"High Technology Elements" in Co-Rich Ferromanganese Crusts from the Scotia Sea

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INTRODUCTION.

Ferromanganese deposits are extended throughout all the ocean basins in the World. They appear covering hard rock substrates in seamounts, plateaus and ridges mostly at depths from 1000-3000 m (Hein et al., 2000). Fe-Mn crusts form by mineral precipitation from the seawater (hydrogenesis) in areas without pelagic sedimentation processes during long time periods. Their growth usually is very slow, a few millimetres by million of years. Ferromanganese crusts generally contain significant quantities of different elements of economic interest: Co, Ni, Mn, Te, Ti, rare-earth elements (REEs), Pt and other metals. Some of these metals are enriched in factors between 100 and 10000 over the average contents in the continental rocks, and they are necessary for the high technology industry development (*high tech elements*) (Hein et al., 2010). In this sense, the European economies are highly dependent on imports of these strategic metals from political and/or economical unstable countries. For these reasons the European Commission considers a priority the investigation of strategic mineral resources in the European Territory, including the seabed (European Commission, 2008).

In this work we present the mineralogical and geochemical analysis of strategic elements in ferromanganese crusts from the Scotia Sea. We discuss the relation between the metals and the mineral phases and finally we propose potential areas for the investigation of this type of deposits in the continental margins of Iberia.

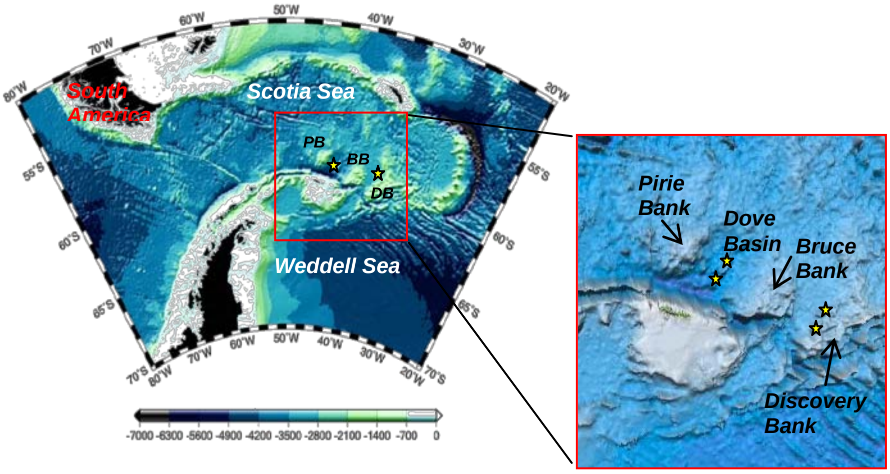

fig 1. *Simplified bathymetric map from the GEOSAT gravimetric anomaly of the Scotia Sea and Weddell Sea (Sandwell and Smith 1997). The rectangle represents the area investigated by different geophysical methods and sampling by dredge. On the right, detail of the studied area and location of the Fe-Mn crusts sampling sites (stars), outside of the Antarctic Treaty area.*

MATERIALS AND METHODS.

A large suite of Fe-Mn crusts was collected by benthic dredges from oceanic ridges and seamounts at 2000-2500 m depth in the Dove Basin (Southern Scotia Sea). The samples were recovered during the oceanographic cruises SCAN-2004 and SCAN-2008 onboard the Spanish research vessel "BIO Hespérides".

For the mineralogical and textural characterization of crusts they were studied by DRX, optical and electronic microscopy (EPMA and SEM). Different spectroscopic methods (ICP-MS, FRX) were employed to determinate the concentration of strategic elements onto the ferromanganese crusts. Platinum Group Elements were analyzed by ICP-MS after nickel sulphide fire-assay collection and tellurium coprecipitation.

GEOLOGIC AND OCEANOGRAPHIC SETTING.

The Scotia plate is situated between the South America and Antarctic plates resulting from the fragmentation of the continental connection of South America and Antarctic Peninsula (Barker et al., 1991). In the southern boundary of the Scotia plate (Fig. 1) appear different basins generated by spreading ridges, probably during the Lower to Middle Miocene, and limited by large blocks of continental crusts (Maldonado et al., 2006). The tectonic evolution with the opening of the Drake Passage and other seaways in the last 32 Ma has controlled the formation and evolution of the circum-Antarctic deepwater flows (WSDW) and the Antarctic Circumpolar Current (ACC) (Lawver and Gahagan, 2003).

RESULTS AND DISCUSSION.

Fe-Mn crusts form botryoidally pavements up to 30 mm thick on tholeiitic oceanic basalts. They are basically formed by Fe-rich vernadite (δ-MnO) and goethite and detrital quartz as accessories.

Manganese oxides form a concentric

palabras clave: Elementos Estratégicos, Costras de Mn, Biomineralizaciones, Recursos Minerales Marinos. | *key words:* High Tech Elements, Mn Crusts, Biomineralizations, Marine Mineral Resources.

