Halogens: Another piece of the puzzle for Fe-Mn crusts

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This study will address the content, bonding, fate, and role of halogens (Cl, F, Br, I) in the formation of marine ferromanganese (Fe-Mn) deposits. Previous investigations show that elements in seawater can be complexed with different chloride species that then bind to the approproately corresponding charged colloid surfaces of the Fe and Mn substrate [1]. However, further evidence is required and we hypothesize that Cl as well as the other halogens play essential roles in the acquisition of metals, especially the critical, green-tech and high-tech metals. The halogens are also of interest due to their long residence time in the oceans, each much longer than the mixing time of the oceans, and thus reflect global ocean processes, trends, and history when complexed with metals with long residence times.

From a dataset of 41 crusts from the global ocean, element concentrations will be determined, including the halogens, which are difficult to quanitify and except for Cl are rarely reported. This dataset includes crusts from well-studied areas, such as the Pacific Prime Crust Zone, as well as areas less well studied, including the Arctic Ocean and the Southern Ocean. Thus, a broad view of halogen distribution will be provided along with trends in their concentration within ocean basins, along bathymetric features, and with latitide, longitude, and water depth. Initial results show that mean Cl concentrations for Fe-Mn crusts from various areas of the global ocean fluctuate from ~0.88% to >1.1%.

Beyond global ocean distributions, correlations of each of the halogens with other metals within the crusts are being calculated in order to determine phase associations, possible bonding environments, and metal incorporation mechanisms. For example, based solely on the zero point of charge for the mineral ferrihydrite (the main iron mineral in Fe-Mn crusts) and the fundamental physiochemical properties of Br and I, it is expected that these halogens should be associated with the iron-oxyhydroxide phase [2], which our data will address for the natural marine system. Our chemical dataset will be the first of its kind for Fe-Mn crusts and provide insights into the mass balance of halogens and their role in the surface chemistry and metal acquistion.

[1] Koschinsky and Hein (2003), *Marine Geology* **98**, 331-351. [2] Axelsson, *et al*. (2001), *Analyst* **127**, 76-82.