %	nmol/mol	2 RSD %
La/Ca	184	1.9	178	1.9
Ce/Ca	328	2.1	202	2.9
Pr/Ca	38.9	2.2	30.7	2.5
Nd/Ca	157	2.6	130	2.8
Sm/Ca	32.9	3.4	26.8	4.4
Eu/Ca	7.28	4.6	7.47	4.2
Gd/Ca	35.3	4.6	31.7	3.3
Tb/Ca	4.94	2.8	4.84	3.4
Dy/Ca	29.0	6.5	32.1	3.1
Ho/Ca	5.68	3.2	7.22	3.3
Er/Ca	15.4	3.0	22.1	3.4
Tm/Ca	2.06	3.6	3.30	4.2
Yb/Ca	13.0	3.4	21.1	3.7
Lu/Ca	1.98	4.0	3.17	3.9

[#] Number of replicate measurements is 63 for coral ST0506 and 70 for foraminifer FORAM-GM.

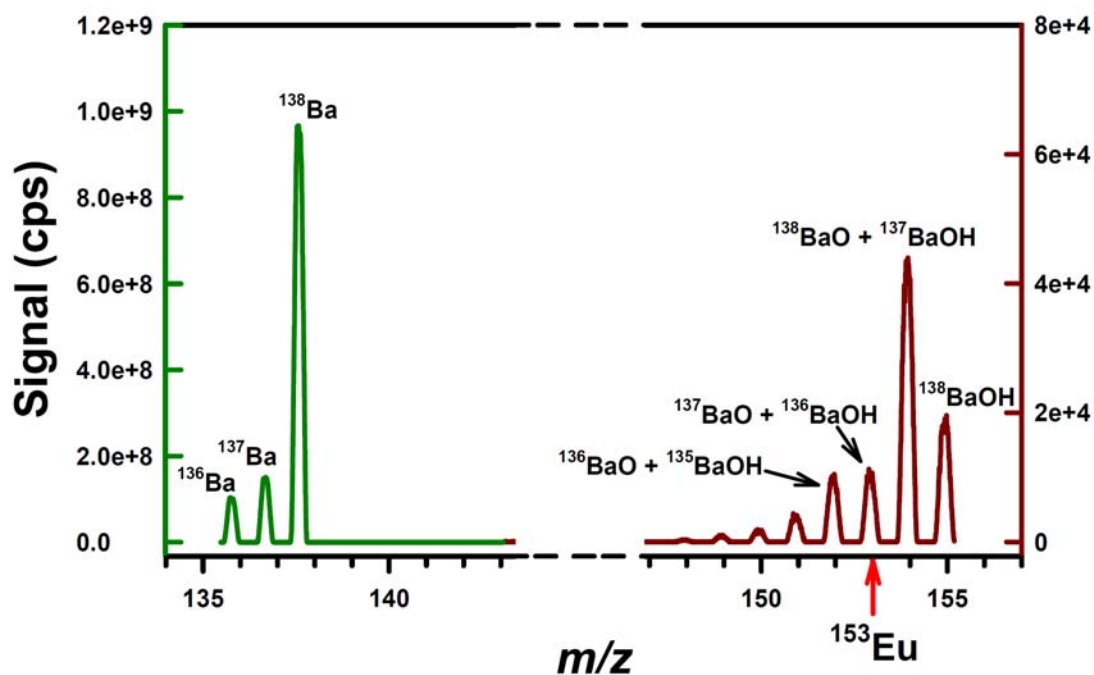


Fig. S1 Mass spectrum for a 1-ppm barium solution at a mass interval, 136-156 amu.

