POTENTIALLY ECONOMIC REE IN Fe-Mn CRUST DEPOSITS FROM THE CANARY ISLAND SEAMOUNT PROVINCE: HIGH RESOLUTION ANALYSIS TO IDENTIFY THE METAL BEARING MINERALS

Egidio MARINO[1,2,3], Francisco J. GONZÁLEZ[1], Luis SOMOZA[1], Thomas KUHN[4], Teresa MEDIALDEA[1], Martin OESER[5], Rosario LUNAR[2,3]

[1] Marine Geology Division, Geological Survey of Spain (IGME), <Rios Rosas 23, 28003 Madrid>, <Spain>
[2] Mineralogy and Petrology Department, Geology Faculty, Complutense University of Madrid (UCM), <Jose Antonio Novais, 2, 28040 Madrid>, <Spain>
[3] Geosciences Institute (IGEO-UCM-CSIC), <Severo Ochoa 7, 28040 Madrid>, <Spain>
[4] Federal Institute for Geosciences and Natural Resources (BGR), <Stilleweg 2, D-30655 Hannover>, <Germany>
[5] Leibniz Universität Hannover Institut für Mineralogie, <Callinstraße, 3, 30167 Hannover>, <Germany>

emarino@ucm.es, fj.gonzalez@igme.es, l.somoza@igme.es, Thomas.Kuhn@bgr.de, t.medialdea@igme.es, m.oeser@mineralogie.uni-hannover.de, lunar@ucm.es

Fe-Mn crusts grow on hard surfaces, usually on seamounts, plateaus and ridges of all the oceans worldwide. They are formed by the precipitation of nanometric floccules formed by Mn oxides and Fe oxyhydroxides. The accumulation and growth of Fe-Mn crusts take place according to three main genetic processes: diagenetic, hydrothermal and hydrogenetic. Hydrogenetic crusts are formed by the precipitation of Fe and Mn oxyhydroxides from the cold seawater in presence of currents sufficiently strong to keep the substrate rock clean of sediments. Due to their slow growth (0.5-5 mm/Myr) hydrogenetic Fe-Mn crusts concentrate high contents of several valuable metals in their structure, between them there are Co, Ni, Cu, Mo, Te, Platinum Group Elements (PGE) and also Sc and Rare Earth Elements plus yttrium (REY)[1].

Fe-Mn crusts from the Canary Island Seamount Province (CISP) have been recently studied and the results obtained demonstrate a predominantly hydrogenetic origin[2,3,4]. The main minerals are Mn-oxides (essentially vernadite with small amount of birnessite, asbolane and todorokite) and Fe oxyhydroxides (goethite group metals with metastable phases as feroxyhyte and ferrihydrite). Chemically they are characterized by high bulk contents (based on ICP-MS analysis) of Co, Ni, Mo (0.5, 0.3, 0.03 wt. % respectively). Sc and REY are highly concentrated in CISP Fe-Mn crusts (35 µg/g and 0.30 wt. % respectively) and between them the most enriched are the LREE (La, Ce, Pr and Nd) ranging from 400 to 2000 µg/g. REY elements can be found dissolved in seawater as mono- and di- carbonate complexes and are concentrated in Fe-Mn crusts with a preferential scavenging (especially for LREE) on the freshly precipitated surface of the Mn oxides and Fe oxyhydroxides due to their surface charge[5,6,7].

High resolution analysis performed on selected CISP samples show that REY are differently distributed in the Fe and Mn oxy-hydroxides that form the crusts. EPMA analysis show that diagenetic Mn minerals (asbolane/buserite) have high Mn (up to 45 wt.%) with less Fe (max 10 wt.%) and low contents of Ce (200-600 µg/g). On the other hand, hydrogenetic vernadite, which represents more than 85% of the total oxy-hydroxides content in CISP crusts, have similar contents of Mn (22-25 wt.%) and Fe (18-22 wt.%) with high contents of Ce (2200-3000 µg/g).

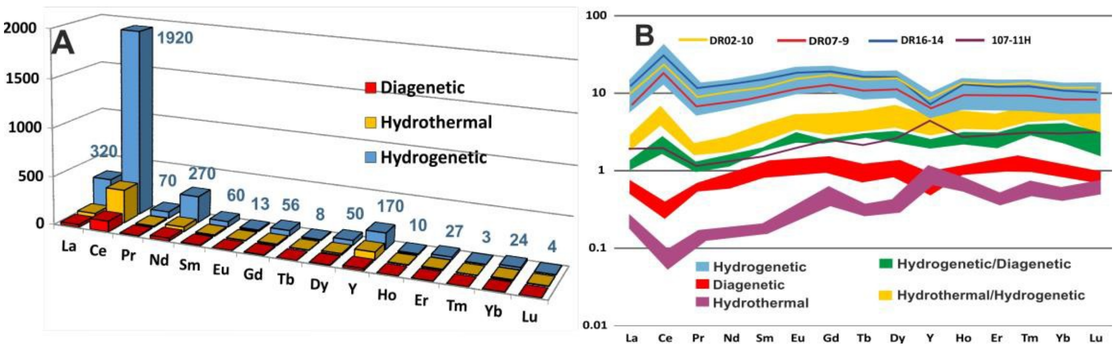

Figure 1. A) LA-ICP-MS average contents (in µg/g) of the mineral laminae formed by different genetic processes. B) PAAS normalization of the different genetic processes based on laminae (colored areas) and bulk sample (solid lines) analysis.

