

Rare and Valuable Metals for High-Tech Applications Found in Marine Ferromanganese Nodules and Crusts: Relationships To Genetic Endmembers

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Introduction

Ferromanganese crusts have traditionally been considered a potential ore for Co, whereas ferromanganese nodules have typically been considered a potential ore for Ni and Cu. However, both nodules and crusts sequester high concentrations of many metals (Table 1) from sediment pore waters and seawater, many of which are essential for high-tech applications.

The resource potential of these rare and valuable metals is poorly known and they are the subject of considerable current research. The need for adequate and dependable supplies of these metals is essential for the development of new technologies. The rare-earth elements have recently received much attention in the scientific and popular press because of their use in so many high-tech applications and because more than 95% of the production comes from China (e.g., Service 2010); consequently, there is concern about the possibility of a significant decrease or even curtailment in exports from China. The lack of a primary source and the inadequate supply of Te have prohibited the development of a Cd-Te photovoltaic solar-cell industry (Hein et al. 2010). Inadequate supplies of many of the elements listed in Table 1 are limiting the development of key high-tech industries, forcing the use of alternative metals that

Table 1

Qualitative Assessment of Resource Potential for Rare and Valuable Metals for High-tech Applications Found in Marine Ferromanganese Deposits

	Fe-Mn Crusts	Abyssal Fe-Mn Nodules
Bi	L	-
Co	G	L
Cu	L	G
Li	-	L
Mn	G	G
Mo	L	L
Nb	G	-
Ni	G	G
Pt	L	-
REEs-Y	G	L
Te	G	-
Th	G	-
Ti	G	L
W	L	-
Zr	L	-

G = Good potential; L = Longer-term potential - = not applicable

may result in less efficiency or less favorable properties for a product. The rare-earth elements, Te, and other elements listed in Table 1 occur in high abundances in marine hydrogenetic and diagenetic ferromanganese deposits. Here, we look at the mechanisms by which these rare and valuable metals are incorporated into different genetic types of marine ferromanganese deposits.

Hydrogenetic and Diagenetic Deposit Types - Occurrences and Mechanisms of Formation

Hydrogenetic ferromanganese crusts and nodules, diagenetic nodules, and mixed-type nodules occur in different geological settings that are characterized by specific environmental and geochemical conditions (Hein et al., 1997). Ferromanganese nodules occur throughout the global ocean, predominantly on abyssal plains to water depths of up to 6,500 m. Nodules are less common on continental shelves and slopes and on oceanic plateaus and seamounts. The most extensive deposits have been found in the Pacific, especially in the Clarion-Clipperton Fracture Zone (CCFZ, Halbach et al. 1981; Morgan 2000), the Peru Basin (Von

Stackelberg 2000), and the Central Indian Ocean Basin (Jauhari and Pattan, 2000). Nodule size ranges from 0.5 to 25 cm, with a global average of 4 cm. Nodule coverage on the sediment surface can locally exceed 90%. Nodules are most abundant at the seabed with oxygenated bottom waters and in areas with low sedimentation rates, less than 10 cm/ka. Nodules can also occur within the upper meters of the sediment column.

The growth mechanisms most responsible for the formation of abyssal ferromanganese nodules are hydrogenetic and diagenetic processes (Halbach et al. 1988; Takematsu & Okabe 1989). Nodules in abyssal basins form by accumulation of Mn (and Fe) oxides around a nucleus, thereby forming concentric layers. The oxides precipitate from sediment pore waters that undergo redox reactions in the uppermost sediment layer. The supply of Mn, Ni, Cu, Zn, and other trace metals to the nodules takes place by early diagenetic mobilization of these metals in the upper part of the sediment column during the oxidation of organic matter. Dissolved Mn in the pore water re-precipitates during oxidation with oxygen from the bottom waters. Diagenetic growth in suboxic pore water produces todorokite as the major mineral, a hydrated crystalline Mn oxide (10Å manganate). Birnessite, a 7Å manganate, occurs less commonly. Accordingly, Mn is the major metal in diagenetic nodules with concentrations of up to about 40%. Diagenetic nodules have high Mn/Fe ratios (≥ 4), a coarse and porous texture, often cauliflower-like structures, and form at rates of up to several cm per million years.