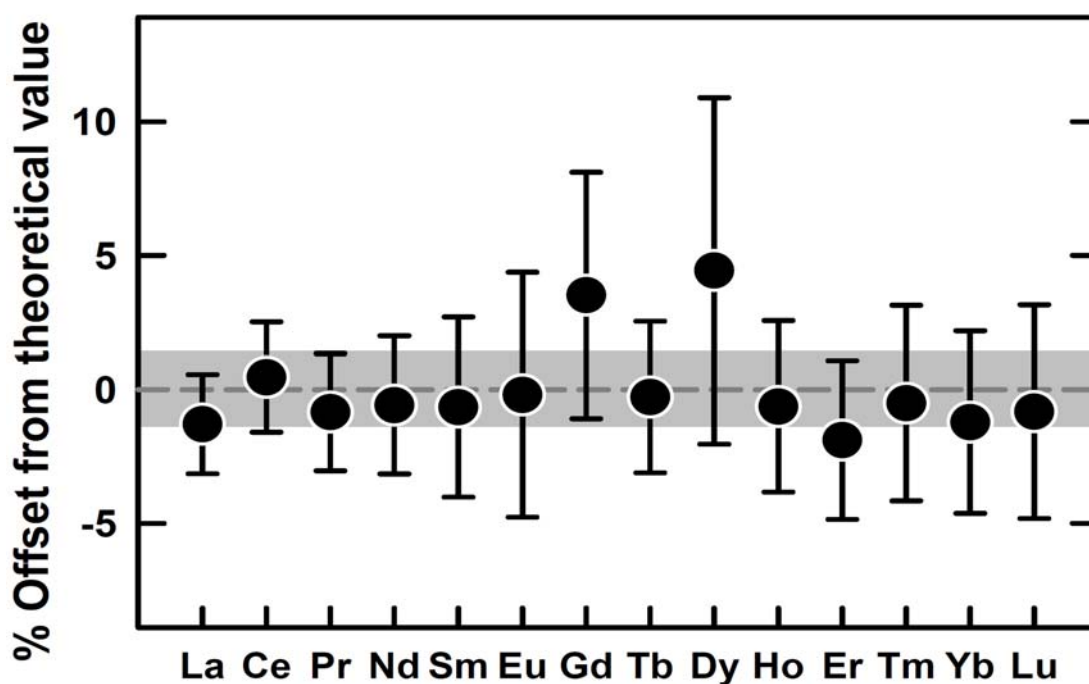


Fig. S2 Percent offset of measured REE/Ca ratios with long-term 2RSD error bars (Table S4) from theoretical values in CoralM-REE standard solution. Shaded area denotes the uncertainty of REE/Ca in the standard.

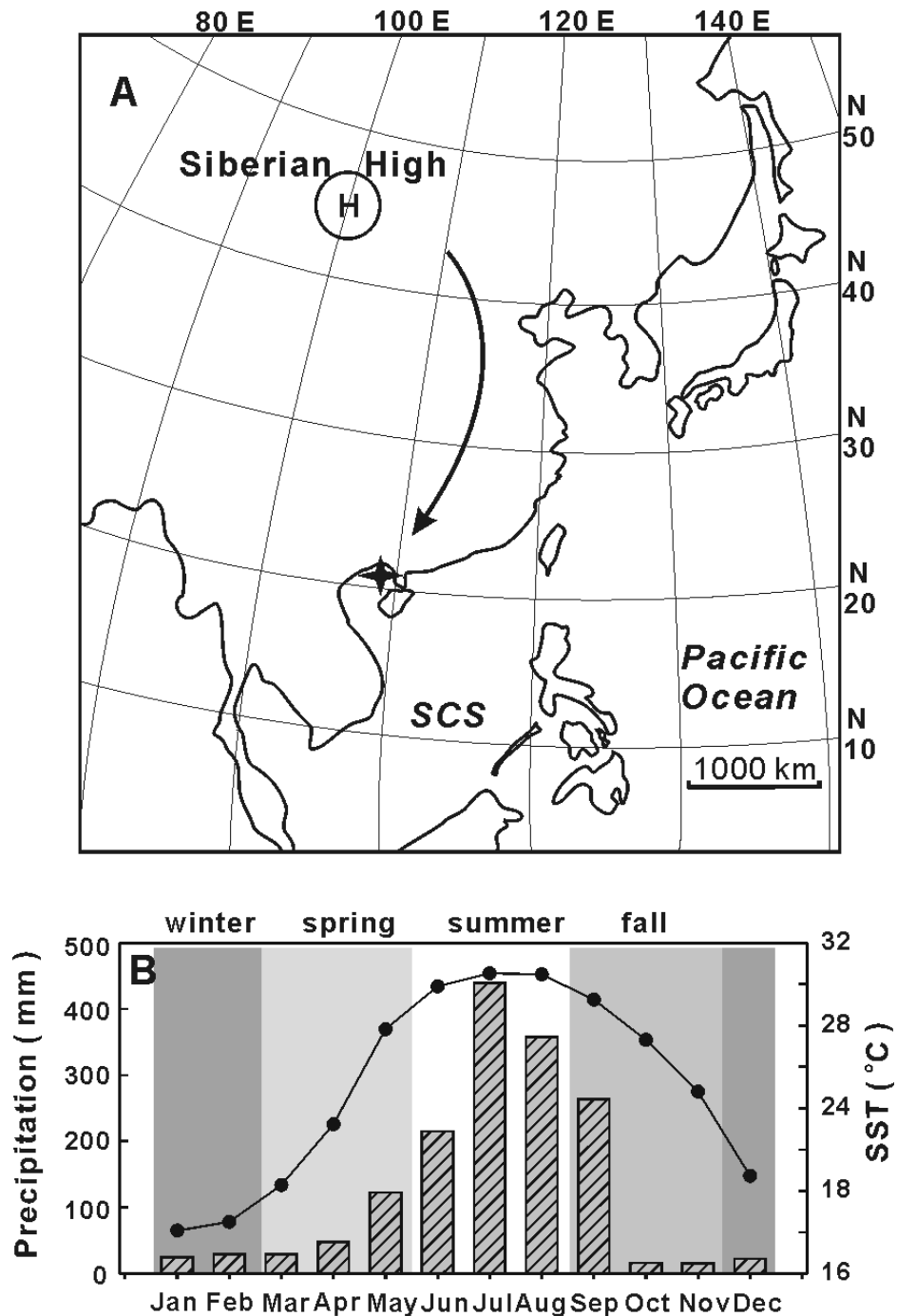


Fig. S3. (A) A modern *Porites* coral core, WZI-1 (star), was drilled offshore of Weizhou Island (21°01'N, 109°04'E) from Gulf of Tonkin, northern South China Sea (SCS) in 2009. A solid arrow indicates the winter monsoon from Siberian High. (B) Local monthly sea surface temperature (SST) and precipitation from an island meteorological station (AD 2002-2005). More than 88% of the yearly precipitation, 1400 mm, falls in the wet season from May to September. During the dry season, the prevailing winter monsoon brings cold and dry continental air masses, and dust, from the Siberian High.

