



Influence of diagenetic and post-sampling processes on biogenic carbonate oxygen and carbon stable isotope in suboxic sediments

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Diagenetic and post-sampling processes may largely imprint the sedimentary records, and particularly oxygen and carbon isotopic records from biogenic carbonates. In order to study and decipher such effects, a multi-proxy approach was conducted on core MD02-2520, retrieved in the Gulf of Tehuantepec (Mexico) (IMAGESVIII-MONA, 2002) at 750 meters water depth. The core lies within the modern Oxygen Minimum Zone and exhibits millimeter-scale laminations composed of alternating terrigenous-rich and carbonate-rich silty-clay layers. The 35 m of sediments recovered span the last 40 kyr, as indicated by a series of calibrated ^{14}C dating.

Oxygen and carbon isotopic composition was analyzed in several planktonic and benthic foraminiferal species and in diagenetic calcite. Additionally, we performed stable sulfur isotope measurements on gypsum crystals ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and conducted Scanning Electron Microscope observations and semi-quantitative counting of foraminiferal abundances.

Although the oxygen isotope records show coherent glacial/interglacial changes, all oxygen and carbon isotopic records are punctuated by large excursions reaching +3 ‰ in $\delta^{18}\text{O}$ and -5 ‰ in $\delta^{13}\text{C}$. In the glacial sediments, millimeter-scale gypsum crystals were recovered from the sieved samples, associated to a lower number of foraminifers. The $\delta^{34}\text{S}$ measured on several gypsum crystals ranges from -10 to +15 ‰.

Since the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ excursions cannot be explained by paleohydrological changes, different hypothesis are discussed. After already published results, dissolution of the ontogenetic calcite alone cannot explain such large excursions. Mass-balanced estimations of the amount of secondary calcite needed to produce the isotopic anomalies show that the $\delta^{13}\text{C}$ excursions could be produced by integration of low- $\delta^{13}\text{C}$ carbon originating either from organic matter degradation (due to contact with oxidants during diagenesis or post-sampling storage) or from methane-rich environment (during methane formation, migration from below or clathrates decomposition). However, the $\delta^{18}\text{O}$ excursions are too ample to be explained by precipitation of calcite during clathrates decomposition and subsequent anaerobic oxidation of methane (generally inducing excursions of up to 1.5 ‰), but they might be explained by precipitation of calcite linked with oxidation of organic matter during post-sampling storage (at 4 °C) or during diagenesis (at ~ 5 °C). The wide range of $\delta^{34}\text{S}$ values show that gypsum crystals could integrate sulfates originating from sea-water, oxidized organic matter and re-oxidation of iron sulfides. These results therefore point to re-oxidation processes occurring after sediment deposition or after core recovery. Oxygen and carbon isotopic measurements of calcite aggregates will help to assess the first interpretations.