Discovery of ferromanganese hydrocarbon-related nodules associated with the Meknes mud volcano (Western Moroccan margin)

F. J. González[1], L. Somoza[1], T. Medialdea[1], R. León[1], T. Torres[2], J. E. Ortiz[2], J. A. Martín Rubí[1]

1 Geological Survey of Spain (IGME). C/ Ríos Rosas 23, 28003 Madrid, Spain. E-mail: fj.gonzalez@igme.es

2 Laboratorio de Estratigrafía Biomolecular (ETSIM/UPM). C/ Ríos Rosas 21, 28003 Madrid, Spain

REGIONAL SETTING, STUDY AREA AND SAMPLE SUITE

The Gulf of Cadiz is located at the westward front of the Betic-Rifian Arc, in the easternmost sector of the Azores-Gibraltar segment of the Africa/Eurasia collisional plate boundary (Fig. 1). It has a complex geological history and has undergone several episodes of rifting, compression, and strike-slip motion since the Triassic. The African-Eurasian convergence has promoted fault reactivation and widespread mud-salt diapirism and hydrocarbon-rich fluid venting structures (mud volcanoes, diapiric ridges, carbonate mud mounds, pockmarks and hydrocarbon-derived authigenic carbonates (HDACs)) (Medialdea et al., 2009).

Fig. 1. Geological setting and bathymetry of the Gulf of Cadiz with the location of sampling site in Meknes mud volcano (A) and ferromanganese nodule fields in the Iberian margin (B). Partially modified from León et al. (2012).

Fig. 2. Multi-beam bathymetric image (Simrad EM12-120S) and 3-D Fledermouse visualization of the Meknes mud volcano. Below, ultra-high resolution seismic profile through the Meknes mud volcano with the position of sampling stations and, below side-scan sonar image (MAK-1M at 100 kHz, TTR-15). Meknes MV has a flat summit, an elongated crater in the N-S trend and high steep slopes in the flanks. The profiles show low penetration, probably due to the presence of authigenic precipitates, and transparent to chaotic facies in the mud volcano and carbonate mounds. There are also evidences of bottom current activity and erosion as the presence of contourite deposits and outcroppings of carbonate mounds and HDACs.

Fig. 3. A suite of ferromanganese nodules, HDACs and cold water corals were sampled by dredging in the discovered field after detailed bathymetric surveys. Mud-breccia was sampled by gravity coring at top of Meknes MV. Selected nodules were analysed by different methods in order to define their physical, mineralogical and geochemical characteristics.

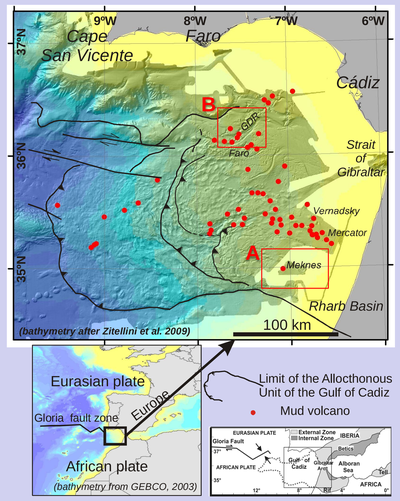

Figure 1

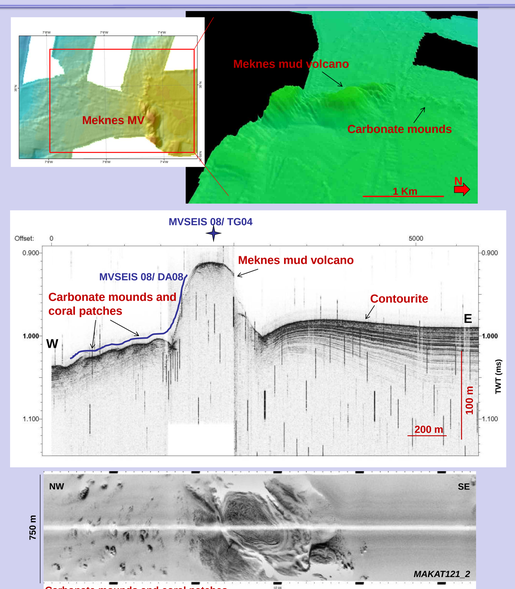

Figure 2

ABSTRACT:

A suite of ferromanganese nodules were sampled during the MVSEIS-2008 cruise aboard of the R/V Hespérides in the flanks of Meknes mud volcano (Moroccan margin, NE Central Atlantic). The nodules were collected at water depths between 750-850 m within a seabed area characterized by high acoustic backscatter values. Debris of cold water corals and hydrocarbon-derived authigenic carbonate crusts were sampled at same time. The nodules show tabular morphology, up to 20 cm in maximum diameter and 2 kg of weight, brown-reddish external color and they are internally composed by a concentric to complex arrangement of laminae. The results of X-ray diffraction analysis show that these ferromanganese nodules are essentially composed of goethite and lepidocrocite, being Mn-oxides, silicates (quartz and clay minerals) and carbonates (calcite, dolomite and siderite) accessory to occasional minerals. All the samples display micritic to micro-sparitic mosaic under the petrographic microscope which forms massive, laminated or dendritic-mottled textures. The nodules show a high abundance of Fe, minor Mn and low contents of trace metals and REEs. Mature hydrocarbons, as n-alkanes derived from marine bacterial activity, and phenanthrene have been detected in all the ferromanganese nodules analyzed.

These nodules display analogous characteristics (textural, mineralogical and geochemical) to the nodules studied by González et al (2009) in the carbonate mud-mounds in the Gulf of Cadiz, offshore Iberian margin. In this way, the same preliminary genetic model proposed for these nodules might be applicable to those find in the Meknes mud volcano. Therefore, the anaerobic oxidation of hydrocarbon-rich fluids within the mud-breccia sediments in the flanks of Meknes mud volcano would induce the formation of early diagenetic Fe-(Mn) carbonate nodules. Thus, the nodules were later exhumed by the erosive action of sea bottom currents generating the replacement of ferromanganese carbonates by Fe-Mn oxy-hydroxides. Thus, the hydrocarbon-rich fluid venting from deep seated reservoirs and erosive action of bottom currents must have been essential actors, as mineralization controls, for ferromanganese nodules generation and evolution.

These findings imply that this type of nodules must be considered as new product as derived from the anaerobic/aerobic oxidation of hydrocarbons in areas of active seepages.

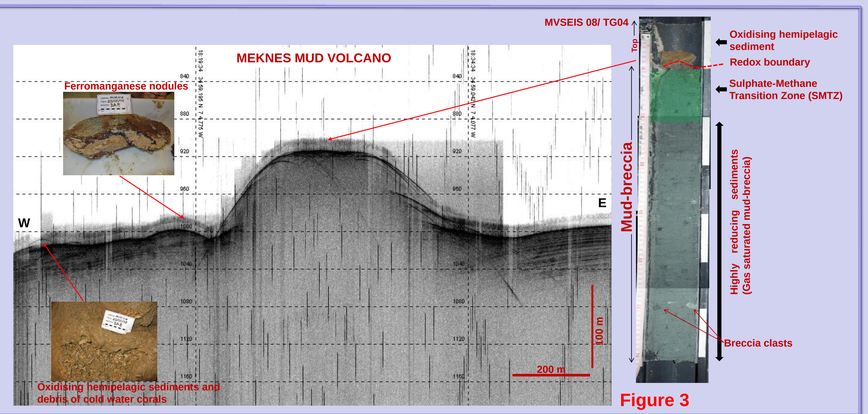

Figure 3

INTERNAL FEATURES AND MINERALOGY

The nodules have tabular-to-irregular morphologies and sizes ranging from 1 to 20 cm. Surface and internal colour varies between orange and black and reflects the fundamental mineralogical composition of the samples: iron-manganese oxy-hydroxides.

