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Discriminating between different genetic types of marine ferro-manganese crusts and nodules based on rare earth elements and yttrium

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ABSTRACT

Marine ferro-manganese (Fe–Mn) crusts and nodules are metal-rich chemical sediments that are archives of paleoceanographic proxies and potential metal resources and targets of deep-sea mining. Traditionally, crusts and nodules are subdivided into hydrogenetic, diagenetic, and hydrothermal types. Because these are characterized by different compositions and hence economic resource potential, a useable genetic classification is not only a tool for geochemical studies but may also help to characterize potential exploration targets. We propose two easy-to-use, yet robust discrimination diagrams based on geochemical relationships controlling the rare earths and yttrium (REY) inventory of marine Fe–Mn (oxyhydr)oxide deposits. The REY are a set of trace elements that show coherent behavior, are routinely determined in geochemical studies, and for which the analytical quality can easily be evaluated. Graphs of Ce anomaly *vs* Nd concentration and Ce anomaly *vs* Y anomaly effectively discriminate between the different types of precipitates, regardless of their diverse mineralogical composition. Both hydrogenetic crusts and nodules show positive Ce anomalies, negative Y anomalies and high Nd concentrations of >100 mg kg^{-1}, although nodules tend to have slightly lower Nd concentrations than crusts. In marked contrast, hydrothermal deposits generally yield negative Ce anomalies, positive Y anomalies, and low Nd concentrations of <10 mg kg^{-1}, in spite of their large geochemical, mineralogical and sedimentological diversity. Diagenetic nodules show negative Ce anomalies, negative Y anomalies, and intermediate Nd concentrations, between 10 and 100 mg kg^{-1}. We discuss the geochemical background of these diagrams, the respective sources of REY in the different precipitates, and address the processes that control their REY inventory. Besides the three end-members, we also use REY systematics to define mixed-type diagenetic–hydrogenetic nodules and classify well-studied international reference standards.

1. Introduction

Ferruginous and manganiferous chemical sediments, such as ferromanganese (Fe–Mn) crusts and nodules, ironstones, manganese formations (MnFs), and banded iron formations (BIFs), are typical components of the marine sedimentary record of Earth's geological history and are widely used as archives of geochemical proxies. While Precambrian BIFs and MnFs are world-class metal resources, Fe–Mn nodules and crusts in the modern global ocean are currently being explored and evaluated as potential targets of deep-sea mining, predominantly because of their high contents of critical high-technology metals, such as Cu, Ni, Co, rare earths and yttrium (REY), Mo, Te, Li, and Pt, among others (e.g., Hein et al., 2013).

In discussions of Cenozoic marine Fe–Mn (oxyhydr)oxide precipitates, it is commonly distinguished between hydrothermal deposits, hydrogenetic crusts, hydrogenetic nodules (also referred to as hydrogenous nodules) and diagenetic nodules. This terminology is based on the type of aqueous fluid from which the Fe–Mn (oxyhydr)oxides precipitate. Hydrogenetic crusts and nodules are composed of Fe–Mn (oxyhydr)oxides that precipitated from seawater as initially colloidal particles within the water column, at the surface of solid substrates such as seamount basalts (Fe–Mn crusts), or by accretion around a nucleus on soft sediment (Fe–Mn nodules). They are characterized by very slow growth rates of only a few millimeters per million years. The Fe–Mn (oxyhydr)oxides of diagenetic nodules form from metal ions in sub-oxic porewaters either within the soft sediment or at the sediment-water interface. Hydrothermal Fe and Mn (oxyhydr)oxides precipitate from marine medium- to low-temperature hydrothermal fluids when these mix with cold seawater after exiting the seafloor, or

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they form below the seafloor as stratabound hydrothermal deposits. While the hydrogenetic and diagenetic types are not very diverse, several types of hydrothermal deposits exist (Hein et al., 1997, 2008), such as (i) hydrothermal stratabound Mn deposits that form below the seafloor, (ii) hydrothermal, intimately mixed, Mn and Fe oxide mounds that form at the seafloor with a network of conduits, (iii) intimately mixed Mn and Fe oxides with conduits parallel to the seafloor, that form hardgrounds, (iv) diffuse-flow seafloor Fe–Mn oxides, (v) hydrothermal plume fallout, (vi) mixed hydrothermal-hydrogenetic crusts, and (vii) hydrothermal Fe oxides (ironstones) that are usually phosphate-rich.

For convenience, we here define a marine precipitate as purely hydrogenetic when all constituents are derived from ambient seawater, as diagenetic when all constituents are derived from cold porewater, and as hydrothermal when precipitation occurred in the vicinity of hydrothermal vent sites and when, in marked contrast to hydrogenetic crusts, an exchange equilibrium between ferro-manganese (oxyhydr) oxides and ambient seawater had not yet been established for those elements that form surface-complexes on the metal (oxyhydr)oxide surface (addressed below in detail). While pure hydrogenetic Fe–Mn crusts are abundant, pure diagenetic nodules are less common. The extent of hydrothermal deposits is not known, but they likely are widespread along 89,000 km of volcanic ridges.

While hydrogenetic Fe–Mn crusts are a potential resource for Co, Te, Pt, and REY, nodules are enriched in Cu, Ni, Mo, and Li, and hydrothermal deposits may be enriched in individual metals such as Mo, Ba, and Li, depending on the temperature and composition of the hydrothermal fluid. The different types of marine oxidic Fe–Mn precipitates, therefore, have different economic potential. Hence, a robust classification is not only helpful in the general geochemical characterization of such precipitates (and as such is a useful teaching tool, for example), but may also simplify the evaluation of their importance as a potential metal resource, which helps to prioritize exploration targets for deep-sea mining.