Most of these abyssal nodules also have at least a small hydrogenetic component, such as part of the accumulated metals precipitated directly from seawater. They are called mixed-type nodules; if seawater was the major source of metals, then they are called hydrogenetic nodules.

Hydrogenetic ferromanganese crusts form up to 25 cm-thick coatings on rocks of seamounts, ridges, and plateaus in places where sediment does not accumulate. Both hydrogenetic nodules and crusts grow at very slow rates of a few mm per million years from precipitation of mixed Mn-Fe oxide phases from seawater and strongly enrich trace metals by scavenging processes from the water column (Hein et al., 2000, 2010). They have an extremely high surface area (mean 325 m²/g) and a high porosity, promoting a very effective sorption of

trace metals on the Fe-oxyhydroxide and Mn-oxide phases (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003).

Hydrogenetic nodules and crusts consist of mixed Mn-Fe oxides, basically a Fe-bearing vernadite (δ -MnO₂) intergrown with an X-ray amorphous Fe oxyhydroxide (FeO(OH)) phase. Major metal concentrations range from about 17 to 25% Mn and 7 to 15% Fe.

Because the distinctions between hydrogenetic-, diagenetic-, and mixed-type deposits are based on chemical composition, it is important to understand the behaviours of individual elements in aqueous systems and their processes of accumulation. Accordingly, the elements of interest will be discussed in the following sections in specific groups: transition metals Co, Ni, Cu, and Zn; lanthanide rare-earth elements and yttrium (REY); high field-strength transition elements (HFSE, i.e. Ti, Zr, Hf, Nb, Ta); potentially redox-sensitive elements (Ce, Co, V, Mo, W, Te, Pt); platinum-group elements (PGE, with a focus on Pt); and Li.

Transition Metals (Cu, Zn, Ni, Co)

The quasi-amorphous Fe-Mn oxyhydroxide-oxide mixture in hydrogenetic precipitates is an effective scavenger of dissolved transition metals in seawater. Dissolved metals in seawater are surface complexed by the functional groups of the Mn and Fe oxides and are incorporated into the oxide structure in various ways. The resulting accumulation of transition metals averages about 0.8% Co, 0.5% Ni, 0.1% Cu, and 0.08% Zn for crusts from the Central Pacific (Hein et al., 1997); incredibly high concentrations of Co of up to 2 % have been reported (Halbach et al. 1989b).

Diagenetic nodules are characterized by high concentrations of these valuable metals (up to about 3% for Ni + Cu + Zn) because diagenetically formed todorokite preferentially incorporates them in its crystal structure; these metals are mobilized from the sediment during early diagenesis. In contrast, concentrations of Co are often below 0.1% (e.g., about 0.05 % in the Peru Basin nodules; von Stackelberg, 2000).

REY (rare-earth elements and yttrium)

The REY distribution in hydrogenetic crusts represents the exchange equilibrium between REY(III) seawater solution-complexes (mono- and di-carbonate complexes) and REY(III) Fe and Mn phase surface-complexes (mostly hydroxide complexes, such as REYOH₂⁺; Bau et al., 1996). As a consequence, hydrogenetic Fe-Mn crusts are characterized by very similar REY distribution pattern regardless of their place of origin.

Compared to the strictly trivalent REY, the behaviour of Ce (which is redox-sensitive in oxic Earth-surface systems) is markedly different. After the initial surface-complexation of Ce(III) on hydrogenetic Fe-Mn crusts, a small fraction of the Ce is oxidized at the solid surface. This now tetravalent Ce no longer participates in the exchange reactions between REY solution and surface complexes and, with time, these Fe-Mn oxides preferentially accumulate Ce over the other REY, which results in the positive Ce anomalies characteristic of hydrogenetic Fe-Mn crusts (Bau and Koschinsky 2009, and references therein). Due to the rather slow reaction kinetics of Ce(III) oxidation, a slow growth rate is required to produce a positive Ce anomaly in a Fe-Mn crust. Purely hydrogenetic Fe-Mn nodules show REY patterns that are similar to those of hydrogenetic Fe-Mn crusts, suggesting that the scavenging mechanism is the same for both deposit types.

