UNUSUAL FE-RICH FRAMBOIDS FROM DEVONIAN CARBONATE MOUNDS (SAHARA DESERT, MOROCCO) INVESTIGATED BY HR-SEM AND TOF-SIMS: FOSSIL ANALOGUES OF MOA-SRB CONSORTIA?

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Introduction: Finding a solution to the enigma of the origin of the Devonian Ca-carbonate mounds cropping out in the Western edge of the Sahara Desert (Anti-Atlas, Morocco), requires a combination of large (field) scale and micro-scale investigations. The biological composition of these conical mounds is still incomplete as is knowledge of their facies distribution and field (and subsurficial) geometries. There are, however, several lines of evidence that indicate obvious relationships with hydrothermal venting and hydrocarbon fluid seepage during the development of the mounds [1-3]. The recent finding of carbonate deposits on Mars [4], associated with the detection of methane in the Martian atmosphere [5], make these carbonate mounds astrobiologically significant. The Moroccan carbonate bodies can be considered as martian analogues and their study will help develop strategies for detecting traces of past (fossil) life, especially in view of the future selection of Mars landing sites. Here we present the results of the microscopic investigations of iron-rich framboidal structures (~6µm diameter) recovered from ^{13}C depleted Ca-carbonate cements filling veins crosscutting the mounds at Hamar Laghdad Ridge (fig. 1).

Fig. 1: Outcrop of vent-generated mounds in the eastern Anti-Atlas, Morocco, and detail of veins (acting as fluid channels) generated by a diffusive hydrocarbon seepage active ~400milion years ago during the development of the mounds.

Framboids are minute raspberry-shaped spherical aggregates (2-50 μm in diameter) composed of assemblages of tiny, 0.5-2 μm-sized crystallites often in geometrical arrays. The presence of pyrite framboids is a common feature in modern (and fossil) hydrocarbon seep environments and deposits [6], where a high density of chemosynthetic microbes is reported. Although there is much discussion on the direct origin of framboids (bacterial vs. organic vs. inorganic), it is accepted that they have a very close association with decaying flesh or organic matter and form during early diagenesis [7-8]. Moreover, it has recently been suggested that framboidal pyrites can be produced by the activity of methane oxidizing archaea (MOA) and sulphate reducing bacteria (SRB) colonies [9].

Results: Investigation by optical and high resolution scanning electron microscopes (HR-SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffractions (XRD) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), show that framboids in the carbonate facture-infillings of the Maroccan cold seeps consist of spheroidal clusters of discrete, Fe-rich octahedral and equidimensional microcrystals with a distinct internal architecture (fig.s 2-5). Fe-rich framboids are characterized by an inner core and an outer layer

Fig. 2: Optical microscope image showing framboids. They are isolated or but some appear to be joined by a meniscus (arrow). Framboids range in size from 1-2 to 11 μm in diameter.

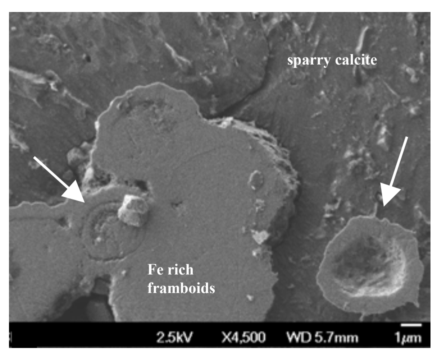

Fig. 3: HR-SEM image showing (HC etched surphace) zoned framboidal structures (arrows) that exhibit bacteriomorph structures (see [9]).

generating a zoned spherical aggregates. EDX and ToF-SIMS analysis of the framboids show that they are mainly composed of Fe-O with traces of S, P, NH and non-identified organics (fig. 5). The Ca-carbonate (calcite) matrix lacks significant Fe, but includes Na-Si minerals. P, S and N was not detected by EDX.

