Mineralogy and Geochemistry of Ferromanganese Crusts

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Contributor: Francisco González , Dominik Zawadzki , Lukasz Maciag , Iker Blasco del Barrio , , Egidio Marino , Gabriela A. Kozub-Budzyń , Adam Piestrzynski , Rafal Wrobel , Kevin McCartney

Late Pleistocene–Holocene rocks from the western part of Cocos-Nazca Spreading Centre (C-NSC) include ferromanganese crusts that elucidate the geochemistry and mineralogy of a deep-sea geological setting. Geochemical, mineralogical and petrological signatures indicate complex formation influenced by mild hydrothermal processes. These crusts consist mostly of mixed birnessite, todorokite-buserite, and Mn-(Fe) vernadite with traces of diagenetic manganates (asbolane), Fe-oxides and oxyhydroxides or hydrothermally associated and relatively pure Mn-oxyhydroxides (manganite). The average Mn/Fe ratio is 2.7, which suggests predominant mixed hydrogenous-early diagenetic crusts with hydrothermal influences. The mean concentrations of three prospective metals (Ni, Cu and Co) are low: 0.17, 0.08 and 0.025 wt %, respectively. The total content of ΣREY is also low, and ranges from 81 to 741 mg/kg (mean 339 mg/kg).

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1. Introduction

Despite more than 40 years of research on marine ferromanganese (Fe-Mn) crusts, knowledge remains limited and new discoveries provide added geochemical and mineralogical data on formation mechanisms, from either Exclusive Economic Zones (EEZ) [1][2][3][4], or from waters outside national jurisdictions [5][6][7]. Recently, high-resolution analyses of critical minerals and elements have focused on crusts formation to distinguish hydrogenetic and diagenetic origins [8]. In addition, numerous studies have addressed the identification and distribution of critical metals, such as rare earth elements and yttrium (REY), cobalt or platinum in mineral phases [9][10][11]. Studies of crusts from the South China Sea, Western Pacific Ocean and Canary Island Seamount Province note that light REY are preferentially adsorbed onto δ-MnO_2 (vernadite), while heavy REY are associated with amorphous Fe-oxides and hydroxides, mainly FeOOH. Several authors concentrate on growth rate estimation and crustal formation stages reconstruction [12][13], while others focus on mineral resource assessment at regional and local scales, with particular emphasis on critical elements (e.g., Co, Te, REY) [14][15]. The Be isotope age models indicate continuous growth from ocean substrate to surface at Takuyo-Daigo Seamount, NW Pacific, with a fairly constant growth rate of 2.3–3.5 mm/Myr during the past 17 Ma [13].

Marine Fe-Mn deposits are traditionally divided into three genetic classes: hydrogenetic, diagenetic and hydrothermal [16][17]. Additionally, mixed-signature crusts have been found [10]. Hydrogenetic Fe-Mn crusts form by precipitation from cold ambient bottom waters, or by a combination of hydrogenetic-hydrothermal input in areas of hydrothermal venting, such as oceanic spreading centres, volcanic arcs, and hotspot volcanoes [18]. Hydrogenetic Fe-Mn crusts contain subequal amounts of Fe and Mn, enriched in Co, Pb, Te, Bi, and Pt relative to concentrations in lithosphere and sea water [19]. These Fe-Mn crusts usually form at hard rock substrates throughout the oceanic basins, including flanks and summits of seamounts, ridges, plateaus, and abyssal hills, at depths between 400 and 7000 m where rocks have been swept clean of sediments at least intermittently for millions of years. In some instances, the Fe-Mn crusts form oxyhydroxide-rich pavements up to 250 mm thick (mean thickness varying within 2–4 cm), mostly on rock outcrops, or coatings on talus debris [20]. The thickest crusts occur in a depth interval of 800 to 2500 m and indicate high concentrations of critical metals [21]. Some studies set this depth in the anoxic zone at depths of about 1 to 1.5 km [22][23][24]. Crust nucleation is extremely slow, with mean growth rates of 1–5 mm/Myr. Mn-oxide hydrothermal crusts, sometimes called “stratabound”, precipitate directly from low temperature hydrothermal fluids, and usually grow significantly at a more rapid rate, even up to 1600–1800 mm/Myr [25].

