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Ferromanganese nodules in the Gulf of Cadiz: Geochemical evidences from deep-seated fluids migration

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Mud volcanism and mud diapirism are widely extended in the Gulf of Cadiz (Eastern Central Atlantic). In 2001, during the *TASYO* oceanographic cruises, Fe-Mn nodule fields were discovered along the bases and flanks of mud volcanoes at the Guadalquivir Diapiric Ridge area. In order to determine genetic pathways in the nodules generation we have studied their physico-chemical properties and mineralogy using different techniques. Special attention was given to looking for geochemical signs of the presence of fluid migration in the nodules (GC-MS, chemical leaching sequences, $^{87}Sr/^{86}Sr$ determinations).

Nodules are essentially composed of a mixture of goethite and Mn-oxides derived

from the oxidation of previous siderite-rhodochrosite nodules. Nodule growth has been fuelled by early diagenesis from the pore water fluids at shallow depth within the mud breccia sediments. Hidrogenetic growth of nodules, related to the MOW action, is observed in their most external parts. Selective dissolution procedures of nodules have allowed separation of the major mineral phases and their associated elements. Ca and Mg carbonates are specially enriched in K, Li, B, Sr and Se in respect to the bulk sample. Mn-oxides present large enrichments of Na, K, Mg, Ba, Sr, B, Se and other trace metals. Relative to average continental crustal abundance, several elements are enriched in the nodules from the Gulf of Cadiz by different order factors: As (159), Mo (47), I (44), Mn (43), B (28), Fe (6), Co (3), P (2) and V (2). Mature hydrocarbons (n-alkanes) have been discovered in the nodular nucleus and layers, also with presence of aromatic hydrocarbons as phenanthrene, characteristic of petroleum. Isotopic values of δ^{13}C of these compounds range between -20 and -37 per mil (vs. PDB) supporting the idea of deep thermal maturation. ^{87}Sr/^{86}Sr determinations in Mn-oxides from six nodules range between 0.709677 and 0.710443. These values are larger than the actual medium oceanic water value (0.70917) indicating more radiogenic Sr sources.

Geochemical observations suggest that significant interaction has occurred between fluids and continental crust materials. Sr enrichments in Fe-Mn nodules with respect to seawater are in agreement with the hypothesis of leaching from clay minerals at moderate to high temperatures. Also high concentrations of Li, B, Sr and other elements support the hypothesis about clay dewatering. Topographic highs as Guadalquivir Diapiric Ridge may act as sites for crustal fluid discharge of fluids and the consequent accumulation of mineral deposits. Mud volcanoes and diapiric ridges present large heat flow and geochemical anomalies with respect to the surrounding area and related with faulting structures. These structures facilitate fluid flow between deep crustal materials and the ocean, being mud volcanoes and diapiric ridges the expression of crustal fluids discharge, and probably recharge sites for seawater. Detailed studies across the growth layers of the nodules may show us the different physico-chemical environmental conditions along the time of nodule accretion, reflecting pulses of fluid migration (tectonic events) or changes into the oceanic circulation.