Mineralogy and geochemistry of critical metals in Fe-Mn crusts from the Canary Islands Seamount Province

Egidio Marino[1,2,3], Francisco Javier González[1], Rosario Lunar[2,3], Luis Somoza[1], Jesús Reyes[1], Teresa Medialdea[1], Eva Bellido[1], Thomas Kuhn[4], Anna Wegorzewski[4], Martin Oeser[5].

[1] Geological Survey of Spain, (IGME), C/Ríos Rosas, 23, 28003 Madrid, Spain. email: emarino@ucm.es

[2] Mineralogy and Petrology Dpt., 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), Geozentrum Hannover Stilleweg 2, D-30655 Hannover

[5] Leibniz Universität Hannover Institut für Mineralogie, Callinstr. 3, 30167 Hannover

Ferromanganese crust deposits from Canary Islands Seamount Province (CISP) have been recovered from slopes and tops of six seamounts within the Spanish EEZ and Extended Continental Shelf: Las Hijas, Bimbache, The Paps, Tropic, Echo and Drago seamounts (NE Central Atlantic). They form extensive pavements up to 25 cm of thickness covering hard substrates and sediments on slopes and summits of Mesozoic seamounts. Bulk studies, made on 49 selected crusts, show that the mineralogy and geochemistry of CISP crusts reflect a general hydrogenetic origin. Mineralogy is represented essentially by Fe and Mn oxyhydroxides. Vernadite is the main Mn oxide with contents up to 80%, birnessite, buserite/asbolane and occasionally todorokite are also present in smaller amounts. Fe oxyhydroxides are poorly crystalline goethite group minerals and amorphous feroxyhyte. Detrital and authigenic minerals could also be recognized in some samples represented by quartz, feldspar, calcite CFA and phyllosilicates. Textural features recognized under the petrographic and electronic microscopes show that Fe-Mn oxyhydroxides are packed with 3 main typologies: I) dendritic to mottled, II) columnar and III) dense parallel.

Bulk geochemistry reflects mineralogical data with high average contents of Fe (23 %) and Mn (14 %). Silicate filiation elements show lower contents: Si (3.8 %), Al (1.7 %), Mg (1.2 %), Na (1 %) and K (0.4 %). Ca (3 %) and P (0.6 %) are usually linked to the presence of calcite, bioclasts and CFA formation in crusts or substrate fragments at the base of them.

Trace elements are usually enriched in Fe-Mn crusts from CISP compared to average continental crust. Metals considered for their economic potential in CISP crusts are Co (up to 8000 µg/g), Ni (up to 4800 µg/g), Cu (up to 1200 µg/g). Our studies indicate that Fe-Mn crusts are an economic source for other trace elements like V (up to 1200 µg/g), Mo (up to 600 µg/g), Tl (up to 140 µg/g) and especially Te with average contents of 45 µg/g and maximums up to 65 µg/g. The total content of all these economic elements ranges from 0.13 to 1.1 %.

Rare earth elements (REE) and yttrium are also considered with economic potential in Fe-Mn crusts. These elements are enriched in CISP Fe-Mn crusts with total contents ranging from 1300 to 3300 µg/g. LREEs and MREEs are the most enriched with the highest contents represented by Ce with up to 2000 µg/g. If normalized to PAAS the samples show a clear positive Ce anomaly typical of hydrogenetic crusts. PGEs bulk contents have been analyzed in 30 crusts from CISP and show an average total of 260 ppb. Pt is the most abundant, containing up to 340 ppb in diagenetically influenced crusts.

Recent high resolution studies using HR-TEM, EPMA and LA-ICP-MS made on selected samples show that Fe-Mn crusts from CISP did not grow only due to hydrogenesis but they have been subject to the influence of diagenetic processes, of volcanic-hydrothermal episodes, and Sahara eolian dust. Diagenetic growth is restricted to local covering of freshly precipitated Fe-Mn oxyhydroxides with sediments and/or mineral replacements within the crust layers. Diagenetic layers studied with high resolution methods show average contents of Mn (up to 40 %), Ni (up to 2 %) and Cu (up to 1 %) and lower Co (0.3 %) similar to diagenetic nodules from CCZ. The different diagenetic processes lead to a change of content of several strategic metals. Diagenesis enriches CISP crusts in Ni and Cu but deplete them in several other elements like Co, REEs plus yttrium, Mo and V.