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Palaeoredox indicators from the organic-rich Messinian early post-evaporitic deposits of the Apennines (Central Italy)

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Bottom redox conditions in marine and lacustrine ancient basins are often inferred by the occurrence of peculiar sedimentological structures and microfaunal assemblages. The co-occurrence, in such environments, of authigenic uranium, framboidal pyrite, barite and Fe-Mn nodules and encrustations, provides a good constraint for palaeo reconstructions. Authigenic uranium is a common constituent of hydrocarbon source rocks: it forms at the sediment-water interface under oxygen-deficient conditions and accumulates together with organic matter (OM). Its precipitation is triggered by the reduction of the soluble U^{6+}ion in seawater to insoluble U^{4+}. With respect to black shales, uranium content has even been used to estimate the TOC. Also authigenic pyrite forms under anoxic conditions and replaces organic matter: 1) the increase in pyrite content and in organic matter are directly correlated; 2) the size distribution of framboidal pyrite (consistent with sulphate-reducing bacterial activity) is considered a measure of redox conditions within the sediment. Barite is an authigenic mineral related to Corg content, since its organic precipitation is triggered by sulphate-reduction processes occurring in decaying OM-bearing microenvironments. Finally, also Fe-Mn oxyhydroxide are typical indicators of redox conditions.

About 6 My ago the Mediterranean Sea underwent a giant event of concentration referred to as Messinian Salinity Crisis, which can be roughly subdivided into an evaporitic and a post evaporitic phase. The post evaporitic phase (p-ev; 5.61-5.33 Ma) developed in a context of humid conditions and can be further distinguished into two steps: p-ev1 (early post evaporitic phase) and p-ev2 (late post evaporitic phase). Previous works focused on pev2, which is interpreted to represent the establishment of brackish water conditions (Lago-Mare biofacies). In other respects, the palaeoenvironment of p-ev1 deposits, mostly represented by resedimented evaporitic deposits or barren laminated sediments, hasn't been thoroughly clarified yet.

The aim of the present study, dealing with messinian p-ev1 deposits from Marche and Maiella successions, is to provide more details in the definition of the environment developed during the early post-evaporitic phase. Since the lamination and the absence of benthic fauna suggest the occurrence of anoxic conditions, the following indirect proxies for the detection of organic matter have been investigated: 1) sedimentary fabric and microfacies; 2) framboidal pyrite size distribution; 3) natural radioactivity (authigenic uranium values, Th/U ratios). Natural radioactivity has been achieved through gamma spectrometry, with field and laboratory specific techniques.

In the Maccarone section (Marche region), p-ev1 deposits are constituted by: barren greyish shales; laminated black shales interbedded with calcitic and ankeritic horizons; thin intercalations of sandstones. Organic-matter and framboidal pyrite commonly occur. Size analysis of framboids populations yielded a mean diameter of $4 \div 8$ μm, typical of disaerobic facies. Microfacies analysis yielded also the presence of crystals aggregates of barite, up to 50 μm in size, and of isolated detrital (silicilastic) crystals. Without considering γ-ray values of the volcaniclastic layer (52-65 Cps) occurring within the p-ev1 interval, black shales horizons revealed the maximum natural radioactivity (NRD of about 50 Cps) recorded inthe studied section. Lower γ-activity characterizes the calcitic layers (i.e. "Colombacci") and the ankerites. Field NRD spectra acquired on different lithologies, showed variable contributions of ^{238}U, ^{232}Th and ^{40}K. Both the blue-greyish shales and the black shales are characterized by total NRD related to the three main radioelements: ^{40}K is associated to abundant ^{238}U content (Thppm/Uppm $<< 1$) and variable amounts of ^{232}Th have also been detected. The black laminated shales show higher ^{238}U values, due to the higher contribution of the authigenic uranium. The ankerite NRD-spectra point to a prevalent contribution of ^{238}U (Thppm/Uppm $<< 1$). Conversely, the sandstone horizons have a higher Th-content, marking an increase in the input of extra-basinal grains (Thppm/Uppm $>>1$). The ^{238}U content is primarily referable to processes of

organic matter enrichment (authigenic uranium) and secondarily to the input of detrital grains. In contrast, ^{40}K and ^{232}Th are entirely ascribed to the clastic fraction.

P-ev1 deposits from Maiella section consist of thinly-laminated grey-brownish pelites, enclosing carbonatic lenses and interrupted horizons. The pelitic fraction contains Fe-Mn-Ni encrustated micronodules. The carbonate portion is made up of locally brecciated calcitic limestones, associated with calcitic concretions and discontinuous laminae. Traces of organic matter and bitumen have been observed in thin section. Framboidal pyrite occurs both as single element and as aggregate, reaching dimensions up to about 10 μm. Barite and celestite occur as well. NRD measurements yielded high values of radioactivity both in carbonates (20-63 Cps) and in terrigenous sediments (21-70 Cps). Limestones NRD-spectra showed a ^{238}U-dominant (5 ppm in content) radioactivity. ^{238}U is totally referable to an authigenic origin, since the γ-activity of limestones is devoid of contributions from ^{40}K and ^{232}Th (proxies for the detritic fraction).

In the latest Messinian frame, authigenic uranium, barite, ankerite, Fe-Mn oxyhydroxide and framboidal pyrite indicate strongly palaeoredox conditions (from disaerobic to fully anoxic). In particular, with respect to NRD data, this peculiar environment is confirmed by the Th/U ratio, mostly $<<1$. Th/U ratio provides in fact a measure of the oxygen conditions in the depositional environment: Th/U$<<1$ indicates anoxic conditions; Th/U$>>1$ indicates oxic conditions; the ranges $1<$Th/U>1 point to dysoxic conditions.