

Structures of weakly binding anions at the interfaces of Fe-polymers and Fe-oxides: Evidence from X-ray and infrared spectroscopic studies

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Halides and oxoanions (e.g. CO_3^{2-} , NO_3^-) are common in all aquatic systems, and play an important role on the interfacial reactions of both cations and anions. Several of these ions (e.g. Cl^- , Br^- , NO_3^- , SO_4^{2-}) are considered to interact weakly at the mineral-water interfaces, and thus are used as inert-electrolytes in aqueous geochemical studies for decades. However, our X-ray and infrared spectroscopic data suggest that these ions form strong complexes at the interfaces of Fe-oxides, and play an important role in Fe-oxide transformations.

We examined the reactions of Cl^- , NO_3^- , SO_4^{2-} , and SiO_4^{4-} with soluble Fe-polymers, and freshly prepared Fe-oxhydroxides. The coordination environments of several of these ligands are highly disputed, and experimental evidence was presented for the formation of both inner- and outer-sphere complexes using different macroscale and molecular methods. We examined the coordination environments of these ions using the X-ray and vibrational spectroscopy techniques. We found that these ions exhibit a variety of complexes at the Fe-oxide-water interfaces; however, H-bonded complexes are identified as the predominant complexes for these ligands at the Fe-oxide-water interfaces.

Differences in the molecular structures of these ions at the Fe-oxide-water interfaces are attributed to the rates at which freshly prepared Fe-oxides transformed to goethite. Our studies indicate that goethite appeared first in freshly precipitated Fe-oxides in the presence of SO_4^{2-} and NO_3^- , when compared to that of Cl^- . However, the rate at which the concentration of goethite increased was much lower in the presence of SO_4^{2-} . In addition, the crystallinity of goethite was affected significantly in the presence of these ligands indicating that these weakly coordinating ligands play a central role on the stability and crystallinity of Fe-oxides. Details of these interactions will be presented.

Strontium Isotope Anomalies and ^{26}Al - ^{26}Mg Chronology in CAIs from CV Chondrites

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Many nucleosynthetic isotope anomalies have been documented in calcium and aluminum rich inclusions (CAIs). Recently, Moynier *et al.* [1] found positive $^{84}\text{Sr}/^{86}\text{Sr}$ anomalies in Allende CAIs, suggesting excess of the p-process component or deficit of the r-process component in the CAIs. In contrast, Brennecke *et al.* [2] measured Ba, Nd and Sm isotopic compositions in Allende CAIs and discovered that the CAIs have r-process excesses only for Ba isotopes. If these anomalies in CAIs were caused by the injection of refractory materials via a nearby supernova, isotopic anomalies could vary due to difference in time and/or location. To reveal the timing of injection toward the early solar system or processes that caused excesses of nucleosynthetic isotope anomalies in CAIs, we first measured Al-Mg ages in type B CAIs from Allende and NWA 2364 and type C CAI from Allende, then we measured Sr isotopic anomalies in the same CAI. For Al-Mg ages, we used NanoSIMS at the AORI, the Univ. of Tokyo, and for Sr isotopic analysis, we used TIMS, Triton plus at Tokyo Tech.

Al-Mg internal isochrones of type B CAIs yielded initial $^{26}\text{Al}/^{27}\text{Al}$ ratio which are consistent with the canonical value of 5.11×10^{-5} [3]. Two Allende CAIs show $^{84}\text{Sr}/^{86}\text{Sr}$ anomalies of 187 ppm (type B) and 46 ppm (type C) higher than terrestrial standard, whereas the CAI from NWA 2364 has no anomalies. In addition, we also measured $\delta^{88}\text{Sr}/^{86}\text{Sr}$ ratio to trace the degree of mass dependent isotope fractionation. Allende type B CAI has 0.3 ‰ higher and other two CAIs have values lower than terrestrial standard. These results suggest that Sr isotope signatures in individual CAIs inherited isotope signatures of their formation locations. The excesses of a p-process nuclide (^{84}Sr) in CAIs are most likely caused by irradiation from the proto-sun, and their heterogeneous isotope signature is attributed to the distance from proto-sun to formation region of individual CAIs.

[1] Moynier *et al.* (2012) *Astrophysical Journal*, 758:45, [2] Brennecke *et al.* (2011) *LPSC Abstract #1302* [3] Jacobsen *et al.* (2008) *EPSL* 272, 353-364.