



Pyrite nucleation induced by sulphate-reducing bacteria in carbonate chimneys from the Vernadsky Ridge, Moroccan Margin (Gulf of Cadiz)

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More than 40 hydrocarbon-derived carbonate chimneys, crusts and their fragments were sampled during the TTR-15 cruise in the Atlantic Moroccan Margin of the Gulf of Cadiz. A large variety of them was recovered from the Vernadsky Ridge, where an extensive field of carbonate chimneys and crusts was discovered in a high backscattering area at 500 m of depth. Observations from an underwater camera revealed a high density of pipe-like chimneys laying over the sea floor, and some protruding from muddy sediment. The collected chimneys show a wide range of sizes and morphological types (spiral, cylindrical, branched, conical, massive, etc). The surface texture generally is irregular and very porous in the chimneys recovered, frequently with ramified fluid channel-ways. Based on the external colour these chimneys were divided into two groups: **Group I** of chimneys with a dark brown colour. These samples, with oxidised surface, were submitted to an oxygen rich environment. They are speckled with iron oxides. The **Group II** of chimneys presents a greyish-green colour. They are samples submitted to an oxygen depleted environment, and these are speckled with sulphides micro-crystals. The chimneys from both groups are mainly composed of authigenic carbonates classified as intrapel-biomicrite (Mg-calcite and Fe-dolomite to ankerite) with a minor quantity of opaque minerals (goethite, Mn-oxides, pyrite and chalcopyrite) apatite, forming micro-crystalline aggregates, and detritical miner-

als (quartz, feldspars, clays, apatite and zircon). Bioclasts of planktonic foraminifera, ostracods and pellets were observed. SEM observations reveal microbes like structures, which indicate microbial activity in the carbonates generation (methanotrophs activity). Pyrite appears in four different forms in the chimneys from the Group I: 1- Pyrite filling intra-clast porosity of foraminifera and ostracoda bioclasts (filling of chambers). 2- Pyrite infilling and forming pseudomorphs in the bioclast skeletons. 3- Pyrite disseminated in the carbonate matrix. 4- Pyrite filling inter-clast porosity and secondary porosity (cracks burrows). Framboidal aggregates ($< 100\mu\text{m}$), spherical, are the most typical pyrite morphology in the samples from the Group I of chimneys. They are formed by a variable number of subidiomorph to idiomorph micro-crystals ($< 5\mu\text{m}$) of pyrite. Organic matter around and within pyrite micro-crystals was observed. Framboidal aggregates can be isolated or forming groups. Framboids of pyrite described in this work correspond to the first states of the textural, mineralogical and geochemical evolution. Fe-Mn oxy-hydroxides pseudomorphs after pyrite are present, especially in the external part of the chimneys affected by oxidation. In the chimneys from the Group II, pyrite is filling and cementing the space exist between carbonates crystals. In these samples we can not observe framboidal aggregates. Pyrite forms heterogeneous massive cement between subidiomorph to idiomorph Fe-dolomite and it could represent an advantage stadium of textural evolution between framboids and euhedral crystals. Pyrite replacements (Fe-Mn oxyhydroxides) were not observed. Pyrites from the first and second group of chimneys have similar geochemistry. They are characterised by the high contents in trace metals (Mo, Pb, Bi, Co) and negative $\delta^{34}\text{S}$ isotopic composition (-34 permil) linked to sulphate-reducing bacteria activity. Bacterial cell walls could act as a nucleation sites for pyrites, and probably the framboidal aggregates represent bacterial colonies. These samples present a micro-crystalline aggregate of apatite surrounding framboidal aggregates and massive pyrites. It could be related with products expelled by bacterial activity. Sulphides precipitation is related with anoxic sediments (sulphate-methane interface) or anoxic micro-niches in oxidised sediments where bacterial sulphate reduction is very active and an amount of available metals, especially iron, is sufficient. Incorporation of trace metals into pyrite may proceeds both by co-precipitation and adsorption, and it depends on concentration of metals in the environment of deposit.