4.1.P01

A technique for the separation and isotopic analysis of Fe and Zn in seawater

J. BERMIN[1], D. VANCE[2] AND P. STATHAM[3]

[1] Department of Geology, Royal Holloway University of London, Egham, Surrey TW20 OEX, U.K (j.bermin@gl.rhul.ac.uk)
[2] Department of Earth Sciences, University of Bristol, Wills Memorial Building, Bristol BS8 1RJ, U.K (d.vance@bristol.ac.uk)
[3] Southampton Oceanography Centre, University of Southampton, European Way, Southampton SO14 3ZH, U.K (pjs1@soc.soton.ac.uk)

In the open oceans, the concentration versus depth profiles of Fe and Zn, like those of the macronutrients, show surface depletions and deep enrichments[1,2], indicating that the dominant control on Zn, and perhaps Fe, in the oceans is biological cycling. Both Fe and Zn are vital constituents of many enzymes, which are expected to preferentially use the lighter isotopes. Such properties suggest that the isotopic systems of Fe and Zn will behave analogously to the C isotopic system, which is a well-established tracer for biological cycling of macronutrients in the oceans. The extreme relative depletion of Zn in surface waters relative to carbon suggests an even greater potential as a tracer of deep water origin.

It is now possible to measure Zn and Fe isotopes with good precision and reproducibility[3,4]. The isotopic analysis of seawater, however, presents a number of further challenges - notably the very low concentrations. Here we describe a method to extract Fe and Zn from large quantities of seawater at low blank and with no artificial isotopic fractionation. The procedure includes preconcentration of the samples through a Chelex 100 column[5] and purification using an AGP MP-1 column[3]. The potential problem of uncontrolled fractionation occurring during the chemical procedures is counteracted by the addition of a double spike prior to any chemical treatment. These techniques have been tested on samples from the English Channel. A large quantity of seawater was collected using trace metal clean techniques and the Fe and Zn separated using the above approach. Four aliquots of this sample measured on the Royal Holloway IsoProbe gave $\delta^{66}Zn$ -0.4± 0.07‰ relative to the Lyons JMC standard. Data for the Fe isotopic analysis of these samples will also be presented.

References
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4.1.P02

Experimental modeling of the transformation of terrigenic iron(III) and aluminum phosphates in seawater

A.V. SAVENKO

Department of Geology, Moscow M.V. Lomonosov State University, Moscow, Russia (Alla_Savenko@rambler.ru)

Iron (III) and aluminum phosphates are among the most abundant minerals of phosphorus. They for an array of compounds from simple monophosphates $FePO_4$ and $AlPO_4$ to mixed hydroxophosphates $Me(I)_xMe(II)_yFe(PO_4)_q(OH)_z$ and $Me(I)_xMe(II)_yAl(PO_4)_q(OH)_{z,}$, the latter ones contain ions of hydrogen, alkalies and alkaly-earth elements. Thermodynamic properties of compound phosphates are poorly investigated. This makes it difficult to clarify their role in hypergenic geochemistry of phosphorus.

This paper presents the results of experimental study of interaction of iron (III) and aluminum phosphates with seawater and river water. The results make it possible to explain several issues of chemical transformation of these compounds at the "river–sea" geochemical barrier.

Synthetic low-temperature phases of iron (III) and aluminum phosphates were used for experiments. Three sets of experiments were run for every phase: with water from the Moscow River, water from the Don River, and seawater of the Mediterranean Sea. Every set included two stages. The weight ratio solid : solution changed from 1 : 500 to 1 : 4000 at the first stage. The weight ratio solid : solution was fixed at 1 : 1000 at the second stage, but the effect of $CaCO_3$ (0.10–0.75 g/l) was examined. The pH value varied 5.9–8.3 during the experiments. The temperature was equal to 25±2°C. The time of exposure was 6 months.

According to the experimental results the concentration of dissolved phosphorus in equilibrium with iron (III) and aluminum phosphates (35–710 µM) more than ten times as higher as the mean concentrations of phosphorus in river waters and seawater (1–2 µM) and substantially higher than the solubility of natural phosphorites in seawater (1–30 µM). It was evidenced that these minerals are thermodynamically unstable. Constancy of the product of Na^{2+} and HPO_4^{2-} activities was observed in all of the experiments. The logarithms of these values for iron (III) and aluminum phosphates were closely spaced and equal to –8.16 ± 0.17 and –7.95 ± 0.18, correspondingly. It was more than ten times as lower as solubility product of brushite ($CaHPO_4·2\ H_2O$).

On the based of experimental results we set up the hypothesis about the mechanism of terrigenic iron (III) and aluminum phosphates transformation in seawater with formation of mixed hydroxophosphates of iron (III)–calcium and aluminum–calcium. The part of these minerals is incongruently dissolved with formation of iron (III) and aluminum oxyhydroxides.