

Organic nitrogen cosmochemistry of ultracarbonaceous micrometeorite

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Nitrogen is expected as a critical diagnostic tracer to determine the origin and evolution of organic compounds in the early Solar System. In the meteorite studies, nitrogen molecular and isotopic compositions have been debated separately for some of soluble organic compounds (e.g., amino acids) and insoluble organic solids, respectively. However, more than 10000 kinds of high molecular weight CHONS compounds remained unidentified in the solvent extract of Murchison meteorite (Schmitt-Kopplin *et al.* 2010). For understanding the formation of every discrete N-bearing organic compounds, it is very important to link soluble and insoluble components, by tracing back to more primitive organic chemistry than that of chondritic meteorites.

Amicrometeorite collected from the snow near the Dome Fuji Station, Antarctica, was investigated by SIMS, FIB-SEM, μ -XANES, and TEM in this study. From the micrometeorite, we have found an organic material in size of $\sim 10 \times 20 \mu\text{m}^2$, that is more than twenty times as large as those in chondritic meteorites. The organic material is seeping into epoxy (embedding media), implying partial solubility. Its C- and N-XANES spectra are rich in a variety of nitrogen functional groups, such as imine (C=N), nitrile (C \equiv N), and amide (NHx(C=O)C). The N/C ratio is estimated order of 0.15, which is around five times higher than those of insoluble organic solids from chondritic meteorites (Alexander *et al.* 2007) but similar to some of comet 81P/Wild 2 dust particles (Cody *et al.* 2008). The isotopic imaging reveals that the organic material is likely sulfurized by the surrounding sulfide. The N- and S-rich organic chemistry may be related to a number of soluble CHONS compounds found by Schmitt-Kopplin *et al.* No isotopic anomalies in hydrogen, carbon, and nitrogen are observed ($\delta\text{D} = \sim +100 \pm 300\text{‰}$, $\delta^{13}\text{C} = \sim 0 \pm 70\text{‰}$, $\delta^{15}\text{N} = \sim +100 \pm 110\text{‰}$). The nitrogen isotopic range covers that of α -amino acids in CR chondrite (Pizzarello and Holmes, 2009), but is distinct from that of insoluble organic solids in the same meteorite group (Alexander *et al.* 2007). The TEM mineralogical characterization records a very slight degree of aqueous alteration (Yabuta *et al.* 2013). Thus, the observed N-rich organic chemical characteristics could reflect a original source of amino acids and the other CHONS in meteorites.

REE Geochemistry of ~ 3.2 Ga old BIFs from the Mapepe Formation and Msauli Member, Barberton, South Africa

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A popular mechanism for Banded Iron Formation (BIF) deposition is that Fe-oxides were precipitated in deep-water setting by oxidation of dissolved Fe^{2+} supplied from submarine hydrothermal activity, by dissolved oxygen supplied from oxygenic photosynthesis in the surface ocean. When Fe-oxides precipitated, rare earth elements (REEs) were adsorbed on their surface. REE compositions of seawater have been recognized to reflect redox state of seawater and the extent of input from hydrothermal activity. In this study, we aimed to estimate Mesoarchean seawater chemistry based on REE signatures of 3.2 Ga old BIFs.

Samples were collected from outcrops of the Mapepe Fm at the bottom of the Fig Tree Gp and Msauli Member in the Onverwacht Gp, both belonging to the Swaziland Supergroup. Powdered rock samples were analyzed for their major element compositions by XRF at AORI, REE compositions by ICP-MS at JCAC, and oxygen isotope compositions. Samples with $<1.0 \text{ wt.}\% \text{ Al}_2\text{O}_3$ are considered to be "pure chemical precipitates" and thus used for further discussion.

Chondrite-normalized REE patterns of the Mapepe samples show positive Eu anomaly, elevated Y/Ho ratios, and LREE>HREE. Furthermore, there exist positive correlations among the extent of positive Eu anomaly, $\Sigma\text{Fe}_2\text{O}_3$ contents, and Y/Ho ratios. The maximum Y/Ho ratios are surprisingly comparable to the those of the modern ocean. These characteristics suggest a coherent story for BIF deposition; Fe^{2+} emanated from submarine hydrothermal activity was oxidized to Fe^{3+} , which, with enhanced particle reactivity, absorbed dissolved REEs and Y in the 3.2 Ga ocean, producing elevated near-modern Y/Ho ratios. The Msauli samples are mostly enriched in Al_2O_3 and have clastics-dominated REE patterns, suggesting deposition at shallower, more proximal setting.

We also estimate temperature of seawater 3.2 Ga ago from which the BIF precipitated, based on their oxygen isotope compositions of silicate- and Fe-oxide phases.