Marine hydrogenetic, diagenetic, and hydrothermal Fe–Mn (oxyhydr)oxide precipitates are traditionally distinguished using the ternary Mn–Fe-10(Ni + Co + Cu) discrimination diagram of Bonatti et al. (1972), and essentially all other discrimination diagrams that are in use are based on transition element plots using Fe, Mn, Co, Ni, Cu, and Zn (e.g., Bonatti et al., 1972; Rona, 1978; Dymond et al., 1984; Nicholson, 1992; Roy, 1992; Winter et al., 1997; Banerjee et al., 1999; Frank et al., 1999; Jung and Lee, 1999). However, this approach cannot be used to clearly distinguish between hydrothermal and diagenetic precipitates. Moreover, because of the diverse mineralogical composition of the marine precipitates one of the challenges to any chemical discrimination scheme is that it must effectively distinguish different types of crusts and nodules regardless of potential differences between their mineralogical compositions.

We suggest two simple and user-friendly, yet very robust discrimination diagrams that are based on the REY signature of a precipitate, because the REY are known for their coherent behavior in natural environments, are routinely measured in studies of marine Fe–Mn deposits, and allow easy evaluation of the analytical quality of the data. Moreover, a large body of REY data for marine oxidic Fe–Mn precipitates has been published in the past decades, but numerous data sets are also "hidden" in unpublished theses, cruise reports and company reports. As these studies did not necessarily aim at evaluating the economic potential of the Fe–Mn precipitates, concentration data may have only been determined for a small subset of the elements known today of being of economic interest. Our discrimination diagrams, therefore, provide an opportunity for making use of such data sets.

2. Discrimination diagrams based on rare earths and yttrium

In the 1990s, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) became a widely used technique in trace element analysis and today concentration data for the full set of naturally occurring REY are routinely determined in trace element geochemical studies of Fe–Mn deposits. Moreover, the behavior of the REY during scavenging by Fe and Mn (oxyhydr)oxides is sufficiently well understood from many studies of natural and experimental systems to design discrimination diagrams not only based on statistics but on a combination of process understanding and knowledge about element sources. For decades, the REY have been used as geochemical probes because of their coherent behavior during geochemical processes and because of their predictable fractionation. Furthermore, the smoothness of a shale-normalized REY pattern (subscript 'SN'; shale is Post-Archean Australian Shale, PAAS, of McLennan, 1989) is a simple but reliable criterion to test the quality of a chemical analysis and to eliminate questionable data sets. REY_{SN} patterns may show anomalies for redox-sensitive Ce and Eu, and anomalies for La, Gd and Y because of subtle differences among the stabilities of chemical REY complexes. Except for these anomalies, REY_{SN} patterns are smooth functions of ionic radius. If, however, they show irregularities this is usually an indication of questionable analytical quality.

Hence, we screened a very large database (published data and own data) and eventually focused on 319 analyses of REY concentrations in marine Fe–Mn (oxyhydr)oxide deposits. As these data have been determined during the past four decades and with different analytical techniques, the analytical quality likely covers a rather large range. Moreover, many older data sets do not provide concentrations for the full set of all fourteen naturally occurring lanthanoids and particularly Y data are missing. As the first step, we therefore focus on our own data (see online supplementary material) that have exclusively been determined by ICP-MS following an established analytical protocol and using international certified reference materials for quality control (Bau et al., 1996; Dulski, 2001; Alexander, 2008). As shown in Fig. 1A, REY_{SN} patterns of the different types of marine Fe–Mn precipitates differ significantly from each other. However, except for small anomalies of La, Eu, and Gd, and larger ones for Ce and Y, that can *all* be explained by the unique physico-chemical properties of the respective element, the REY_{SN} patterns are smooth, which indicates excellent analytical quality. We emphasize that we conservatively *a priori* eliminated all samples from the data set that contain more than 0.5% P_2O_5, because the primary REY distribution of marine Fe–Mn crusts and nodules is significantly altered (Fig. 1A) and (except for the Ce anomaly) becomes similar to that of seawater (Fig. 1B) during secondary phosphatization (Bau et al., 1996; Koschinsky et al., 1997).

As a starting point for defining the different types of marine Fe–Mn (oxyhydr)oxide precipitates, we used our own datasets for well-characterized *hydrogenetic crusts* from the Central Pacific (published in Bau et al., 1996), *diagenetic nodules* from the Peru Basin (described by Von Stackelberg, 1997), *hydrogenetic nodules* from the Pacific, and *hydrothermal* iron and manganese *deposits* from the Mariana volcanic arc and the Hawaii Rift Zone; the hydrothermal samples show positive Eu_{SN} anomalies — a feature inherited from high-temperature hydrothermal fluids (Fig. 1B), hence indicating the presence of hydrothermal REY; (e.g., Michard and Albarède, 1986; Bau, 1991; Bau and Möller, 1992). We plotted the REY data of these samples on graphs of Ce_{SN}/Ce_{SN}^* *vs* Nd concentration (Fig. 2A) and Ce_{SN}/Ce_{SN}^* *vs* Y_{SN}/Ho_{SN} (Fig. 2B), where Ce_{SN}^* is calculated from

$$Ce_{SN}* = 0.5La_{SN} + 0.5\,Pr_{SN} \tag{1a}$$

or, if no Pr data were available,

$$Ce_{SN}* = 0.67La_{SN} + 0.33Nd_{SN}. \tag{1b}$$

We focus on Ce-REE and Y-REE relationships, because Ce and Y produce the most significant anomalies in patterns of REY partition coefficients and normalized REY concentrations (e.g., Bau et al., 1996). Minima, maxima, median, and mean values for Nd concentration, total