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 $\delta^{13}$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 moder-
te to high temperatures. Also high concentrations of Li, B, Sr and other elements
support the hypothesis about clay dewatering. Topographic highs as Guadalquivir Di-
apiric 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 ma-
terials 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 environmen-
tal conditions along the time of nodule accretion, reflecting pulses of fluid migration
(tectonic events) or changes into the oceanic circulation.