In marked contrast to hydrogenetic nodules and crusts, diagenetic nodules show a negative Ce anomaly or no Ce anomaly. Because of the limited data for REY distribution in sub-oxic and oxic marine pore waters this observation is not fully understood and may be related to a negative Ce anomaly in the pore-water and high nodule growth rates. This paucity of data highlights the need for more work on diagenetic Fe-Mn nodules, especially on pore waters in areas where nodules form. Regardless, the REY distribution is a diagnostic feature of diagenetic Fe-Mn nodules and clearly distinguishes them from hydrogenetic crusts and nodules.

HFSE (Ti, Zr, Hf, Nb, Ta)

Titanium reaches high concentrations of up to nearly 3% in crusts and nodules. Concentrations of Zr (190-1150 ppm), Hf (2.7-19 ppm), Nb (11-127 ppm), and Ta (0.24-2.7

ppm) in marine ferromanganese nodules and crusts are strongly variable within and between the different genetic types, but correlate well with Ti. All of these elements are enriched in hydrogenetic crusts relative to mixed-type nodules and tend to be lowest in dominantly diagenetic nodules (Fig. 1). Especially the Nb and Ta concentrations clearly separate diagenetic nodules from mixed-type crusts and nodules. Compared to pelagic shales and igneous rocks, Zr and Nb are significantly enriched in mixed-type nodules and crusts, whereas Ta is not. The precipitates display strongly fractionated, superchondritic Zr/Hf (46-92) and Nb/Ta (33-133) ratios, Relative to the average continental crust and pelagic shales with close to chondritic values. This signature of HFSE excludes an enrichment via the incorporation of detrital aluminosilicates but rather results from scavenging of dissolved complexes from seawater.

The good inter-correlation between Zr and Hf (Fig. 1) as well as Nb and Ta is evidence for a similar enrichment process. Results from sequential leaching suggest that the HFSE are predominantly associated with the Fe-oxide phase (Koschinsky and Hein, 2003) Similar to other highly charged, easily hydrolyzing elements like Ti and Th, the incorporation of Zr, Hf, Nb, and Ta is suggested to occur via the initial formation of inner-sphere surface complexes, followed by surface precipitation of specific hydroxide compounds as solid solutions with the original solid (Farley et al., 1985). The HFSE concentrations thus depend on the exposure time of the mineral surface to seawater. The good correlation of HFSE with the size of the positive Ce anomaly (see above) in hydrogenetic crusts strongly supports the interpretation of a time-dependent enrichment process. The generally higher concentrations of Zr, Hf, Nb, and Ta in hydrogenetic crusts (Fig. 1) relative to mixed-type nodules can be explained with the relatively higher growth rate of ferromanganese nodules relative to crusts, but is also related to the generally higher Fe content in ferromanganese crusts.

Bulk and depth profile data of hydrogenetic ferromanganese crusts display a systematic variation of the Zr/Hf ratio and the absolute concentrations, with decreasing ratios with increasing element concentrations. The Zr/Hf ratios in nodules and crusts are always significantly lower than those of seawater, which suggests preferential removal of Hf over Zr during the formation of the ferromanganese precipitates. Differences in complex stabilities and the type of chemical bonding between the geochemical pairs Zr-Hf and Nb-Ta are required to produce the strong fractionation between these elements during removal from

solution and incorporation into the solids. However, because the properties of HFSE in aqueous solutions are poorly constrained and thermodynamic data are scarce, interpretations of these observations are tentative.

