



Record of methane paleofluxes in the Mediterranean Sea: evidences from the Messinian deposits of the Maiella Mts (Central Apennines, Italy)

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This paper deals with the upper Messinian deposits of the Adriatic foreland basin, connected to the major phases of the Messinian Salinity Crisis (MSC). The deposits of the evaporitic phase are characterized by a cyclical alternation of primary selenitic gypsum beds and sapropelitic layers, truncated on top by the Messinian unconformity. Early post-evaporitic deposits (p-ev₁) consist of barren shales with lenses of brecciated carbonates, in turn overlain by marls with Paratethyan ostracods (late post-evaporitic deposits, p-ev₂). The study section predates the Mediterranean Early Pliocene flooding, responsible for the deposition of bathyal clays.

The post-evaporitic deposits have been characterized by compositional (XRD and EDAX microprobe), microfacies, stable isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) and natural radioactivity (NRD) analyses to define the paleoenvironment.

The p-ev₁ deposits of the N-western Maiella area (Colle Votta quarry) consist of brown laminated shales, grey-brownish marls and yellow-brownish brecciated limestones. The bulk mineralogy of the terrigenous sediments is dominated by calcite and quartz, with minor amount of fillosilicate, plagioclase and ankerite. Calcitic fraction is made up of different types of microconcretions: 1) single and double tubular structures; 2) microbrecciated clasts. The brecciated limestones, which are enclosed within the ter-

igenous succession, outcrop as isolated and lenticular bodies, thus showing chaotic, nodular and biolaminated meso- and microfabrics. The chaotic fabric results from microbrecciated areas and from a complex framework of microfacies (micrite, microsparite, yellow calcite, banded/botryoidal calcite), with corrosion contacts. Micrite, microsparite and yellow calcite are rich in inclusions like peloids, framboidal pyrite, organic matter and pseudomorphs. The detected microfacies can be referred to authigenic carbonate phases, whilst only minor late diagenetic phases are present. In spite of the manifold microfacies, compositional analysis yielded no or slight differences, mainly related to strontium enrichments in patchy microareas.

The $\delta^{13}\text{C}$ isotopic analysis carried out on the post-evaporitic deposits provided a wide range of negative values: the less negative ones have been obtained by bulk analysis of marls (-10.89‰, \div -3.82‰, PDB), whilst their own constituents exhibit more negative values. In particular microbrecciated botryoidal grains show mean values of 11‰, PDB and tubular microstructures even reach the most negative values recorded in the studied deposits (-39‰, and -28‰, PDB). The $\delta^{13}\text{C}$ values of limestones range from -22.59‰, to 0.59‰, PDB, even though on the average they are assembled in a narrower and less negative range (from -25‰, to -15‰, PDB).

NRD measurements in the p-ev₁ deposits yielded higher values in carbonates facies (20-63 Cps) than in terrigenous sediments (21-47 Cps). Furthermore, field γ tspectra put in evidence different patterns of radioelements contributions: the NRD of the carbonate facies is entirely related to ^{238}U , whereas the NRD of the terrigenous sediments is due to related to ^{40}K , ^{238}U , ^{232}Th . Uranium concentration in the carbonates reaches values up to 5 ppm, which are extremely high if compared to the mean values recorded in carbonate lithofacies.

The data provided by NRD analyses show strong differences between evaporitic and post-evaporitic deposits, both in terms of NRD intensity and gamma-ray profile. A shift in the NRD background value (from 10 Cps to 20-30 Cps) and an increase of peak values, which reach the highest values of the section (55 and 63 Cps), occur above the Messinian unconformity. In the p-ev₁ the gamma-ray profile record doesn't exhibit the typical cyclic pattern related of the evaporitic deposits.

The textural-microfacies data and the isotopic ^{13}C -depletion exhibited by the carbonate cements of the Messinian p-ev₁ deposits, together with the presence of framboidal pyrite, bacterial structures and organic matter, represent the diagnostic criteria that testify a cold seep origin for the post evaporitic carbonates of the Colle Votta section. In this work this classical information is corroborated by a new approach achieved by NRD signal, in particular in terms of organic-enrichment indicated by the high value of ^{238}U .

The $\delta^{13}\text{C}$ signal reveals that the carbonates derive from the microbial oxidation of methane, both aerobic and anaerobic, as even implied by the presence of different microfacies. The complex microfacies framework, due to alternation of oxic and anoxic conditions could be related to different and discontinuous seepage/flux rates. In this context, a possible factor for triggering brecciation is the gas seepage, which is inferred to develop through the microtubular structures resembling the microscale chimneys of the cold seep carbonate deposits. The absence of seep biota may testify a deposition of these p-ev₁ methane-derived carbonates within the sedimentary column, below the sediment-water interface.