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Iron isotope fractionation in river colloidal matter

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Abstract

Temporal variations in the iron isotopic composition, δ^{56}Fe between − 0.13‰ and 0.31‰, have been measured in the suspended fraction in a Boreal river. The major mechanism behind these variations is temporal mixing between two types of particles–colloids, Fe-oxyhydroxides and Fe–C colloids. Data in this study indicate that these two types of colloids have different Fe-isotope composition. The Fe–C colloid has a negative δ^{56}Fe value whereas the Fe-oxyhydroxide colloid is enriched in ^{56}Fe.

These two types of colloidal matter have different hydrogeochemical origin. The Fe–C colloid reaches the river during storm events when the upper sections of the soil profile (O and E horizons) are flooded by a rising water table. Colloidal Fe-oxyhydroxides reach the river via inflow and subsequent oxidation of groundwater enriched in dissolved Fe(II).

Keywords: Fe isotopes; Kalix River; suspended matter; Fe-colloids; temporal variation

1. Introduction

Zhu et al. [1] demonstrated systematic changes in the Fe-isotope composition for the last 1.7 million years in a Fe–Mn crust from the North Atlantic Ocean. They suggested that the variations reflect isotopic variability in the continental sources of Fe fluxes to the oceans. However, Levasseur et al. [2] found no evidence that the observed oceanic Fe isotopic heterogeneity in marine hydrogenetic ferromanganese deposits is controlled by variations in continental sources. Most of the ferromanganese nodules and crusts analysed in the open ocean show clearly negative δ^{56}Fe values [2,3], thus implying an overall negative isotope signal in seawater. However, Levasseur et al. [2] concluded that the overall negative isotope signal and the variations are induced locally within the ocean, although the exact processes for the fractionation remain unclear.

Fantle and DePaolo [4] suggested that the net effect of continental weathering processes is to mobilize small amounts of isotopically light Fe in an “exchangeable”, or dissolved form. They inferred that continental weathering under modern oxidising earth surface conditions

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preferentially releases dissolved Fe with negative δ^{56}Fe, which is transported in rivers to the ocean, and suggested that riverine Fe has a substantial role in determining the δ^{56}Fe of both the modern and ancient oceans.

It is not yet clearly established if the relatively high dissolved Fe concentrations (< 0.45 μm) observed in many organic rich freshwater systems are attributed to Fe-organic (humic) complexes [5] and/or small Fe-oxyhydroxide particles [6]. Recently, both types of colloids, Fe-oxyhydroxides and Fe–C colloidal matter, have been identified as important carriers of dissolved Fe in boreal river systems [7–11]. Data in this study indicate that these two types of colloids have different Fe-isotope composition. This finding provides a mechanism for a variable Fe-isotope signal in river suspended matter and hence opens up the possibility for a changing river introduced Fe-isotope signal to the ocean during geological time. The relative river discharge and conservativeness during estuarine mixing need to be understood for each of these two Fe-colloid forms to properly evaluate the role of river introduced Fe to the Fe-isotope variations preserved in the environmental archive of the ocean.

2. Sampling

Sampling was performed in the Kalix River, Northern Sweden. Detailed description of the river system, general hydrogeochemistry and the sampling procedures for the collection of the suspended phase in the river have been described elsewhere [12–14]. The samples were filtered in situ and filters were kept frozen until analyses. Fe-isotope measurements were performed during 2003 and 2004 on samples collected during the period March 1991 to June 1992. The filters were deliberately clogged during sampling to detect both particles and colloidal matter. Substantial amounts of colloidal particles (< 0.45 μm) rich in Fe–C are enriched on the filters during periods of high TOC (total organic carbon) in the river [7].

3. Analytical methods

The suspended matter was prepared for Fe-isotope analyses using a modified microwave-assisted extraction procedure [13]. The filters were transferred to microwave digestion PFA Teflon vessels, and 5 ml of nitric acid (16 M) and 1 ml of hydrochloric acid (10 M) were added. The samples were then heated in a microwave oven for 60 min. This procedure dissolves most of the Fe in the samples, usually more than 95% of the total Fe (Table 1). Some samples during spring flood in May have up to 10% of total Fe left in un-dissolved particles. A mixture of 24 M HF and 16 m HNO_3 (3:1) was used to dissolve remaining Fe in the silicate residue obtained from the HCl reductive extraction, and the relative amount of Fe in the HCl-leachable fraction was calculated (Table 1).

Table 1
Fe-isotopic composition of suspended matter in the Kalix River

Sample	Date	δ^{56}Fe (‰)	2 STD (‰)	δ^{57}Fe (‰)	2 STD (‰)	Leachable Fe * (%)
91-42	March 30, 1991	0.18	0.04	0.25	0.05	98
91-54	May 8	0.05	0.03	0.06	0.03	
91-63	May 13	−0.05	0.04	−0.07	0.06	95
91-73	May 17	−0.05	0.04	−0.08	0.09	
91-80	May 27	−0.06	0.01	−0.07	0.02	
91-93	June 7	0.00	0.04	0.01	0.08	99
91-137	July 10	−0.13	0.05	−0.18	0.08	96
91-164	August 8	−0.04	0.04	−0.05	0.05	
91-207	September 9	0.08	0.03	0.12	0.03	97
91-231	October 1	0.20	0.03	0.27	0.04	96
91-243	October 8	0.22	0.03	0.32	0.10	98
91-266	November 5	0.16	0.06	0.23	0.08	
91-278	December 3	0.12	0.01	0.18	0.04	
91-280	December 9	0.04	0.03	0.07	0.01	99
92-2	January 10, 1992	0.12	0.05	0.18	0.07	
92-10	February 6	0.22	0.01	0.31	0.03	99
92-21	March 13	0.20	0.03	0.30	0.06	
92-43	April 9	0.31	0.03	0.44	0.05	99
92-60	April 17	0.23	0.05	0.34	0.04	
92-72	May 14	0.14	0.06	0.22	0.09	91
92-73	May 18	0.01	0.09	0.01	0.13	96
92-79	May 22	−0.07	0.02	−0.09	0.03	96
92-120	June 18	−0.08	0.02	−0.12	0.03	97
92-123	June 22	−0.07	0.03	−0.09	0.03	

* Fe released by reductive HCl extraction (see text).

Anion-exchange chromatography was used for chemical purification of Fe. With minor adjustments, the anion-exchange closely followed that employed by Malinovsky et al. [15]. A mass balance estimate of Fe contents on aliquots of each sample before and after anion-exchange separation demonstrated that Fe recovery from the column was always higher than 95%. To eliminate high concentrations of HCl, which were found to affect precise MC-ICPMS measurements of Fe, the Fe fractions after anion-exchange separation were transferred into Teflon beakers, evaporated on a hot plate to dryness and re-dissolved in 0.3 M HNO_3. The samples were then diluted to 5.0±0.5 mg Fe l^{-1} with 0.3 M HNO_3 and spiked with Ni at 5 mg l^{-1}, followed by isotope ratio measurements using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS).

Procedural blanks were prepared for all sample manipulations and found to contain insignificant quantities of Fe relative to that extracted from the filters. Total procedural blanks of Fe for the filters after digestion and