A number of relatively thin Fe-Mn crusts were unexpectedly discovered and recovered during the April–May 2018 Cocos-Nazca cruise (R/V Sally Ride, Leg 1806), recovered in areas close to the regional spreading centre axis. A few samples were recognized as Fe-Mn crust. The aim of this contribution is to provide detailed geochemical and mineralogical study of initial Fe-Mn crusts collected from the western portion of Cocos-Nazca Rift (C-NR), with analysis to determine their formation conditions.

2. Ferromanganese Crust Occurrences in the Cocos-Nazca Ridge

The Galapagos Spreading Center (GSC) located east of the Cocos-Nazca (C-N) region, at approximately 98° W, extensively studied in 1970s and 80s, provide detailed geophysical and geochemical data of the eastern GSC flank [26]. Here, increased heat-flow and associated hydrothermal activity was discovered in a number of localities, especially near seafloor mounds [27][28][29]. Deep Sea Drilling Project (DSDP) Leg 70 provided Fe-Mn crusts with included encrustations of hydrothermal mounds and sedimentary sections [30][31][32]. These localities occur within a zone of high biological productivity associated with sedimentation processes [31]. Sediment thickness consists of foraminifer-nannofossil oozes interbedded with hydrothermally associated nontronite-rich pelagic and siliceous foraminifer-nannofossil oozes [33][34] that increase rapidly and regularly away from the spreading axis. In some cases, the uppermost sediment layer was covered by hydrothermal Fe-Mn crusts and metal-rich muds, especially within intensely oxidized greenish nontronite-rich association [31]. Based on magneto- and biostratigraphy, the hydrothermal activity in the eastern GSC started about 300 ka [35].

The Fe-Mn crusts recovered during Leg 70 consist of brownish-black, flat to saucer-shaped angular fragments, ranging from 10–40 mm width to 1–5 mm thickness. Surface textures were finely granular, though some samples showed botryoidal-concretionary growth patterns [31]. Several fragments were brittle, with freshly broken pieces showing in cross-section dense metallic luster, locally micro-laminated and ubiquitously covered with a thin (<2 mm) coating of soft and porous black Mn-oxides. X-ray diffraction analyses indicated the presence of intermixed todorokite-buserite and birnessite, with lesser unidentified amorphous Fe-Mn phases. Varentsov et al. [36] suggested that the Leg 70 crusts formed in a less oxidized environment, possibly the result of growth at a slightly subsurface level or influenced by discharged hydrothermal plume solutions. Additionally, admixtures of dioctahedral Fe-rich smectite (nontronite), Fe-mica (celadonite), quartz, feldspars, zeolites (phillipsite), calcite, goethite and halite were observed. U-Pb dating estimated that the Fe-Mn crusts formed on mound tops at about 20–60 ka [37].

Moore and Vogt [38] first studied C-N hydrothermal and hydrothermally altered hydrogenetic manganese crusts and described 2–6 cm thick intervals from two sites near the Galapagos spreading axis. Those samples were characterized by low Fe/Mn and $^{232}Th/^{238}U$ ratios, as well as deposition rates several orders of magnitude faster than more common hydrogenetic nodules, with estimated age of these crusts given as 2400 to 300 ka [38]. A few hydrothermal and mixed hydrothermal-hydrogenetic crusts were discovered around hydrothermal vents in the eastern part of GSC during the GARIMAS project (Galapagos Rift Massive Sulphides) during the middle 1980s aboard the R/V Sonne. These samples were dominated mainly by Mn (up to 82% as MnO) and some were characterized by increased Fe content (45–55% as Fe_2O_3). These iron-rich samples were composed mainly of amorphic Fe-oxides, birnessite and clay minerals (mainly montmorillonite and illite) [39][40]. REE concentration in *GARIMAS* samples was low and ranged from 1.3–9.0 mg/kg. The samples are likely younger than previously described crusts, since the collection sites are west of C-NSC at a distance near (16 km) to the spreading axis.

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