

## Organic coatings and sorption of REE and Y on marine Fe-Mn crusts

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### Introduction

Significant amounts of trace elements are scavenged from seawater by Mn oxides and Fe oxyhydroxides of hydrogenetic Fe-Mn crusts. This process is steered by the surface properties of the respective mineral phase and the speciation of the dissolved trace metals. Crusts enrich REE and Y (REY) up to several orders of magnitude from seawater. Our interest was to evaluate whether it is either the hydroxyl groups of the inorganic (oxyhydr)oxide surface or the carboxyl groups of organic coatings on hydrogenetic Fe-Mn crusts, that control sorption of REY from seawater.

### Experiments and results

We carried out sequential leaching experiments with two hydrogenetic Fe-Mn crusts from the Central Pacific, one from the NE Atlantic, and one from the Indian Ocean. The samples were not affected by phosphatization or other secondary processes. With the selective dissolution procedure we separated four fractions: carbonate, amorphous Mn oxide (vernadite), amorphous FeOOH (strongly intergrown with the Mn phase), and a residuum with mostly detrital aluminosilicates. All crusts shared the same characteristics: Only minor amounts of REY were found in the carbonate and in the residual fractions. However, we observed strong fractionation of the REY between the Mn oxide and the Fe oxyhydroxide fractions: the Mn oxides preferentially sorbed the LREE, the Fe oxyhydroxides preferred the HREE.

### Discussion and conclusion

This observation can be explained by the speciation of REY in seawater and by the interaction of these dissolved species with the hydroxyl groups of the inorganic oxide surfaces. In seawater, the LREE predominate as mono-carbonate complexes of the type  $\text{REY}(\text{CO}_3)^+$  and are strongly attracted by the negative surface charge of the  $\text{MnO}_2$  particles. In contrast, the HREE predominate as di-carbonate complexes of the form  $\text{REY}(\text{CO}_3)_2^{2-}$ . As anionic complexes they preferentially sorb on the slightly positively charged FeOOH surface. Organic coatings or biofilms would create a similarly negative surface charge on both, the Mn oxide and the Fe oxyhydroxide. This would eliminate the different surface characteristics between the two, and the contrasting surface-complexation behaviour of LREE and HREE would not occur. We conclude that in the deep ocean inorganic surface complexation controls sorption of REY on Fe and Mn (oxyhydr)oxides and that organic surface complexation is of minor importance.

## Analysis of Fe isotopes in sulphides by laser ablation high-mass resolution MC ICPMS

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The accuracy of Fe isotopic analyses in geological samples has been recently improved by the use of plasma source mass spectrometry which, compared to TIMS, is characterized by a large but less variable mass discrimination of isotopes. Difficulties associated with the ICPMS analysis of Fe include isobaric interference of molecular species present in the ICP gas (mainly  $^{40}\text{Ar}^{14}\text{N}^+$ ,  $^{40}\text{Ar}^{16}\text{O}^+$ ,  $^{40}\text{Ar}^{16}\text{O}^+\text{H}^+$ ,  $^{40}\text{Ar}^{18}\text{O}^+$ ) and O, N and Ca species originating from the sample. In addition, the isobaric interferences of Cr on  $^{54}\text{Fe}$  and Ni on  $^{58}\text{Fe}$  can affect the isotopic measurements of Cr- and Ni-rich samples.

Various methods that have been implemented to reduce the isobaric interferences on Fe include the use of collision and reaction cell, cold plasma and reduction of interfering molecular species by the use of HCl instead of  $\text{HNO}_3$  for sample introduction or the use of dry plasma. While the molecular interferences can be substantially reduced, they can still significantly affect the isotopic measurement of samples with low Fe content. The mass discrimination of Fe isotopic analyses by solution ICPMS has been corrected using simultaneous measurements of  $^{65}\text{Cu}/^{63}\text{Cu}$  or a  $^{58}\text{Fe}$ - $^{54}\text{Fe}$  tracer or by the use of external Fe isotopic standard. The reported external precision of ICPMS isotopic measurements of Fe are 0.05 – 0.2 and 0.5 – 1 ‰  $\delta^{56}\text{Fe}$  (2 sigma) for solution and laser ablation sampling, respectively.

In this study we have used a Finnigan Neptune high-mass resolution MC ICPMS coupled to a UV laser to analyze Fe isotopes in natural sulphides. The mass resolution of ca 6500 is sufficient to resolve the Ar-, O- and N-based interferences; as all molecular interferences are heavier than the Fe isotopes, the Fe isotopic signals were measured on the flat-top peak shoulders that are at least 15 m.u. wide. The measured isotopic ratios were corrected for mass discrimination from measurements of IRMM-14 isotopic standard before and after each analysis. The internal precision of  $^{56}\text{Fe}/^{54}\text{Fe}$  ratios was better than 0.2 permil and the external precision was better than 0.4 permil for isotopically homogeneous samples.

Despite the lower precision of Fe laser ablation data compared to the conventional solution analyses, the technique can still be useful for studying natural Fe isotopic variations (ca 3.5 ‰). The capability of in-situ laser ablation analysis of Fe isotopes is especially important for analysis of small biomineralised sulphide and iron-oxide-hydroxide grains.