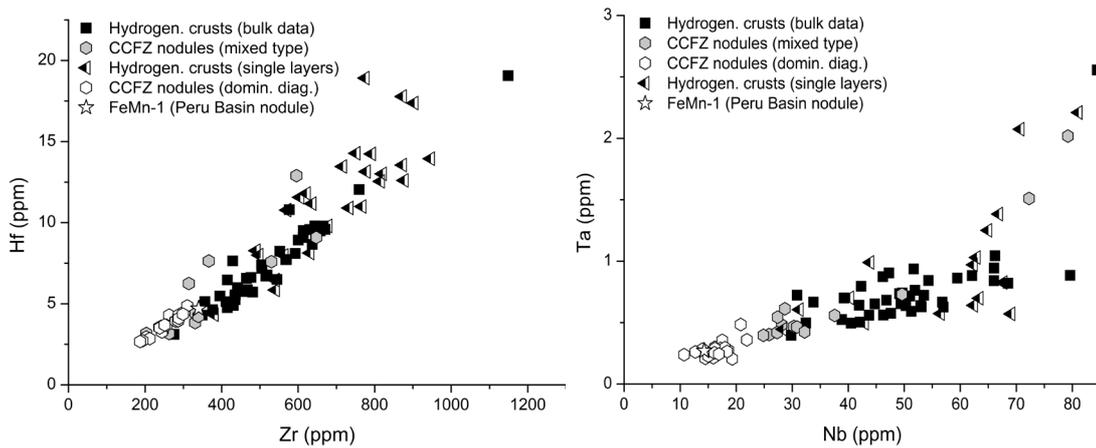


Figure 1. Plot of Zr vs. Hf (1a) and Nb vs. Ta (1b) in crusts and nodules, with the diagenetic Peru-Basin nodule lying within the CCFZ nodule field and hydrogenetic crusts having the highest Zr and Hf and Nb and Ta concentrations.

Potentially Redox-sensitive Elements (Co, Ce, Te, Pt, V, Mo, and W)

Some redox-sensitive trace metals undergo surface oxidation during sorption on the Fe and Mn mineral phases in hydrogenetic precipitates. Because this surface oxidation is a very efficient scavenging mechanism, hydrogenetic crusts and nodules are rich in these elements compared to diagenetic nodules. This surface oxidation had first been suggested for Co (Co^{2+} in seawater \rightarrow Co(III) on the MnO_2 surface; Murray & Dillard 1979) and for Ce (Ce^{3+} in seawater \rightarrow Ce(IV); see above, and Goldberg et al. 1963), which were confirmed by structural analysis using synchrotron methods (Takahashi et al. 2007). A similar surface oxidation mechanism has been suggested to explain the pronounced enrichment of Te compared to its geochemical twin Se in hydrogenetic precipitates (Te(IV) in seawater \rightarrow Te(VI) in the Fe-Mn phases; Hein et al. 2003), which has also been supported by synchrotron radiation XANES data (Hein et al. 2007). Pt may also undergo surface oxidation (see below). In contrast, there are no indications from enrichment factors (deposit/seawater or deposit/Earth's crust) or structural analyses such as using EXAFS and XANES that V, Mo, and W undergo surface

oxidation during incorporation into the oxide carrier phases (e.g., Kashiwabara et al. 2009). These three elements are predominantly present in their highest oxidation states (V(V), Mo(VI), W(VI)) both in seawater and in the precipitates, indicating that their incorporation into nodules and crusts is the result of surface complexation or structural incorporation without redox transformation. In contrast to the surface-oxidized elements, which are significantly more enriched in hydrogenetic deposits, V, Mo, and W concentrations do not differ significantly between different genetic types of nodules and crusts.

PGE

The noteworthy high concentrations of Pt in hydrogenetic precipitates range from about 0.4 to 1 ppm for regional mean values, with a maxima measured concentration of 3 ppm (see compilation in Hein et al. 2005 and abstract by Halbach et al. this volume). These high concentrations have been under discussion for many years and explanations have varied widely, from both oxidation and reduction of seawater Pt during uptake to external Pt sources such as cosmic spherules (Halbach et al. 1989a,b, 1990; Hein et al. 2005). Recent investigations based on sorption experiments with Pt(II) in seawater and determination of the oxidation state of the sorbed Pt support an oxidative scavenging process (Pt^{2+} in seawater as $\text{PtCl}_4^{2-} \rightarrow \text{Pt(IV)}$) on the hydrogenetic Mn-Fe phases; Koschinsky et al. 2005). This sequestration by surface oxidation explains the strong fractionation between Pt from the other platinum group elements, especially Pd.

Diagenetic nodules have low Pt concentrations, which may reflect the low mobility and limited migration of Pt in sediment pore water during early diagenesis (Terashima et al. 2002), the relatively fast growth rates of diagenetic nodules, and differences in their mineralogy (compared to hydrogenetic deposits), which may not provide surface-chemical environments conducive to surface oxidation of Pt.

