

## Siderite-rhodochrosite nodules as precursors of ferromanganese-oxide nodules in carbonate-mud mounds related to fluid venting (Gulf of Cadiz)

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From 1999 a great variety of hydrocarbon seep-related geomorphic features have been discovered on the sea floor along the continental margin of the Gulf of Cadiz (eastern Central Atlantic) (León et al., 2007). During the Anastasya-01 cruise (TASYO project), extensive nodule fields were discovered and sampled for the first time at water depths ranging from 850 to 1000 m. The fields of Fe-Mn nodules occur at the Guadalquivir Diapiric Ridge area, where the influence of the Mediterranean Outflow Water (MOW) is strong and hydrocarbon-derived carbonate crusts and chimneys also occur. The underwater images show a variable density of nodules overlying the seafloor, affected by intensive erosive processes, at the base of carbonate-mud mounds related to fluid venting (González et al., 2006). Thirty six selected nodules among the various morphological types were used for the laboratory analysis of mineralogy (XRD, optical and electronic microscopy) and geochemistry (XRF, AAS, ICP-MS, EPMA, GC-MS).

Tabular to irregular nodules show an internal structure characterised by a layered disposition of Fe-Mn oxides surrounding a carbonated nucleus. Only in some samples is possible distinguish clearly their cores and layers. Fe-Mn layers and carbonated cores display the same microtextural features, composed by zoned rhombohedral crystals (authigenic Fe-Mn oxides in layers, and siderite to rhodochrosite in the nuclei) surrounded by detrital grains (silicates) and framboidal associations (fresh pyrite or totally pseudomorphised by goethite). The center of the rhombohedral crystals are enriched in manganese and their exterior edges are iron enriched for both, Fe-Mn oxides and Fe-Mn carbonates. Mature hydrocarbons have been discovered in their nucleus and layers. Nodules reveal variations in chemical composition from the center, where Mn are concentrated, to the outer edges, where Fe is more abundant, suggesting changes in physico-chemical conditions in their growth process.

Bacteria-mediated oxidation of hydrocarbons through Mn<sup>4+</sup> and Fe<sup>3+</sup> reduction, might be related to the precipitation of Fe-Mn carbonates, forming siderite-rhodochrosite concretions bellow the redox boundary within the mud-breccia extruded sediment, that later were transformed into ferromanganese-oxide nodules by exhumation (MOW action) and exposition to the sea bottom oxidising waters. The determination of stable isotopes in carbonates, hydrocarbons and biomarkers contained into the nodules will be the next step in our investigation.

### References

- González, F. J., Somoza, L., Lunar, R., Martínez-Frías, J., Martín Rubí, J. A., and Díaz del Río, V. (2006). *Boletín Geológico y Minero* 117, 491- 497.
- León, R., Somoza, L., Medialdea, T., González, F.J., Díaz-del-Río, V., Fernández-Puga, M.C., Maestro, A., and Mata, M.P. (2007), *Geo-Marine Letters*, DOI 10.1007/s00367-007-0074-2