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Organic Matter Preservation and in Situ Humification in Phosphatic Pellets from Tunisian Phosphatised Sediments

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SUMMARY

The phosphatic "pellets", from Ypresian ore of Ras-Draâ, Tunisia, are rounded grains, with some hundreds of micrometers in mean diameter. These pellets are embedded in a sedimentary, more or less carbonated or shaly, matrix. The pellets studied in this ore contain between 28 and 38 % of P₂O₅ and between 0.30 and 1.62 % of TOC. Surprisingly - with regards to the age of the pellets - this organic matter (OM) is very rich in humics (>75.60 % of humic C). Curiously also, the OM present in the matrix of the pellets is by far not as rich in humic compounds (>21.42 % of humic C, % of TOC). The composition of the OM of the matrix is quite usual for a 50 My old, epicontinental, never buried (over a maximum of 200 m depth), sedimentary layer. It is a low-rank kerogen. Pellets appear therefore as chemically individual bodies whose diagenetic story has been quite different, and independent, of that of their embedding sediment. These bodies have been demonstrated to have derived from fish feces (Ben Hassen, 2007).

The phosphatic "pellets", phosphate-bearing grains in the Ypresian ore of Ras-Draâ, Tunisia, dated ca. 50 My old, are rounded grains, with some hundreds of micrometers in mean diameter. These pellets are embedded in a sedimentary, more or less carbonated or shaly, matrix. The pellets studied in this ore contain between 28 and 38 % of P_2O_5 and between 0.30 and 1.62 % of TOC.

Surprisingly – with regards to the age of the pellets – this organic matter (OM) is very rich in humics (up to 75.60 % of humic C). Curiously also, the OM present in the matrix of the pellets is by far not as rich in humic compounds (up to 21.42 % of humic C, % of TOC). The composition of the OM of the matrix is quite usual for a 50 My old, epicontinental, never buried (over a maximum of 200 m depth), sedimentary layer. It is a low-rank kerogen. Pellets appear therefore as chemically individual bodies whose diagenetic story has been quite different, and independent, of that of their embedding sediment. These bodies have been demonstrated to have derived from fish feces (Ben Hassen, 2007).

The humification of their OM and the remarkable preservation of the resulting humics, during ca. 50 My, address the following questions and lead to the following answers:

- a. The origin of the OM is marine planktonic, as deduced from elemental analysis, Rock-Eval pyrolysis and photonic microscopy. This OM has been ingested by planktivorous fishes.
- b. The early diagenesis of the OM excreted by fishes was carried in sulfate-reducing conditions, as shown by the following data : **(i)** Humic acids contain large amounts of organic sulfur, up to 12-14%, **(ii)** if the gas chromatographic spectra of n-alkanes and iso-alkanes in the pellets witness commonly to mixed phytoplanktonic and microbial sources for the OM, they can also display a purely microbial composition for the OM, suggesting that the original phytoplanktonic constituents were decomposed by bacteria. Conversely, the alkanes present in the matrix-sediments surrounding the pellets are typically phytoplanktonic in origin.
- c. The preservation of these humics, under such a state during 50 My, is due to some early physical properties of the pellets **(i)** as early as their egestion by the fish, the feces are embedded in a phosphatized external membrane which protects them from tearing during their transfer through the water column and during their reworking by bottom currents **(ii)** the growth of apatite crystals inside the pellets puts a pressure on the organic particles and isolates them from any circulation of fluids at their contact.
- d. Finally, the mainly reactional opportunity offered to the phytoplanktonic OM in the feces of carnivorous fishes was redox microbial sulfate reduction reactions. The abundance of S in the OM and the easy Maillard reactions between abundant carbohydrates and amino compounds derived from phytoplankton were both favourable to the stabilization of these humics. In the absence of heat input and of fluid circulation at their contact, the humic particles were protected from any further diagenesis and evolution.

REFERENCES

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