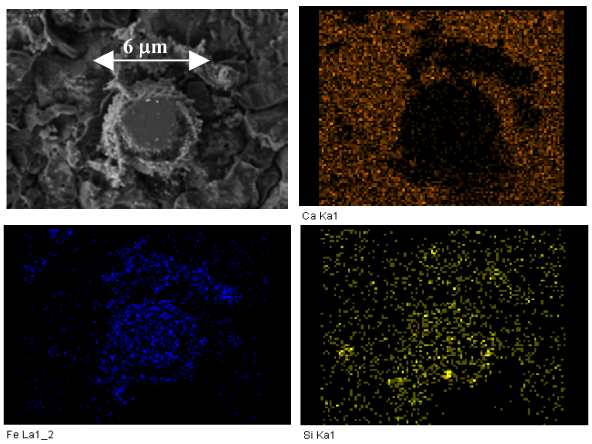

Fig. 4: *EDX analyses show a correspondence between framboids and Fe and a small amount of Si. The Ca-carbonate matrix lacks Fe.*

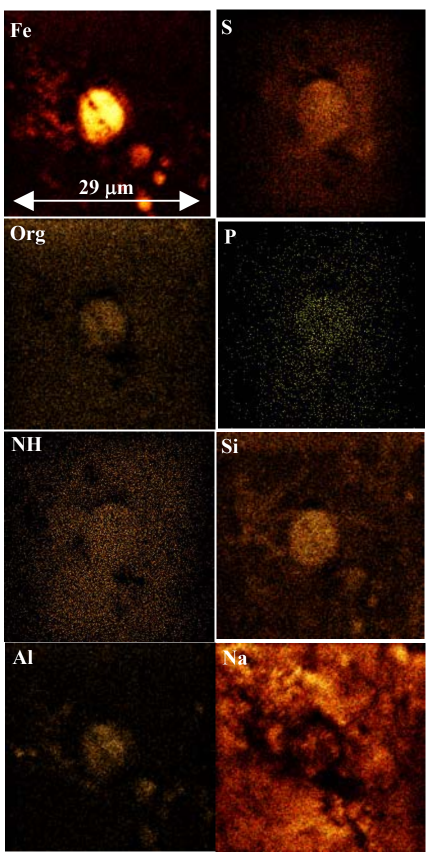

Fig. 4: *ToF-SIMS analysis of framboids confirm their Fe concentrations as well as traces of Al, S, P, N and non-identified organics.*

Discussion: The presence of biologically-important elements, S and P, associated with organic carbon within the zoned spherical structures – Fe-rich framboids – in the Hamar Laghdad Ridge seep-related mounds, suggests that there is a relationship between the framboids and the presence of biological materials. The bacteriomorph forms of the framboids are suggestive but not conclusive evidence that they represent the the fossilised remains of microorganisms. The framboids may simply have incorporated degraded biological matter during their growth and the meniscus-like links between individual framboids may be fortuitous associations.

The trace of S in the framboids could be explained by a number of processes. It could be related to the enrichment of S in degraded organic matter during diagenesis through the activities of microorganisms such as sulphur reducing bacteria (SRBs). Alternatively the framboids may originally have consisted of pyrite but later hydrothermal flushing could have removed most of the anion (S), replacing it with SiO_2. Indeed, the ToF-SIMS results show that the framboids have been silicified, thus adding support to the latter hypothesis. Further evidence of post-diagenetic fluid circulation is the distribution of Si-Al-Na deposits occuring as meniscus-like structures around framboids as well as in the interstices between the calcite grains.

Whether or not MOA and SRBs have been fossilized in the Devonain methane seeps, the Fe-rich framboids exhibit a clear relationship to the presence of biological matter in an anaerobic environment in which such microorganisms could be expected. The characteristics of the Fe-rich framboids in ^{13}C depleted Ca-carbonate filling veins acting as fluid conduits at Hamar Lahgdad Ridge seep system, where MOA and SRB bacteria were probably abundant, therefore represent useful geological and astrobiological indicators of Ca-carbonate biologically controlled fabrics produced during methane seep.

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Acknowledgements: This study was supported by the European Commission-Research Infrastructure Action under the FP6 "European Integrated Activity of Excellence and Networking for Nano and Micro-Electronics Analysis" - Project number 026134(RI3) ANNA (to FW and BC), by MIUR-PRIN grant 2004-2006 (to RB), and le Studium®, Institute for advanced studies, region Centre, France.