

Speciation of colloidal Fe in terrestrial and marine environments using synchrotron X-ray spectroscopy and microscopy

SATISH C.B. MYNENI^{1*}, BJORN P. VON DER HEYDEN²,
ALAKENDRA N. ROYCHOUDHURY², GUSTAVO A. MARTINEZ³,
TOLEK TYLISZCZAK⁴

¹Department of Geosciences, Princeton University,

²Department of Earth Sciences, Stellenbosch University,

³Department of Crops and Agroenvironmental Science, University of Puerto Rico,

⁴Advanced Light Source, Lawrence Berkeley National Laboratory,

*Corresponding author: smyneni@princeton.edu

Iron is an essential element for all organisms, and it is a limiting nutrient in many parts of the oceans, including the unproductive regions of the Southern Ocean. Although Fe is not a common limiting nutrient in terrestrial aquatic systems, Fe-minerals control the solubility and bioavailability of several nutrients and contaminants. While the dominant fraction of Fe occurs in the form of particulates in aquatic systems, its speciation and mineralogy are less well understood. Here we show how Fe *L*-edge spectroscopy can be used to study the speciation of iron in Fe-rich colloids.

Previous studies have shown that Fe *L*-edge XANES spectra can be used to identify the distribution of ferrous and ferric species accurately. Our study shows that the spectral features in the *L*_β-edge XANES spectra are sensitive not only to the oxidation state of Fe, but also to small changes in the structural environment of Fe. We use the differences in energy and the spectral intensities of different Fe *p-d* transitions to identify different iron oxides and oxyhydroxide phases. However, saturation and self-absorption problems, associated with transmission and fluorescence spectra of Fe-rich compounds respectively, make positive identification of some of the Fe-phases difficult.

Using the *L*-edge XANES spectroscopy studies on crystalline and amorphous Fe-oxides and oxyhydroxides, we conducted speciation of Fe in the colloidal fraction of Southern Ocean water, and in several South African streams flowing into the Atlantic Ocean. We find that the Fe in the riverine environments is present in the ferric form, which is associated primarily with amorphous Fe-oxides. These Fe-oxides also often exhibit Al substitution. The colloidal Fe-speciation also changed dramatically with distance away from South Africa, and with different Fe-species in different frontal zones in the Southern Ocean. Characterization of colloidal Fe in freshwater lakes also indicates the abundance of amorphous Fe-oxide phases. Although crystalline iron oxides are found in several samples, amorphous Fe-oxides appear to be much more abundant than the crystalline phases, at least in the colloidal pool. A detailed discussion of the method, and its application to the identification of different Fe-phases will be discussed.

²⁶Al-²⁶Mg and ¹⁰Be-¹⁰B systematics in CAIs from CO and CV chondrites

KUNIHRO MYOJO^{1*}, TETSUYA YOKOYAMA¹, YUJI SANO²,
NAOTO TAKAHATA², AND NAOJI SUGIURA³

¹Department of Earth and Planetary Sciences, Tokyo Tech,
myojo.k.aa@m.titech.ac.jp (* presenting author)

²Atmosphere and Ocean Research Institute, The Univ. of Tokyo

³Department of Earth and Planetary Science, The Univ. of Tokyo

Fine-scale chronology is very important to discuss the dynamic evolution of the early solar system. Most of the critical events such as the formation of Ca, Al-rich inclusions (CAIs) and chondrules as well as the accretion and early differentiation of planetary bodies have occurred within several Myr from the collapse of the molecular cloud [1]. Short-lived chronometers are extremely useful to obtain highly-precise ages for a variety of extraterrestrial materials. In contrast to the most commonly used ²⁶Al-²⁶Mg system, the ¹⁰Be-¹⁰B chronometer has been rarely used because of the uncertainty if the parent nuclide (¹⁰Be, T_{1/2}=1.5 Myr) was homogeneously widespread in the solar nebula. In order to attest the usefulness of the ¹⁰Be-¹⁰B system, we have measured the ¹⁰Be-¹⁰B ages in CAIs from two CO chondrites (Moss and Felix) and one CV chondrite (NWA 2364) coupled with their ²⁶Al-²⁶Mg ages. CO chondrites are known to have chemical and mineral compositions similar to those in CV chondrites. However, *in-situ* analysis of CAIs in CO chondrites has been hindered by their relatively small mineral sizes compared to CV CAIs. In this study, fine-grained CAIs were measured by NanoSIMS installed at the AORI, Univ. of Tokyo.

The meteorite fragment containing CAIs was mounted in a resin, and thoroughly polished. Because boron contamination is one of the major problems in SIMS analysis for B-poor samples, we cleaned the polished sample surface with diluted HF prior to analysis. The mineral compositions of CAIs were observed by the SEM-EDX at the Univ. of Tokyo. We found some melilite grains (~50 μm) in CAIs from Moss and Felix, which were subject to the ¹⁰Be-¹⁰B and ²⁶Al-²⁶Mg analyses using NanoSIMS. We found no melilite in CAIs from NWA 2364, and only the ²⁶Al-²⁶Mg system was analyzed by using hibonite grains.

We observed excess ¹⁰B/¹¹B ratios in Moss CAIs, which yielded an initial ¹⁰Be/⁹Be = (1.05±0.56)×10⁻³. This is consistent with the canonical value of Allende CAI, (1.04±0.09)×10⁻³, within analytical uncertainty [2]. In contrast, we were unable to obtain the initial ¹⁰Be/⁹Be ratio for Felix CAI, because of the limited Be/B ratios in the melilite grains analyzed. We speculate that this is caused by B contamination, because we cleaned the mounted Felix by relatively mild HF (0.01M), while Moss was cleaned by 0.1M HF. This implies that the removal of B contamination is critical for the measurement of ¹⁰Be-¹⁰B system in CAIs. For the ²⁶Al-²⁶Mg system, all CAIs yielded initial ²⁶Al/²⁷Al ratios identical to the canonical value (5.11×10⁻⁵, [3]) within analytical uncertainties. This reinforces the usefulness of the ¹⁰Be-¹⁰B system as for a chronometer in the early solar system.

[1] Kleine, T. et al. (2009) *GCA* **73**, 5150-5188. [2] McKeegan, K.D. and Davis, A.M. (2007) *Treatise on Geochemistry* **1**, 1.16. [3] Jacobsen, B. et al. (2008) *EPSL* **272** 353-364.