Fig. 4. Section and detail of one ferromanganese nodule showing the internal structure formed by a complex arrangement of laminae.

Fig. 5. Mineralogy and internal micro-textures of the nodules, photomicrographs (optical microscope and back-scattered electrons). (a) XRD characteristic pattern. (b) Oxide layer showing goethite-birnessite rhombic crystals (goe + Mn ox) surrounded by phyllosilicates and Mn-oxides (sil + Mn ox). (c) Pyrite aggregates, formed by framboid, partially speudomorphised by goethite, paragenetic with Fe-Mn rhombical crystals (goethite after siderite). (dtr), detrital minerals. (d) Pseudomorphs of Fe-Mn oxides formed by oxidation of Fe-Mn carbonate crystals.

Figure 4

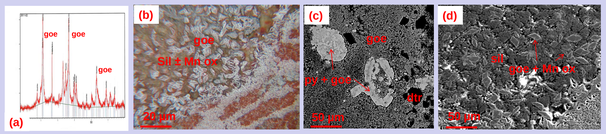

Figure 5

GENETIC MODEL AND FINAL CONSIDERATIONS

Partially and totally oxidised siderite nodules associated with hydrocarbon-rich fluid venting systems and contourites have recently been discovered on the Iberian continental slope of the Gulf of Cadiz (González et al., 2012). They are very similar to the ones preliminary studied in this paper and we can infer an analogous genetic-evolutionary model which require for further studies in Meknes MV (Fig. 9).

Fig. 8. High $^{87}Sr/^{86}Sr$ isotopic values (up to 0.70993±0.00025) observed in the inner parts of nodules from the Iberian margin are related to the influence of radiogenic fluids fuelled by deep-seated fluid venting. The outermost parts show imprints of the Mediterranean Outflow Water (MOW) with low $^{87}Sr/^{86}Sr$ isotopic values (down to 0.70693±0.00081) (Data from González et al., 2012).

Fig. 9. Genetic model. Relationships between sulphate, methane, Fe^{2+} and Mn^{2+} concentration gradients in the pore waters. We also present the location of the redox boundaries and the sulphate–methane transition zone. The nodule may grow below the redox boundary within the sediments, forming an original concretion composed essentially of Fe–Mn carbonates. The erosive action of the MOW during the glacial periods produces the exhumation of Fe–Mn carbonate nodules that are replaced by Fe–Mn oxides through the action of the oxidising sea-bottom water (Data from González et al., 2012).

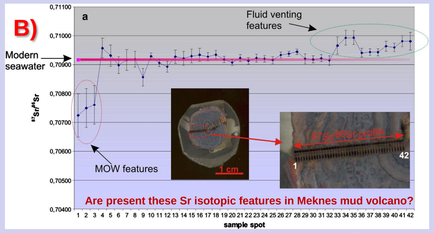

Figure 8

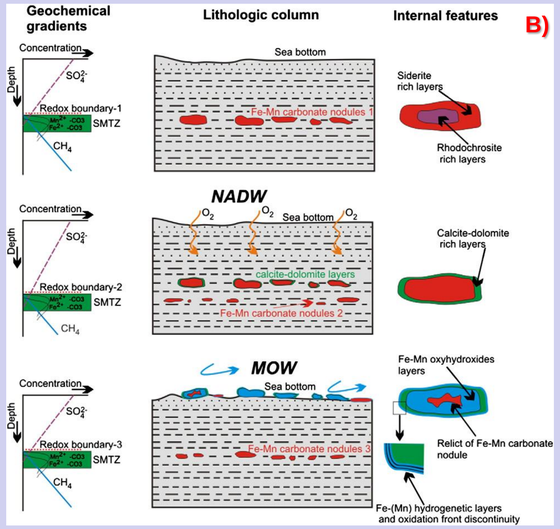

Figure 9

GEOCHEMISTRY

We have obtained geochemical discriminating signatures to explore genetic models.