As the other PGE, such as Rh and Pd, are present in nodules and crusts in significantly lower concentrations than Pt (i.e. a few ppb to a few tens of ppb), they are not considered as potential targets for resource research in our paper.

Lithium

Apart from the metals discussed above, Li is another element of economic interest that is enriched in Fe-Mn nodules. Li is especially important because of its use in batteries for hybrid and electric automobiles as well as for other applications. The sorption of monovalent cations on the negatively charged Mn-oxide surface is less effective compared to the surface sorption of the divalent transition metal cations, hence leading to limited Li enrichments in hydrogenetic crusts and nodules. In contrast, Li can be accommodated in the crystal structures of diagenetically formed Mn oxides such as todorokite (Jiang et al., 2007), leading to high average concentrations of Li in diagenetic nodules (around 300 ppm in Peru Basin samples and 160 ppm in Clarion-Clipperton nodule samples; Hein et al., 2000).

High-tech Metals in Hydrogenetic-diagenetic Mixed-type Nodules

Knowledge about the characteristic chemical composition of endmember diagenetic and hydrogenetic Mn-Fe nodules and crusts allows for the characterization of these precipitates according to their typical metal concentration ranges and distribution patterns. Apart from ternary diagrams in which Co concentrations or Cu+Ni concentrations are plotted against Fe and Mn contents (Bonatti et al. 1972; Halbach et al. 1988), the contents of trace metals, their ratios, and relationships between each other provide criteria for the genesis of the nodules. We analysed a set of 56 nodules from the German claim area of the CCFZ (see abstract by Kuhn et al. this volume) and compared the data with those of hydrogenetic and diagenetic endmembers. All data indicate a mixed-type origin for CCFZ samples, with a strong diagenetic component identified by high Cu and Ni concentrations (average about 1 %), low Co (average 0.2 %) and high Li (up to 480 ppm). The hydrogenetic component is identified by concentrations of HFSE, Pt (around 0.1 ppm), and Te (1.3-5.3 ppm), which are mostly higher than in the endmember diagenetic Peru Basin nodules and significantly lower than in endmember hydrogenetic crusts. In contrast to those elements, Mo and W do not show differences.

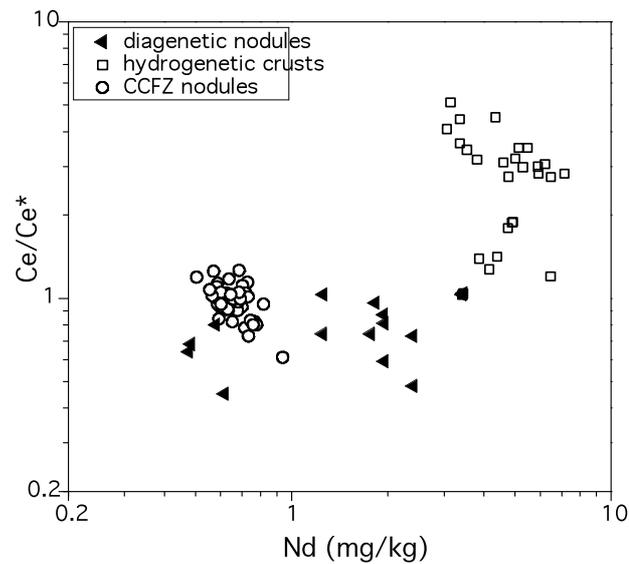


Figure 2. The Ce anomaly plotted vs. the Nd concentration (representing REY concentrations in general) indicates that the CCFZ nodules show a strong diagenetic component and plot away from the field of hydrogenetic crusts.

The CCFZ nodules investigated in this study show slightly positive to slightly negative Ce anomalies with significantly lower REY concentrations compared to hydrogenetic crusts (Fig. 2), reflecting a strong diagenetic component mixed with slight hydrogenetic contributions, and illustrating the usefulness of the REY for discriminating between hydrogenetic and diagenetic endmembers. The Ce anomaly shows a small positive correlation with the HFSE and Te, but not with Co, Mo and W in this sample group.

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