

Dominance of tetravalent cerium in various types of ferromanganese oxides formed in marine environment

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The oxidation state and mineral phase association of Co, Ce and Pb in hydrogenetic, diagenetic, and hydrothermal marine ferromanganese oxides were characterized by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy and chemical extraction.

Among these elements, Ce L_{III}-edge XANES data showed that Ce is exclusively tetravalent in all samples, regardless of genetic origin (Fig. 1). In general, Ce oxidation is considered to be responsible for the positive Ce anomaly in REE patterns of ferromanganese oxides (Fig. 2). The rationale is that Ce(IV) is taken up preferentially over Ce(III) by solid phases in contact with seawater because Ce(IV) is much less soluble than Ce(III). This explanation does not seem to be valid for diagenetic and hydrothermal ferromanganese oxides because they have a negative, or at best moderately positive, Ce anomaly when the data are normalized to PAAS (shale), as is often observed (Fig. 2). However, it was shown that this discrepancy disappears when the REE concentrations in the solid phase are normalized to their abundances in deep seawater. In doing this, the Ce anomalies are all positive, which agrees with the dominance of Ce(IV) in all samples. The reason is that REE in deep seawater, where hydrogenetic nodules occur, are more strongly depleted in Ce than the more reducing interstitial and hydrothermal waters, where the two other types of ferromanganese oxides occur. Also, Ce normalization by PAAS is unsuitable because Ce is not removed by the same geochemical processes in shales and marine nodules.

If we assume that Ce(III) in ferromanganese oxides is in equilibrium with Ce(III) in water, and that Ce(III) is the only soluble species, then the normalized abundance of Ce(III) in the solid phase, denoted Ce*,

can be obtained from the interpolation of the normalized abundances for La and Pr: $(Ce^*)_{SW} = (La^{1/2}Pr^{1/2})_{SW}$, where SW stands for normalization by REE abundances in seawater. The $(Ce^*/Ce_{total})_{SW}$ ratio calculated for FG352 is 15 %, and could be detected by XANES spectroscopy. This ratio is a maximum value among the samples examined, because this sample has the lowest Ce anomaly in the dataset. The CeCl₃ : Ce(SO₄)₂ spectrum shows that 10 % of Ce(III) in a mixed-valence sample manifests itself in the appearance of a shoulder at 5724 eV. None of the sample spectra have such a shoulder including FG352. Also, the maximum of the 1st derivative of this composite spectrum is at 5724.4 eV, while this maximum is between 5726 and 5727 eV in the sample spectra and Ce(IV) references. This analysis confirms the lack of detectable Ce(III) in ferromanganese oxides, even in a sample having a weak Ce anomaly. Therefore, Ce(III) is completely oxidized to Ce(IV) in ferromanganese oxides, and the magnitude of the positive Ce anomaly is not related to a variation of redox conditions, but probably to kinetic factors.

References

[1]Y. Takahashi et al., *Geochim. Cosmochim. Acta* **71** (2007) 984-1008.

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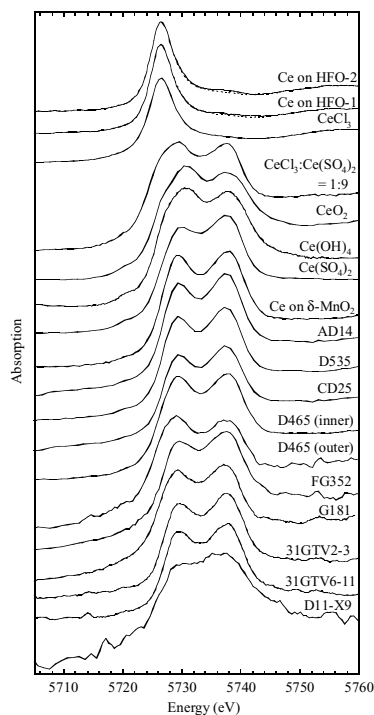


Fig. 1. Cerium L_{III}-edge XANES spectra of a selection of ferromanganese oxides and references.

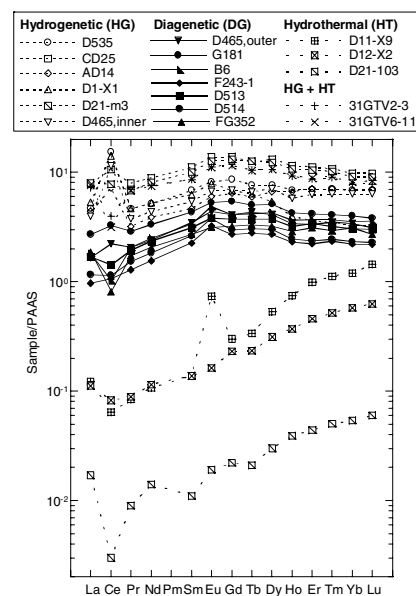


Fig. 2. REE patterns for the three genetic-type ferromanganese oxides normalized to PAAS.