Fig. 6. Selected elements in Fe-Mn nodules compared to the mean Earth's Crust contents (Evans, 1980). Elements above ratio line equal to 1 are enriched in the nodules.

Fig. 7. Nodule section showing sampling areas for GC-MS analysis. Below, chromatogram of hydrocarbon extract showing occurrence of homologous series of normal alkanes (n–Cxx). Presence of unresolved complex mixture (UCM) and high Pr and Ph contents suggest influence of biodegradation.

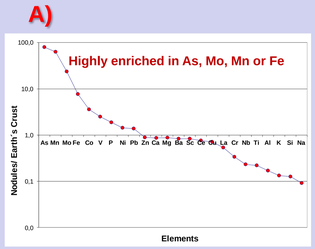

Figure 6

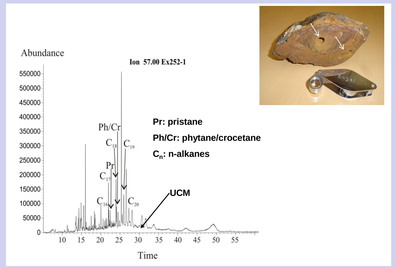

Figure 7

ACKNOWLEDGEMENTS

This investigation is supported by CONTOURIBER project (CTM2008-06399-C04/MAR) of the Spanish Interministerial Commission of Science and Technology (CICYT). The work has also been funded by the European Science Foundation (ESF) under the EUROCORES Programme EUROMARGINS, through projects MVSEIS (O1-LEC-EMA24F, 594 REN2002-11669-E-MAR) and MOUNDFORCE (O1-LEC-EMA06F, 595 REN2002-11668-E-MAR). The authors thank all the scientific and technical personnel who participated in the oceanographic cruises *MVSEIS 08* and *TTR-15*, of the R/V *"Hespérides"* and R/V *"Professor Logachev"*, for the data acquisition and their expertise in collecting the samples, essential for the elaboration of this work.

REFERENCES

- González, F. J., Somoza, L., Lunar, R., Martínez-Frías, J., Martín Rubí, J. A., Torres, T., Ortiz, J. E., Díaz del Río, V., Pinheiro, L., Magalhaes, V. H., 2009. Hydrocarbon-derived ferromanganese nodules in carbonate-mud mounds from the Gulf of Cadiz: Mud-breccia sediments and clasts as nucleation sites. Marine Geology 261, 64-81.
- González, F. J., Somoza, L., León, R., Medialdea, T., Torres, T., Ortiz, J. E., Lunar, R., Martínez-Frías, J., Merinero, R. 2012. Ferromanganese nodules and micro-hardgrounds associated with the Cadiz Contourite Channel (NE Atlantic): palaeoenvironmental records of fluid venting and bottom currents. Chemical Geology (doi:10.1016/j.chemgeo.2012.03.030)
- León, R., Somoza, L., Medialdea, T., Vázquez, J. T., González, F. J., López-González, N., Casas, D., Mata, M. P., Fernández-Puga, M. C., Giménez-Moreno, C. J., Díaz-del-Río, V. 2012. New discoveries of mud volcanoes on the Moroccan Atlantic continental margin (Gulf of Cádiz): morpho-structural characterization. Geo-Marine Letters (doi: 10.1007/s00367-012-0275-1)
- Medialdea, T., Somoza, L., Pinheiro, L.M., Fernández-Puga, M.C., Vazquez, J.T., León, R., Ivanov, M., Magalhães, V., Díaz-del-Río, V., Vegas, R. 2009. Tectonics and mud volcano development in the Gulf of Cádiz. Marine Geology 261, 48-63.
- Zitellini, N., Gràcia, E., Matias, L., Terrinha, P., Abreu, M. A., DeAlteriis, G.,Henriet, J. P., Dañobeitia, J. J., Masson, D. G., Mulder, T., Ramella, R., Somoza, L., Diez, S. 2009. The quest for the Africa–Eurasia plate boundary west of the Strait of Gibraltar. Earth and Planetary Science Letters 280, 13–50