OCCURRENCE, ORIGIN AND MINING OF MESOZOIC MANGANESE NODULES IN COSTA RICA, CENTRAL AMERICA

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The geologic basement of southern Central America is made up of oceanic complexes, partly of ophiolitic affinity, with Jurassic to Early Tertiary ages (Denyer & Gazel, 2009). Most of these rocks are deep-sea tholeiitic basalts, gabbros and serpentinite which are regionally associated with units of volcaniclastic breccias as well as radiolarian cherts (Gursky, 1989). In the Nicoya Peninsula (NW Costa Rica) manganese mineralizations are present within some of these oceanic rocks. They occur mostly as clearly hydrothermal ores: in form of massive stratiform and cross-cutting mineralizations, generally associated with recrystallized bedded cherts or bodies. However, radiolarian cherts of probable Middle Jurassic to Cretaceous ages contain in places sedimentary manganese nodules, which either are set in masses within dark-grey manganiferous siliceous mudstone intercalated in radiolarian chert sequences or occur isolated within red relatively pure radiolarian chert (Gursky, 1989). The manganese ores are of minor dimensions and thus were called 'pockets' by the early miners. Massive hydrothermal deposits were preferentially mined, as shown by the material of relictic dump ores found locally. Documented mining in small open pits and trenches was active mainly from 1916 to 1920 (Roberts, 1944; Webber, 1942) , triggered by the metal shortage during World War I, and was temporarily profitable due to low local salaries and transport expenses. Mining was only once re-activated in the year of 1938, but at a very small scale and without later efforts. All together, some 32,000 metric tons of Mn ore were mined from tens of localities spread over the northwestern part of the Nicoya Peninsula. The mined ore was mostly transported by ox-carts to near-by shipping places, from there on board of small shallow lighters to steamers anchoring offshore in Pacific waters, and then shipped to North America for manganese extraction. The nodules are deep black, with smooth surfaces, discoidal, compact, very dense and generally orientated parallelly to bedding, and show diameters of up to 9 cm. Most nodules are single individuals, aggregated nodules are very subordinate. In alternations with radiolarian chert, nodules may grade horizontally to stratified lenses and layers. Some nodules show tectonic fractures. For some time in the past, all manganese mineralizations were interpreted as being of hydrothermal origin, including the nodules (Kuijpers & Denyer, 1979). This was mainly due to the co-occurrence of nodules and clearly hydrothermal

Fig. 1: Outcrop of manganese nodules interlayered with manganiferous mudstones and radiolarian chert beds. Ancient El Francés Mine, NW Nicoya Peninsula, Costa Rica.

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Fig. 2: Selected typical manganese nodules from the Nicoya Complex, Costa Rica. Samples from the outcrop shown in Fig. 1.

ores, and the observed mineralogy and geochemistry of the nodules. The nodules are mostly characterized by dominating braunite with some hollandite, ?bixbyite, ?manganite, generally much pyrolusite and some quartz. It is visible in polished sections that braunite was successively replaced first by hollandite and later by pyrolusite. The nodules contain 39 – 61 % Mn, 0.9 – 1.6 % Fe, 5 – 26 % SiO_2, 1.3 – 1.9 % Al_2O_3, 1.5 – 3.0 % Ba, 460 – 5,400 ppm Cu, 85 – 340 ppm Ni, and 40 – 130 ppm Co (Halbach et al., 1992).

Modern manganese nodules form the deep-sea are also black and show similar dimensions but, however, are less dense and generally have 'framboidal' or 'globulated' surfaces and consist mostly of todorokite ($[Ca, Mg, Ni, Cu, Zn, Mn]_2$ x Mn_5O_{12} x nH_2O and vernadite/δ-MnO_2 [= MnO_2 x nH_2O mixed with FeOOH x nH_2O and some Ca, Mg, Si]) and up to 25 % water. And they are poorer in Mn and Ba and show a lower Mn/Fe ratio, but are much richer in Ni and somewhat richer in Cu and Co, in comparison to the fossil Costa Rican nodules (Halbach et al., 1992).

The typical association of radiolarian chert, i. e. ancient classical deep-sea ooze, with large numbers of manganese nodules, like on modern ocean-floors, and the concentric internal structure of the fossil nodules seen in polished sections, similar to modern nodules, suggest a sedimentary origin of the Costa Rican ones. To test this hypothesis, a thermal experiment was prepared with sample material of a recent, todorokite/δ-MnO_2 water-rich nodule (Maresch in: Halbach et al., 1992). The material was crushed to powder, welded into thin-walled palladium capsules which then were welded into thin-walled gold tubes, together with the necessary oxygen-buffer mixture plus excess water. Then the p/T experiment was run for 336 hours at 2,000 bar (total), 400, 500 and 600 °C and $10^{-6.5}$, 10^{-5} and 10^{-6} bar (O_2), respectively. X-ray diffraction analysis of the resulting very-fine grained substance showed mainly diffraction lines at 2.706, 1.661, 1.415 Å, 2.701, 1.658, 1.414 Å and 2.705 Å, respectively, all indicative of braunite ($3[Mn, Fe]_2O_3$ x $MnSiO_3$). Thus, this hydrothermal generation of the Mn-silicate braunite synthesized from Mn-oxides of typical modern deep-sea nodules gives evidence of the general possibility of the transformation of original nodule material by hydrothermal processes into the mineralogy observed in the fossil nodules, not regarding the unnatural high temperatures necessary to perform the experiment under laboratory conditions with limited time.

Based on our field observations, the petrography, mineralogy and geochemistry of the Costa Rican nodules, as well as on the laboratory experiment, we conclude the following genetic model for the mineralogical evolution of these nodules (Halbach et al., 1992):

Formation of early diagenetic Mn nodules (*todorokite?*) at the interface between sediment and near-bottom sea-water; possible Mn mobilization (probably Mn^{2+}) from partial solution of micronodules in the underlying sediment layer (as observed in associated radiolarites) under weakly reducing conditions.

Alteration of the primary mineral association due to thermo-metamorphic processes: pretectonic formation of braunite at increased temperature and lowered O_2 partial pressure.

Tectonic compressive deformation and *hydrothermal activity* with Ba input: formation of *hollandite* by partial replacement of braunite at increasing O_2 partial pressure and temperatures of 100 – 200 °C.

Hydrothermal activity: formation of *pyrolusite* at low temperature and under oxidizing conditions (and/or pyolusite formation by near-surface weathering solutions?).

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