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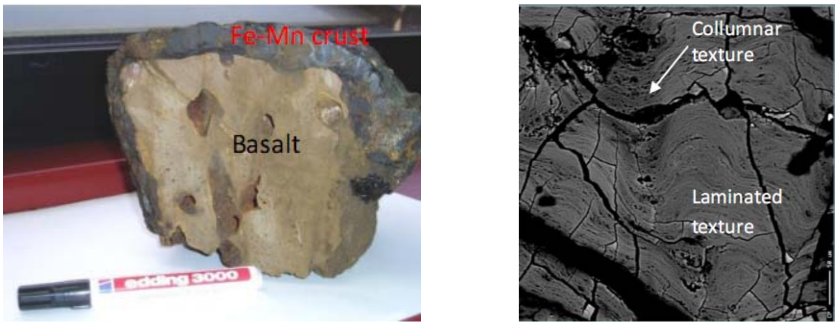

fig 2. On the left, ferromanganese crust section covering a basalt substrate. On the right, EPMA backscatter image on a polished section showing areas enriched in vernadite and goethite, laminated and columnar textures respectively.

pattern of sub-parallel laminate layers. Goethite and detrital silicates generally are abundant in areas with columnar textures (Fig. 2) especially concentrated in the most external part of the crusts.

There are abundant like-microbe micrometric tubular structures, covered by Mn oxides and rich in C and F. These textural features can be due to the Mn-biomineralization action of microorganisms.

In bulk sample ferromanganese crusts are characterised by a similar abundance of Fe_2O_3 and MnO (Table 1). The relation Mn/Fe=1.1 is common in hydrogenetic deposits, and similar to other results obtained for crusts from the Atlantic or South Pacific Oceans (Hein et al., 2000). In addition, the studied samples are enriched in elements of economic interest as cobalt, nickel, thallium, cerium and other REEs relative to their lithosferic concentrations (Table 1). All these metals are adsorbed from the seawater into the Fe-Mn oxide structures during the growth of the crusts.

Total average value of REEs is 0.34%. The most significative are Ce (0.19%), Nd (457 μg/g), La (455 μg/g), Dy (107 μg/g) and Tb (17 μg/g). Rare earths are not rare in the nature, but discovered minable concentrations are less common than for most other ores. In this sense, the ferromanganese crusts may be a potential source for REEs. They could be obtained as by-product of Mn, Co or Ni exploitation.

Pt and other PGE, with economic importance, are present in the crusts. Platinum ranges up to 191 ng/g for individual bulk crusts. Ru, Rd, and Ir contents are up to 13, 16 and 5 ng/g respectively, whereas Pd values are usually at lithosferic contents.

On respect to the distribution of elements in mineral phases, vernadite is enriched in Co, Ni, Ce and Pb; and goethite concentrates Fe, Ti, Zn and V (Table 1).

The laminate facies, which are enriched in vernadite, concentrate strategic elements as Mn (27.5%), Co (0.6%), Ni (0.4%) and Ce (0.2%). On the other hand, the columnar facies, enriched in goethite and silicates, concentrate elements as Fe (42%), Ti (1.6%) and V (0.3%).

On respect to the distribution of crusts on seamounts it is yet poorly known. The studied crusts are situated in the oxygen minimum zone (OMZ) which is where the most Co-rich crusts occur. Factors as gravity processes, sediment cover, water depth and currents control the distribution, metal enrichment and thickness of ferromanganese crusts (Hein et al., 2000). Seamounts with a flat summit and terraced flanks situated between 800 and 2200 m water depth could be favourable to present deposits of economic importance as occur in the Pacific Ocean (Hein et al., 2000). In this way, seamounts, ridges and banks located in the surroundings of the Iberian Peninsula (Atlantic and Cantabrian margins) could be potential areas for prospecting these mineral resources.

	MnO	Fe_2O_3	TiO_2	Ni	Cu	Co	Zn	Ba	Ce	Tl
Lithosphere	0.18	10.1	0.9	0.01	0.008	0.003	0.008	0.025	0.003	0.36
Mn crust1	29.7	28.6	1.4	0.24	0.03	0.4	0.08	0.37	0.19	112
Mn crust2	29.2	25.7	1.6	0.32	<DL	0.43	0.06	0.13	0.23	NA
Vernadite	35.5	24	1.6	0.42	<DL	0.57	0.06	0.16	0.24	NA
Goethite	0.3	54.1	2.7	0.02	0.05	0.06	0.11	0.08	NA	NA

Table 1 Chemical compositions (Wt.%) of two ferromanganese crusts and their mineralogy compared to the Earth's Crust. Thallium content is in μg/g. <DL (below detection limit). NA (Not Analyzed). Continental crust data from Taylor and McLennan (1995).

CONCLUSIONS.

Hydrogenetic ferromanganese crusts from the Scotia Sea are enriched in strategic elements with economic importance as Co, Ni, REEs and PGE. These elements are specially concentrated in the vernadite. It acts as a holder for these metals adsorbed from the cold seawater, because of vernadite could be considered as a strategic mineral. Seamounts from the Iberian Peninsula continental margins are potential areas for the investigation of this type of mineral deposits.

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