Electronic Supplementary Information

Accurate determination of rare earth elements in small volumes of porewater from marine sediments by laser ablation solution sampling ICP-MS

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Equations used for concentration calculation

In this study, quantification for samples was carried out by calibration against the set of reference standard solutions, in conjunction with In used for internal standardization, using the following equations (mainly adapted from Longerich et al.[1]):

$$C_{REE-original\ sample} * V_{original\ sample} = C_{REE-final\ sample} * V_{final\ sample} \#(1)$$

$$\frac{S_{REE-final\ sample}}{S_{In-final\ sample}} = k * \frac{C_{REE-final\ sample}}{C_{In-final\ sample}} \#(2)$$

$$C_{In-standard} * V_{In-standard} = C_{In-final\ sample} * V_{final\ sample} \#(3)$$

where S, C, and V represent the signal intensity (with background signal subtracted), the concentration and the volume, respectively; k is the slop obtained from the calibration curve (Fig. S3); REE-original sample and REE-final sample represent REE in the original sample and in the final dissolved sample; In-standard and In-final sample represent In in the internal standard solution and in the final dissolved sample. By reorganizing the above equations, the following can be derived:

$$C_{REE-original\ sample} = C_{REE-final\ sample} * \frac{V_{final\ sample}}{V_{original\ sample}}$$

$$= \frac{S_{REE-final\ sample}}{S_{In-final\ sample} * k} * C_{In-final\ sample} * \frac{V_{final\ sample}}{V_{original\ sample}}$$

$$= \frac{S_{REE-final\ sample}}{S_{In-final\ sample} * k} * \frac{C_{In-standard} * V_{In-standard}}{V_{final\ sample}} * \frac{V_{final\ sample}}{V_{original\ sample}}$$

$$= \frac{S_{REE-final\ sample}}{k * S_{In-final\ sample}} * \frac{C_{In-standard} * V_{In-standard}}{V_{original\ sample}}$$

where $S_{REE\text{-}final\ sample}$ and $S_{In\text{-}final\ sample}$ are the measured signal intensities, $C_{In\ standard}$ and $V_{In\ standard}$ are the known values, being 10 ng mL^{-1} and 100 uL, respectively.

Reference:

1. H. P. Longerich, S. E. Jackson and D. Günther, *J. Anal. At. Spectrom.*, 1996, **11**, 899–904.

Table S1 Limits of detection (pg mL^{-1}) of REEs analysed by LA-ICP-MS under different laser ablation pulse frequencies, with the laser ablation spot size fixed to 60 μm. It should be noted that this set of values were calculated without consideration of the enrichment factor.

Element	Laser ablation pulse frequency			
	20 Hz	50 Hz	100 Hz	250 Hz
La139	1.9	0.6	0.4	0.1
Ce140	2.8	0.7	0.5	0.1
Pr141	1.9	0.7	0.3	0.1
Nd146	11.1	3.5	1.7	0.6
Sm147	10.9	4.1	2.5	0.7
Eu151	3.3	1.4	0.6	0.2
Gd158	6.7	2.5	1.4	0.4
Tb159	2.4	0.8	0.3	0.1
Dy163	7.8	3.5	1.2	0.5
Ho165	3.4	0.5	0.3	0.1
Er166	7.7	1.6	1.0	0.3
Tm169	2.0	0.7	0.5	0.1
Yb172	11.1	3.1	1.5	0.6
Lu175	3.2	0.8	0.5	0.1

Table S2 Method detection limits (pg mL^{-1}) of REEs analysed by LA-ICP-MS considering different enrichment factors under ablation condition of 60 μm and 250 Hz.

