

# Sulphur and oxygen isotopic composition of sulphates in hypersaline environments, as markers of redox depositional versus diagenetic changes

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## Introduction

The onset of anoxic conditions in hypersaline environments is difficult to distinguish as the scarcity or lack of fauna is not an unequivocal marker for anoxia in restricted settings. Moreover, the existence of pyrite in sedimentary rocks, and even its sulphur isotopic composition, do not differentiate depositional from diagenetic anoxic environments. The results of a study of oxygen and sulphur isotopic variations in sulphates from pre-evaporite marl deposits, prove these markers to be an effective tool in distinguishing syndepositional from diagenetic anoxic environments in hypersaline settings.

## Setting and methods

The Upper Eocene Anoxic Marl Unit at the eastern sector (Vic area) of the South-Pyrenean Foreland Basin represents a distinct change in sedimentation from normal marine deltaic-reef complexes to marine evaporite deposition. The main lithologies are marls with cyclic interbedded sandstone units and iron oxide-pyrite-gypsum crusts.

Sulphur and oxygen isotopic compositions have been analysed in samples (1 pyrite and 30 gypsum samples) from the anoxic marl unit and the underlying deltaic sediments.

## Results and interpretation

The  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values of sulphate are widely scattered ( $-22.44 < \delta^{34}\text{S}\text{‰}_{\text{CDT}} < +23.50$ ;  $-0.72 < \delta^{18}\text{O}\text{‰}_{\text{SMOW}} < +13.47$ ); the sample of still preserved pyrite records the lowest  $\delta^{34}\text{S}$  value ( $-28.86\text{‰}_{\text{CDT}}$ ).

The  $\delta^{34}\text{S}$ - $\delta^{18}\text{O}$  plot (Fig. 1) allows us to identify the trend of isotopic variation between two end members. One end member corresponds

to a cluster of both high  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values ( $+20.03 < \delta^{34}\text{S}\text{‰}_{\text{CDT}} < +23.50$ ;  $+10.96 < \delta^{18}\text{O}\text{‰}_{\text{SMOW}} < +13.47$ ); the other end member is characterised by low  $\delta$  values ( $\delta^{34}\text{S} \sim -22.5\text{‰}$  and  $\delta^{18}\text{O} \sim +1\text{‰}$ ). The samples from the deltaic series show  $\delta^{34}\text{S}$  values between  $-8.06$  and  $+22.40\text{‰}$ , whilst  $\delta^{18}\text{O}$  values are well constrained around  $+1\text{‰}$ : this group thus appears well separated from the main trend (Fig. 1).

Two main clusters of values may be distinguished in the above mentioned trend. One group corresponds to samples with average values of  $\delta^{18}\text{O} \sim +12\text{‰}$  and  $\delta^{34}\text{S} \sim +22\text{‰}$ , which agree with the accepted compositions of Tertiary marine sulphates (Holser and Kaplan, 1966, and Claypool *et al.*, 1980). It is thus inferred that these gypsums were precipitated from a normal marine brine.

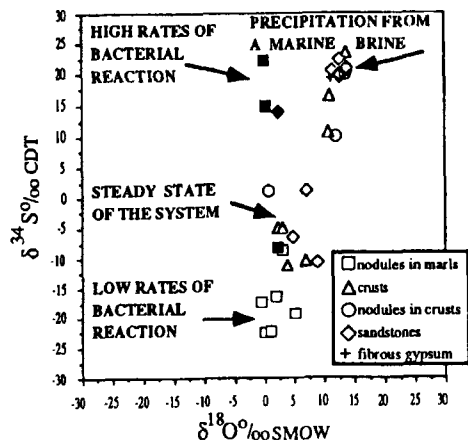


FIG. 1.  $^{18}\text{O}$  and  $^{34}\text{S}$  values of sulphates from deltaic deposits (symbols in bold) and the anoxic marl unit above.

The other group displays lower  $\delta^{18}\text{O}$  values and corresponds mainly to sulphates also with low  $\delta^{34}\text{S}$  values, except for a few samples from the deltaic marls, which exhibit  $\delta^{34}\text{S}$  values similar to the Tertiary marine composition. Most  $\delta^{34}\text{S}$  values in this group range between  $-4.81\text{‰}$  and  $-22.44\text{‰}$ . The large sulphur isotope fractionation between these sulphates and the average marine Tertiary composition demonstrates that these sulphates were formed after the oxidation of a precursor reduced phase (either  $\text{H}_2\text{S}$ ,  $\text{FeS}$  or  $\text{FeS}_2$ ), produced during bacterial sulphate reduction processes.

The application of the Van Everdingen and Krouse (1985) equation gives estimates of the  $\delta^{18}\text{O}$  values of the water in which sulphide oxidation took place. Reoxidation of sulphides was due either to the action of greater or lesser evaporated sea water, during sedimentation or at early diagenetic stages, or to meteoric water circulation (from early diagenetic stages to Recent).

### Discussion

Isotopic compositions similar to Tertiary marine sulphate are found in gypsum samples from sandstone beds and iron oxide-pyrite-gypsum crusts. The largest sulphur isotope fractionation ( $\sim 50\text{‰}$ ) with respect to the Tertiary marine sulphate is characteristic of low rates of bacterial reaction, possibly controlled by limited food supply in a closed system, causing large reservoir effects. Intermediate  $^{34}\text{S}$  fractionation ( $\sim 25\text{‰}$ ) represents the steady state of the system, where food and sulphate supplies are not limiting factors to bacterial sulphate reduction. The lowest  $^{34}\text{S}$  fractionation corresponds to high rates of bacterial reaction due to high amounts of organic matter and no limitation of dissolved sulphate supply.

The constraining parameters of the depositional and early diagenetic environments were thus dissolved sulphate and food supplies, as well as the location of the redox interface relative to the water-sediment boundary. These controlled the rates of bacterial sulphate reduction in an open-versus-closed system, the syngenetic oxida-

tion of precursor reduced phases, or the precipitation of sulphates from a brine in an interstitial environment or at the sediment-water interface.

Cyclic changes in redox conditions can be deduced from the variations of the isotopic composition of sulphates in the studied example. Sulphates would precipitate from a brine under oxic conditions (marine Tertiary  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values) at the sediment-water interface or in the first few centimetres of sediment. The largest  $^{34}\text{S}$  fractionation effects are found in nodules among marls and reflect interstitial anoxic conditions during early diagenesis. The crusts, gypsum and pyrite cements in some sandstones, and a few gypsum nodules in marls, were formed under anoxic bottom water conditions. This assumption is supported by: 1) the  $^{34}\text{S}$  enrichment ( $\sim -25\text{‰}$ ) due to the steady state of the system characterized by a continuous supply of dissolved sulphate, 2) the  $\delta^{18}\text{O}$  values of these sulphates indicate sulphide oxidation in marine waters, and suggest sudden changes from reducing to oxidizing conditions, and 3) the record of marine Tertiary isotopic composition in the crusts indicates that conditions changed from anoxic to oxic.

### Acknowledgements

This work has been supported by the Spanish Government Project DGICYT n. PB91-0801 and by the EC Human Capital and Mobility contract n. ERB-CHRX-CT93-0309. The isotope analyses were performed at the Laboratoire d'Océanographie Dynamique from the Université Pierre et Marie Curie, Paris. Travel and subsistence expenses to perform the analytical work were granted by a joint CSIC-CNRS Cooperation Project and a CIRIT grant.

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