

Data Repository 2006129

Staubwasser, v. Blanckenburg, Schoenberg: Iron isotopes in the early marine diagenetic iron cycle

This item contains the analytical procedure of leaching dispersed reactive solid Fe(III) from marine sediments for Fe isotope analysis and three data tables.

Table DR1 contains measured Fe isotope ratios and concentration data on bulk samples.

Table DR2 contains measured Fe isotope data and concentration data on leached samples.

Table DR3 contains data to verify that unwanted fractionation during leaching or as a result of matrix present during the measurement of isotope ratios can be ruled out.

Leaching Fe oxyhydroxides [reactive Fe(III)] for isotope analysis

A leaching method suitable for the isotopic analysis of reactive Fe(III) must fulfill a number of requirements: 1) it must either not fractionate Fe isotopes or be quantitative; 2) it must not dissolve Fe bearing minerals other than oxyhydroxides in significant amounts, particularly clays or pyrite; 3) it must allow quantitative separation of Fe from the leachate solution matrix to avoid fractionation during subsequent processing and analysis; 4) the reagents must have acceptable levels of blank. These criteria can be met by the classical pH buffered dithionite-citrate-acetate leaching method (Canfield et al. 1993; Haese, 2000). Control leach experiments were conducted with a mixture of synthetic goethite and hematite. Isotope ratios were identical to a full acid digestion regardless of the fraction of Fe oxide dissolved by the dithionite – citrate mixture. This demonstrates that Fe can be leached with established procedures and purified for mass spectrometry without any measurable fractionation (Tab. 3).

The separation of Fe from the leach solution is achieved by repeated hot oxidation in *aqua regia* followed by oxidation in ammonia and H₂O₂. After transfer into vials, Fe hydroxide is precipitated after adding ammonia and H₂O₂. After the first precipitate forms, samples are allowed to stand for several days with occasional addition of H₂O₂ until the supernatant solution becomes colorless. If this is not achieved after 3 – 4 days, another round of oxidation on the hotplate Fe is required. The precipitate may contain whitish sulfate salts, which must be removed by dissolving the precipitate in 1M HCl - HNO₃, precipitating sulfate as barite by adding a BaCl₂ solution and finally precipitating Fe separately from the supernatant by adding ammonia and H₂O₂. Control leach experiments conducted with a mixture of synthetic goethite and hematite were identical to a full acid digestion and demonstrate that Fe can be leached and purified without any measurable fractionation.

References

Canfield, D.E., Thamdrup, B., and Hansen, J.W., 1993, The anaerobic degradation of organic matter in Danish coastal sediments: Iron reduction, manganese reduction, and sulfate reduction: *Geochimica et Cosmochimica Acta*, v. 57, p. 3867–3883.

Haese, R.R., 2000, The reactivity of iron, in Schulz, H.D., and Zabel, M., *Marine Geochemistry*, p 233–261, Heidelberg, Springer.

Table DR1: Bulk sediment concentration and isotope data

Table DR2: Reactive Fe(III) concentration and isotope data

sample	mean depth (cm)	mg_Fe / g_sediment	\pm 1sd	delta 56Fe batch 1	n	delta 56Fe batch 2	n	average delta 56Fe	\pm 1sd ²	mg_Mn / g_sediment	\pm 1sd	mg_Al / g_sediment	\pm 1sd	% Fe from dissolved silicates ³
112KG_00-01_leached	0.5	13.39	0.84	-0.53	3	-0.51	2	-0.52	0.05	0.146	0.010	0.69	0.06	3.7
112KG_01-02_leached	1.5	15.64	0.99	-0.34	3	-0.41	2	-0.37	0.05	0.153	0.011	0.74	0.07	3.4
112KG_02-03_leached	2.5	12.26	0.77			-0.28	2	-0.28	0.05	0.124	0.009	0.69	0.06	4.0
112KG_03-04_leached	3.5	10.82	0.68			-0.18	2	-0.18	0.05	0.128	0.009	0.81	0.07	5.4
112KG_04-05_leached	4.5	7.81	0.49	-0.20	2	-0.18	2	-0.19	0.05	0.120	0.008	0.76	0.07	7.0
112KG_05-06_leached	5.5	6.44	0.41	-0.19	2	-0.27	2	-0.23	0.05	0.113	0.008	0.70	0.06	7.8
112KG_06-07_leached	6.5	5.57	0.35	-0.39	2	-0.32	2	-0.35	0.04	0.108	0.007	0.67	0.06	8.7
112KG_07-08_leached	7.5	5.57	0.35	-0.35	4	-0.36	2	-0.36	0.05	0.107	0.007	0.69	0.06	8.9
112KG_08-09_leached	8.5	5.47	0.35	-0.29	3	-0.34	2	-0.31	0.05	0.103	0.007	0.70	0.07	9.2
112KG_09-10_leached	9.5	5.61	0.35	-0.28	2			-0.28	0.07	0.105	0.007	0.75	0.07	9.6
115KG_00-01_leached	0.5	9.33	0.59	-0.63	2			-0.63	0.07	3.820	0.264	0.65	0.06	5.0
115KG_01-02_leached	1.5	7.98	0.50	-0.71	2			-0.71	0.07	2.402	0.166	0.52	0.05	4.7
115KG_02-03_leached	2.5	7.81	0.49	-0.71	3			-0.71	0.07	1.001	0.069	0.50	0.05	4.7
115KG_03-04_leached	3.5	8.59	0.54	-0.77	2			-0.77	0.07	0.681	0.047	0.52	0.05	4.4
115KG_04-05_leached	4.5	8.63	0.54	-0.57	2	-0.63	2	-0.60	0.06	0.263	0.018	0.61	0.06	5.1
115KG_05-06_leached	5.5	7.28	0.46	-0.32	3	-0.40	2	-0.36	0.05	0.179	0.012	0.57	0.05	5.7
115KG_06-07_leached	6.5	5.89	0.37	-0.28	1	-0.40	2	-0.34	0.05	0.167	0.012	0.52	0.05	6.3
115KG_07-08_leached	7.5	5.69	0.36	-0.33	2	-0.30	2	-0.31	0.05	0.180	0.012	0.51	0.05	6.5
115KG_08-09_leached	8.5	5.00	0.32	-0.30	2	-0.29	2	-0.29	0.05	0.181	0.013	0.48	0.04	6.9
115KG_09-10_leached	9.5	4.82	0.30	-0.29	2			-0.29	0.07	0.170	0.012	0.47	0.04	7.0

¹ calculated as $\sqrt{\{\sum (x_i - \bar{x}_m)^2\} / [\sum (n_{ij}-1)]}$, for the jth sample and the ith replicate² propagated error³ calculated using average silicate Fe/Al for Pakistan margin sediments of 0.72

Table DR3: Isotope data of leaching method validation experiments

sample	method	delta 56Fe ± 1sd	
HG_mix_test_1	dithionite-citrate	0.27	0.07
HG_mix_test_2	dithionite-citrate	0.27	0.07
HG_mix_test_3	dithionite-citrate	0.25	0.07
HG_mix_test_4	dithionite-citrate	0.23	0.07
HG_mix_test_5	dithionite-citrate	0.22	0.07
HG_mix_test_6	HCl-HNO ₃	0.27	0.04
HG_mix_test_7	HCl-HNO ₃	0.28	0.04
HG_mix_test_8	HCl-HNO ₃	0.25	0.04
HG_mix_test_9	HCl-HNO ₃	0.30	0.04
HG_mix_test_10	HCl-HNO ₃	0.27	0.04
HG_mix_test_11	HCl-HNO ₃	0.22	0.04