| Element	Original sample volume			
	2 mL		4 mL	
	Final dissolved solution volume			
	200 μL	100 μL	200 μL	100 μL
	Enrichment factor			
	10	20	20	40
La139	0.01	0.005	0.005	0.003
Ce140	0.01	0.005	0.005	0.003
Pr141	0.01	0.005	0.005	0.003
Nd146	0.06	0.030	0.030	0.015
Sm147	0.07	0.035	0.035	0.018
Eu151	0.02	0.010	0.010	0.005
Gd158	0.04	0.020	0.020	0.010
Tb159	0.01	0.005	0.005	0.003
Dy163	0.05	0.025	0.025	0.013
Ho165	0.01	0.005	0.005	0.003
Er166	0.03	0.015	0.015	0.008
Tm169	0.01	0.005	0.005	0.003
Yb172	0.06	0.030	0.030	0.015
Lu175	0.01	0.005	0.005	0.003
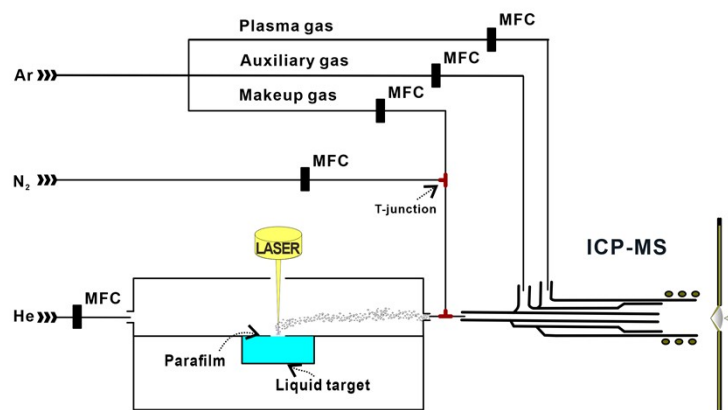