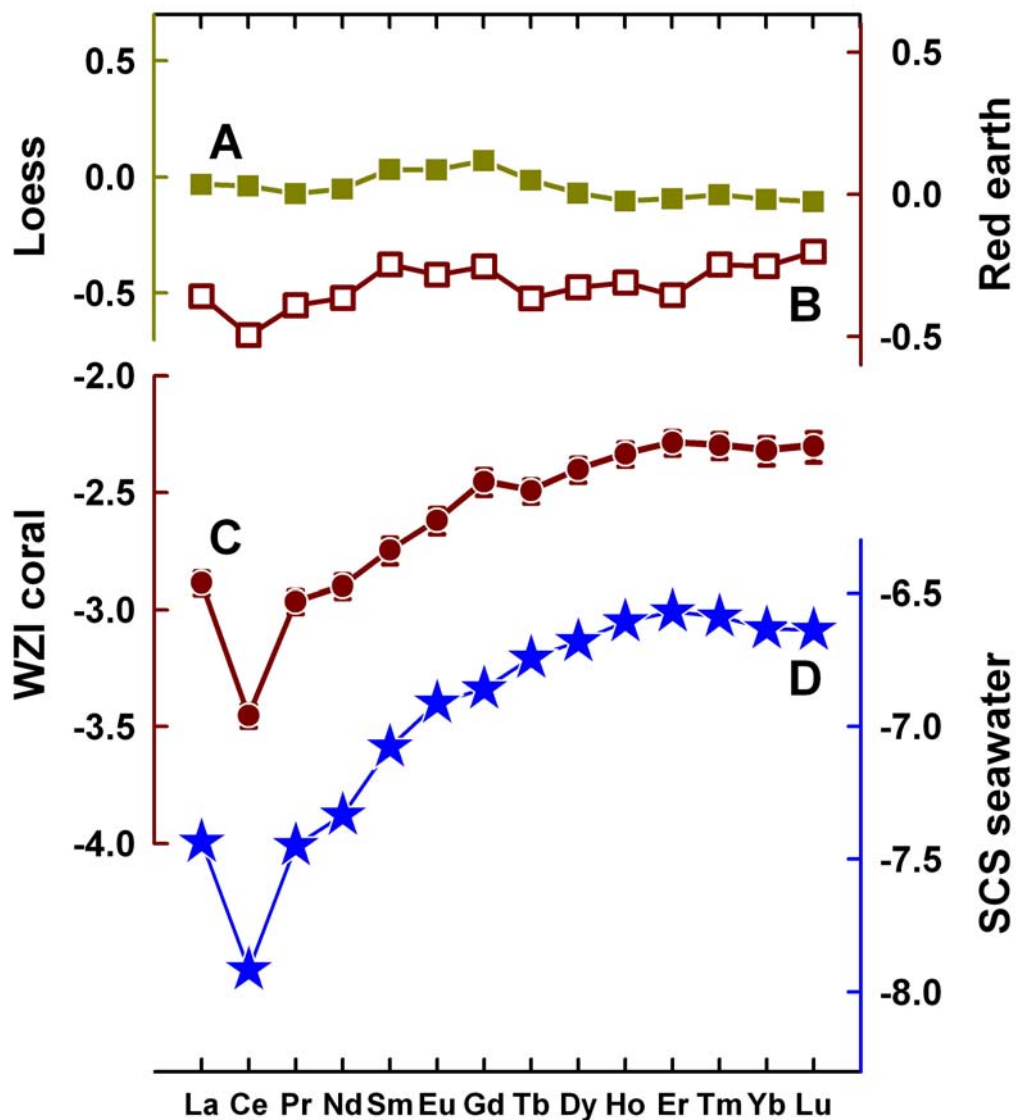


Fig. S4. PAAS-normalized³⁶ REE patterns of (A) Chinese loess,^{S1} (B) red earth,^{S2} (C) WZI coral *Porites*, WZI-1 (4-yr averages of monthly REE data ± 2 -standard deviation of the mean), and (D) South China Sea (SCS) surface seawater³⁷ on logarithmic scale.

Additional References:

(S1) Liu, C. Q.; Masuda, A.; Okada, A.; Yabuki, S.; Zhang, J.; Fan, Z. L. *Chem. Geol.* **1993**, *106*, 359-374.

(S2) Xiong, S. F.; Sun, D. H.; Ding, Z. L.. *J. Quat. Sci.* **2002**, *17*, 181-191.