

NITROGEN ISOTOPIC COMPOSITION OF PORPHYRINS INDICATE IMPORTANCE OF N₂-FIXATION DURING THE DEPOSITION OF ORGANIC-RICH SEDIMENTS

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Introduction

Sedimentary porphyrins are powerful tool for elucidating the biogeochemical processes in the surface water. They are derived mainly from chloropigments, which are synthesized only by phototrophs. Their structural characteristics can be related to those of the source chloropigments, thus enabling us to reconstruct past phototrophic community. Moreover, because porphyrins contain four nitrogen atoms in the tetrapyrrole nucleus, their isotopic records provide constraints on both carbon and nitrogen cycles in the surface water. Here, we report porphyrin distribution and their $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of the shales in Vena del Gesso (Fig. 1a), which are interbedded between gypsum layers deposited during the Messinian Salinity Crisis (5.97-5.33 Ma). $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and sedimentary facies indicate that the deposition of the shale was triggered by continental water inflow occurring in phase with the precessional humid climate periods (Lugli et al., 2010; Fig. 1b), which induced water column stratification and photic zone anoxia (e.g. Keely et al., 1995; Sinninghe Damsté et al., 1995).

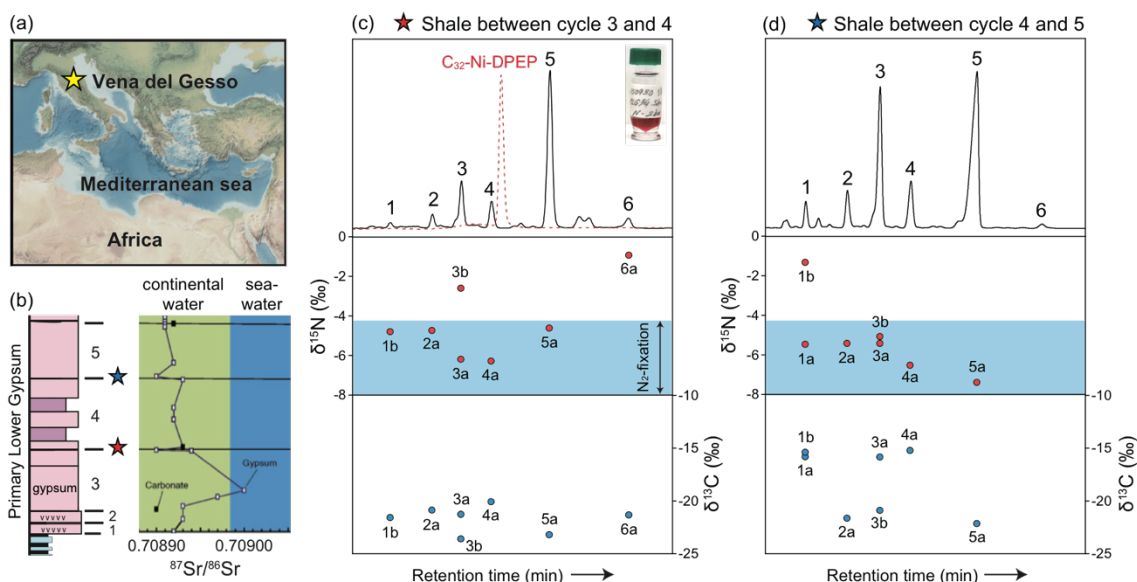


Figure 1 (a) Sampling location. (b) Stratigraphic column and $^{87}\text{Sr}/^{86}\text{Sr}$ variation (Lugli et al., 2010). (c)(d) Reversed-phase HPLC chromatograms of the sample (black solid line) and Ni-DPEP standard (red dotted line) with a picture of purified Ni porphyrin fraction, and $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of each peak.

Results & Discussion

The polar fraction of the total extract was desulfurized and Ni-porphyrin fraction was isolated by silica gel column chromatography. Further isolation and purification was accomplished by dual-step preparative HPLC method (Kashiyama et al., 2007). $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of the purified porphyrins were determined with our modified EA/IRMS. Although structure assignment of each porphyrin with NMR and LC/MS is on-going, C_{32} Ni deoxophylloerythroetioporphyrin (DPEP) was not detected in the shales based on the comparison with the standard material (Fig. 1c). The unique porphyrin composition of our shale samples may reflect unusual degradation pathways under hypersaline, anoxic deep water and/or extraordinary phototrophic community.

$\delta^{13}\text{C}$ values of the porphyrins showed distinct trends between the samples; some from the shale between cycle 4 and 5 showed ^{13}C -enriched values (Fig. 1c, 1d). Because porphyrin compositions of these shales are similar, we speculate that the difference is due to elevated $\delta^{13}\text{C}$ of the dissolved inorganic carbon in the environment during the time of the deposition. $\delta^{15}\text{N}$ values of most porphyrins from both samples range between -7.6 and -4.1% . These $\delta^{15}\text{N}$ values can be explained either by domination of diazotrophic phototrophs as the main primary producer, or suppression of primary production by limitation of nutrients other than nitrate. It is noteworthy that the similar $\delta^{15}\text{N}$ range of porphyrins/chlorins were observed in the black shales of the Cretaceous Oceanic Anoxic Events (Ohkouchi et al., 2006; Kashiyama et al., 2008) and the Mediterranean sapropels (Sachs and Repeta, 1999; Higgins et al., 2010), which concluded diazotrophic cyanobacteria as main primary producer. All these studies indicate that nitrogen cycle strongly controls the phototrophic community and the biogeochemical processes, and evidences are accumulating that diazotrophic phototrophs played an important role during the deposition of organic-rich sediments under stratified, nitrate-depleted condition.

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