Fig. S1 Schematic diagram of the experiment set-up of the laser ablation solution sampling ICP-MS system added with small amounts of nitrogen. MFC denotes mass flow controller.
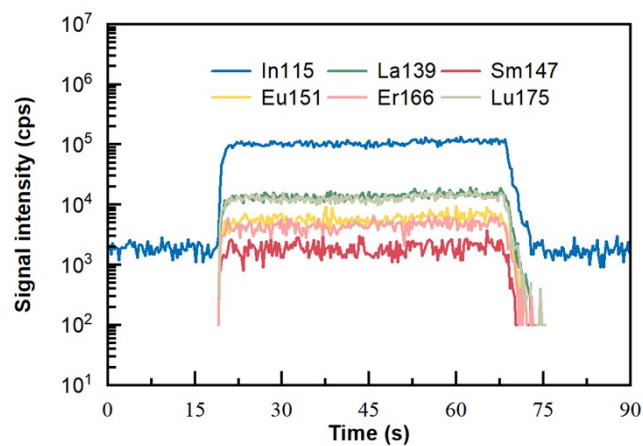
Fig. S2 Signal intensities of analytes (REEs and the internal standard In) versus time in a dissolved $Fe(OH)_3$-precipitate solution analysed by LA-ICP-MS under conditions of 60 μm, 200 Hz. The initial mixed solution was made by about 24 pg mL^{-1} of each REE spiked in a seawater sample.
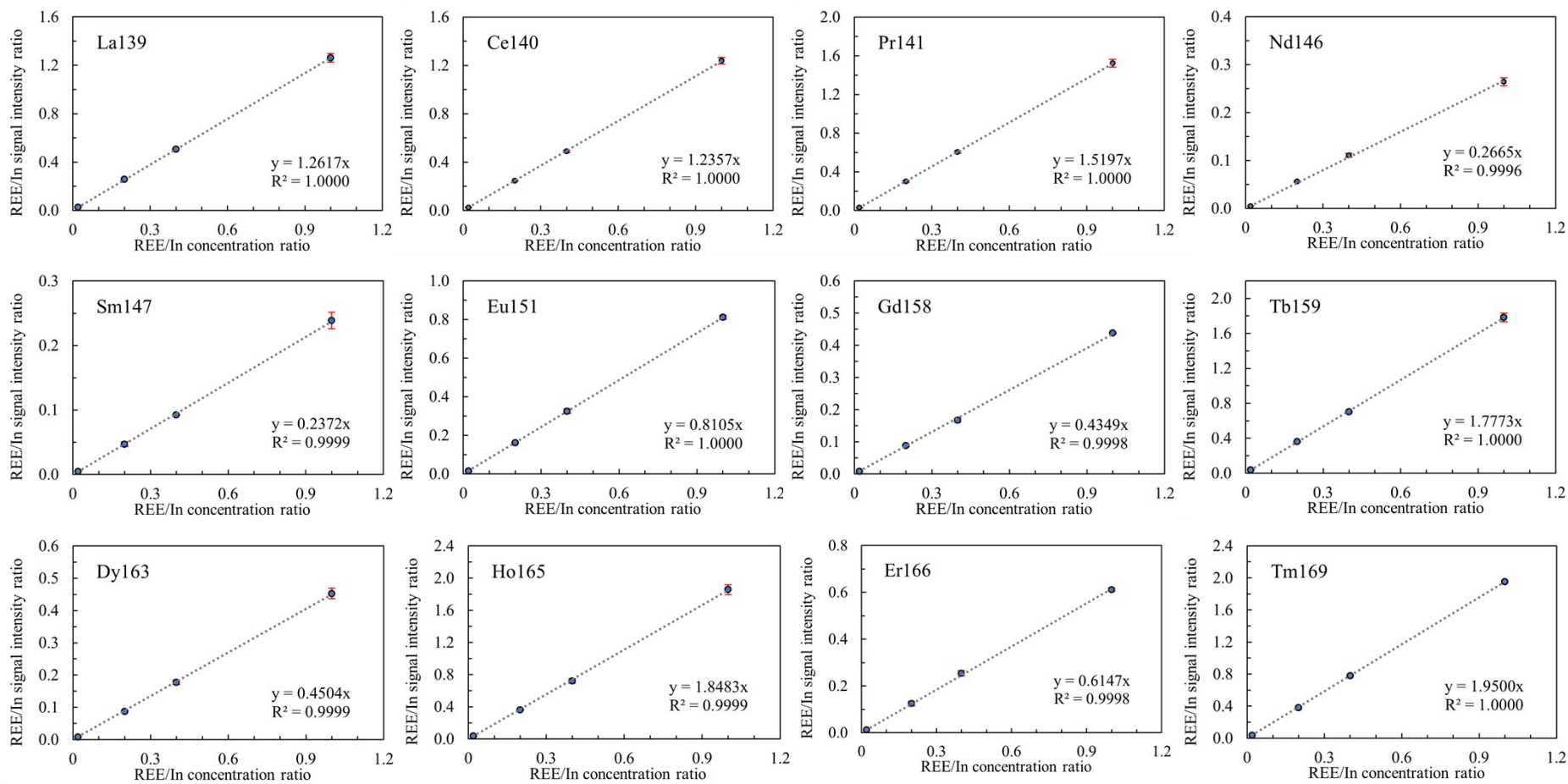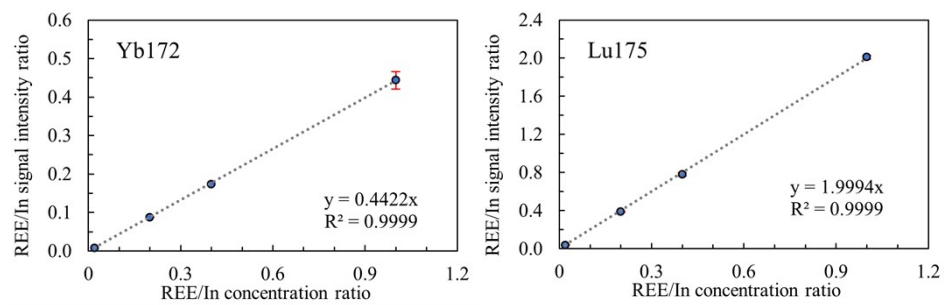
Fig. S3 Calibration graphs for REEs (^{115}In served as the internal standard). Error bars represent sd (n=3).