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ABSTRACT BOOK

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PYRITE, GYPSUM, POTASSIUM-IRON SULFATES, AND CARBONATE DISSOLUTION: ALL IN ONCE IN FORAMINIFERA STEINKERNS

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Pyritization is a well-known fossilization process to preserve 3D non-mineralized tissues of different organisms. Further, pyrite can precipitate later during diagenesis generating molds and steinkerns of buried organisms reproducing, in some cases, very delicate anatomical features. In this contribution, we describe pyrite casts of Pliocene planktonic and benthonic foraminifera from Barcelona (NE Spain). The samples were collected in several cores made for the construction of the high-speed (AVE) railroad through the Barcelona city. The Pliocene deposits, up to 100 m in thickness, consist of three units: a) a basal unit of sandy gravels and sands with some marine bivalves interpreted as high-energy lag deposits linked to the initial stages of the Early Pliocene transgression; b) a middle unit of grey marls rich in bivalves and foraminifera deposited in a sheltered, very shallow setting; and, c) an upper unit consisting of fine to coarse sands formed in shallow coastal environments (beach and foreshore deposits).

Pyritized foraminifera occur in the middle unit. They are preserved as: a) foraminifera filled up with pyrite and preserving their original calcitic tests; b) pyritized steinkerns with the original tests partially dissolved; and, c) pyritized steinkerns with the original tests completely dissolved. Elemental maps of the steinkerns indicate that the outer surface of the pyrite is slightly oxidized and transformed into iron hydroxides. Pyrite occurs as framboids, ranging from 8 μm to 16 μm (eventually, reaching up to 35 μm), as octahedral and dodecahedral (pyritohedral) crystals, and as plate-like crystals. The latter morphology is observed in the contact with the inner surface of the foraminiferal tests, while the other two growth forms fill up the foraminiferal chambers.

Together with the pyrite, there are also gypsum, which occurs as tabular crystals, and rosette-like crystal aggregates of K-Fe sulfate (jarosite?). The gypsum is found as scattered tabular crystals in the chamber cavities and replacing the calcite of the chamber walls roughly preserving the original microstructure. The K-Fe sulfate rosettes occur dispersed, but always associated with pyrite framboids, filling the foraminifera chambers.

Pyrite can precipitate in the interior of living benthic foraminifera inhabiting polluted, very restricted bays. In our study case, the pyrite fills up both planktonic and benthonic foraminifera. This suggests that pyritization took place inside the sediment after the death of the microorganisms. Although pyrite precipitation can locally occur in oxygenated settings due to the presence of heavy metal contaminants, pyritization is mostly related with the activity of microbial sulfate-reduction and iron-reduction in the first few centimeters of the sedimentary column, close to the redox interface, with Fe-rich anaerobic pore-waters. Therefore, we interpret that pyritization in the study foraminiferal casts did occur early after shallow burial of the foraminiferal tests in depleted-oxygen paleoenvironments. The morphology of the pyrite crystals is related with the precipitation conditions. The smooth tabular pyrite developed in the contact with the inner foraminiferal tests most likely replicates the inner foraminiferal membrane. In this case, pyritization could be triggered by the initial decay of the organic carbon of the tissue. The rest of the chambers were filled up with framboids and euhedral crystals due to bacterial activity.

Pyritization produced slightly acid conditions inside the foraminiferal tests, thus promoting the beginning of carbonate dissolution. In addition, oxidation of the pyrite delivers sulfate ions. The combination of these two processes lead to the precipitation of gypsum. This accounts for the transformation of the calcite of the chamber walls into gypsum roughly preserving the original

microstructure and the beginning of gypsum precipitation close to the inner parts of the foraminiferal tests. Finally, the formation of the K-Fe sulfate rosettes is very unusual and remains uncertain. It is also related with the oxidation of the pyrite. Nonetheless, the formation of this mineral occurs in very acid conditions (pH below 6, sometimes even around 2). This acidic microenvironment is incompatible with the preservation of the foraminiferal calcitic tests. Therefore, we need further analyses to account for the presence of these crystal aggregates in the observed mineral association forming the foraminiferal steinkerns.

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