The use of LA-ICP-MS analysis performed on selected crust laminae with different genetic origin allows to obtain their REY contents. Diagenetic minerals show the lowest REY contents (60 to 600 µg/g) that is also evident in their normalization to PAAS (**Fig. 1**), in which the highest contents are represented by La (10-60 µg/g), Nd (13-60 µg/g) and Ce (10-270 µg/g), with very low contents of HREEs (0.1-10 µg/g for each element). The low REY contents in diagenetic minerals can be explained essentially by two causes: i) the high growth rate (up to 100 mm/Myr); ii) their precipitation from pore water within the sediments that isolate them from open seawater. Mixed hydrothermal/hydrogenetic minerals found in CISP Fe-Mn show REY contents between 300 and 800 µg/g, the lower enrichment of diagenetic minerals compared to hydrothermal ones may be caused by the incorporation of REY elements from seawater after their hydrothermal precipitation. In hydrothermal minerals the highest REY contents are represented essentially by Ce (up to 500 µg/g). Finally, hydrogenetic minerals show the highest REY contents in CISP crusts between 2200 and 4900 µg/g. These minerals incorporate the highest Ce contents (up to 3500 µg/g), but also high contents of other REYs like Nd and La (up to 500 µg/g each), Dy (up to 80 µg/g), Eu (up to 25 µg/g) and Y (up to 250 µg/g). Furthermore the U+Th contents of these minerals represent only the 2.5% of the total REY (respectively in average 12 and 67 µg/g), that is good to decrease the radiogenic problems usually associated with onshore mineable ore deposits.

One metal extraction experiment has been probed on studied samples to verify the REY recovery rates obtained in selected samples from CISP crusts. The results show that the highest recovery rates can be found in purely hydrogenetic Fe-Mn crusts (62-85 %), on the other hand mixed diagenetic/hydrogenetic crusts show less recovery rates (58-67 %). These differences can be due to the high crystallinity of the diagenetic minerals that show the worst acid digestion and confirming the hydrogenetic minerals as the best REY carriers and with the highest recovery rates. These findings can be useful on choosing the best routes for processing of submarine Fe-Mn crusts in the future, considering REE a by-product from extraction of other commodities, such as Mn, Co or Ni.

Aknowledgment

This work was supported by the Spanish projects EXPLOSEA (CTM2016-75947-R), SUBVENT (CGL2012-39524-C02); and the European projects EMODnet-Geology (EASME/EMFF/2016/1.31.2-Lot 1/SI2.750862) and H2020 GeoERA-MINDeSEA (Grant Agreement No. 731166, project GeoE.171.001).

References

1. J.R. Hein, K.Mizell, A. Koschinsky, T.A. Conrad. Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: comparison with land-based resources. Ore Geol. Rev. 51 1–14 (2013). http://dx.doi.org/10.1016/j.oregeorev.2012.12.001.
2. E. Marino, F.J. González, L. Somoza, R. Lunar, L. Ortega, J.T. Vázquez, J. Reyes, E. Bellido. Strategic and rare elements in CretaceousCenozoic cobalt-rich ferromanganese crusts from seamounts in the Canary Island Seamount Province (northeastern tropical Atlantic), Ore Geol. Rev., 87 41-61 (2017). https://doi.org/10.1016/j.oregeorev.2016.10.005.
3. E. Marino, F.J. González, R. Lunar, J. Reyes, T. Medialdea, M. Castillo-Carrión, E. Bellido, L Somoza. High-Resolution Analysis of Critical Minerals and Elements in Fe–Mn Crusts from the Canary Island Seamount Province (Atlantic Ocean). Minerals, 8 (7) 285 (2018). https://doi.org/10.3390/min8070285.
4. E. Marino, F.J. González, T. Kuhn, P. Madureira, A.V. Wegorzewski, J. Mirao, T. Medialdea, M. Oeser, C. Miguel, J. Reyes, L. Somoza, R. Lunar. Hydrogenetic, Diagenetic and Hydrothermal Processes Forming Ferromanganese Crusts in the Canary Island Seamounts and Their Influence in the Metal Recovery Rate with Hydrometallurgical Methods. Minerals, 9 (7) 439 (2019). https://doi.org/10.3390/min9070439.

5. A.V. Dubinin, A.G. Rozanov,. Geochemistry of rare earth elements and thorium in sediments and ferromanganese nodules of the Atlantic Ocean. Lithol. Miner. Resour., 36 (3) 268–279 (2001). http://dx.doi.org/10.1023/A:1010485510346.
6. M. Bau, A. Koschinsky. Oxidative scavenging of cerium on hydrous Fe oxide: Evidence from the distribution of rare earth elements and yttrium between Fe oxides and Mn oxides in hydrogenetic ferromanganese crusts. Geochem. J., 43 (1) 37–47 (2009). http://dx.doi.org/10.2343/geochemj.1.0005.
7. M. Bau, K. Schmidt, A. Koschinsky, J.R. Hein, T. Kuhn, A. Usui. Discriminating between different genetic types of marine ferro-manganese crusts and nodules based on rare earth elements and yttrium. Chem. Geol., 381 1–9 (2014). http://dx.doi.org/10.1016/j.chemgeo.2014.05.004.