Refining the δ^{34}S and δ^{18}O values of sulphate in ancient oceans

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Introduction

The isotopic composition of ocean sulphate is essential in the reconstruction of the global sulphur cycle throughout the Phanerozoic. Holser and Kaplan (1966) and Claypool *et al.* (1980) have established the evolution of the δ^{34}S and δ^{18}O values of marine sulphate deposits. Since the residence time of sulphate in the ocean is larger by several orders of magnitude than the time to achieve complete mixing, homogeneous δ^{34}S values are expected. However, the sulphates of the same age, and also from the same basin, may show no constant δ^{34}S and δ^{18}O values, but vary with ranges as large as 10‰ (Claypool *et al.*, 1980). These variations lead to the main question still unsolved: what was exactly the isotopic composition of seawater sulphate at this particular time?.

Several processes taking place within the sedimentary basin have been invoked to account for the variation of the isotope values: 1) fractionation as sulphate precipitates; 2) bacterial sulphate reduction; 3) mixing with sulphate of a different age. Holser and Kaplan (1966) and Claypool *et al.* (1980) propose a compensated mean of the measured δ^{34}S and δ^{18}O values as the best estimate of the isotope composition of seawater sulphate of a particular time.

In the present contribution we propose a method to identify the different processes affecting the isotope composition of sulphate within the sedimentary basin. It is based on the systematic analysis of the δ^{34}S and δ^{18}O values of sulphates sampled throughout a complete evaporite sequence. A computer program has been used to predict the evaporation paths in different scenarios. The comparison of the predictions with the observed isotope compositions has been used to constrain the processes taking place in the basin and to infer the isotope composition of sulphate dissolved in the parental seawater.

Method

The geochemical evolution of the evaporite basin was simulated using the conceptual model of a hydrologically open basin proposed by Sanford and Wood (1991). The main principle supporting the calculations was the conservation of the mass of every solute and the chemical equilibrium between the minerals and the solution. The thermodynamic behavior of the system was described by an ion-ion interaction model at 25°C. A detailed description of the calculations and its application to model the fluid inclusion compositions is found in Ayora *et al.* (1994).

The $\delta^{18}O_B$ and $\delta^{34}S_B$ values of the sulphate in the brine was calculated using the mass balance constraints:

$$\frac{d(Vc_B\delta^{34}S_B)}{dt} = Q_{SW}c_{SW}\delta^{34}S_{SW} + Q_{RW}c_{RW}\delta^{34}S_{RW} -$$

$$Q_L c_B \delta^{34}S_B - \sum_{j=1}^{N_m} \nu_j \frac{d(m_j\delta^{34}S_j)}{dt} \qquad (1)$$

where c_{SW}, c_{RW} and c_B are the sulphate concentrations (mol/l solution), and $\delta^{34}S_{SW}$, $\delta^{34}S_{RW}$ and $\delta^{34}S_B$ are the isotopic composition of sulphate in the sea water, the continental water and the basinal brine, respectively; V the volume of brine; Q_{SW} and Q_{RW} are the water inflows (liter/time unit) from the sea and continent; Q_L the outflow due to reflux to the sea or leakage to aquifers; dm_j/dt are the molar amounts of the j-th mineral formed, m_j is the stoichiometric coefficient of SO_4 in the j-th mineral, and $\delta^{34}S_j$ is the isotopic composition of the j-th mineral. An identical equation can be made for δ^{18}O values. The isotopic composition of the mineral, $\delta^{34}S_j$ and $\delta^{18}O_j$, is calculated from the $\delta^{34}S_B$ and $\delta^{18}O_B$ values and the gypsum-brine enrichment factors of $\delta^{34}S_{min-B}$ and $\delta^{18}O_{min-B}$ of $+1.65$ and $+3.5$‰, respectively.

As Q_{SW} is assumed to be higher than Q_{RW} in a marine basin, and, as the averaged c_{SW} is one order of magnitude higher that of river water c_{RW},
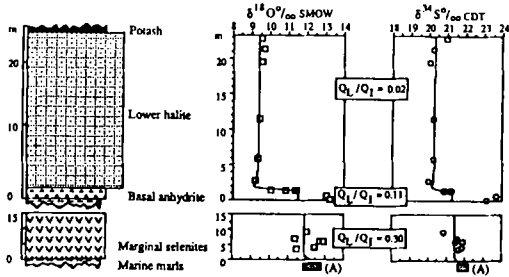
FIG. 1. Evolution of the isotopic composition of sulphates from the Southern Pyrenean potash basin. (A) Early sulphate precipitated from the deduced range of $\delta^{34}S$ and $\delta^{18}O$ values of seawater.

the mass of sulphate of continental origin ($Q_{RW}c_{RW}$) has been discarded as a first approximation.

As discussed in detail in Sanford and Wood (1991) the only reasonable mechanism to accumulate significant thicknesses of an evaporite lithology is the evolution of the basin under a steady state regime: constant volume and solute concentration of the brine. Changes from one lithology to another are due to different degrees of the restriction of the basin. Restriction can be easily described by leakage ratio: the value of leakage outflow relative to total inflow, Q_L/Q_{SW}. The leakage ratio, Q_L/Q_{SW}, ranges in value from 0 in a completely closed basin, to 1 for the open ocean. For any given Q_L/Q_{SW} value a steady state will develop after some time.

Very useful information on the isotopic composition of the source water can be deduced if the lithology as well as the isotopic composition of the sulphates is observed not to vary through a section of an evaporite sequence. Developing the mass balance equation (1) with the brine isotopic composition held constant, and assuming a unique and constant value of the isotopic enrichment factor for all the sulphates throughout evaporation, the following expression is obtained:

$$\delta^{34}S_{SW} = \delta^{34}S_B + \Delta^{34}S(1 - \frac{Q_L}{Q_{SW}}\frac{c_B}{c_{SW}}) \qquad (2)$$

The second term is a correction to be added to the value of $\delta^{34}S_B$ empirically determined from mineral samples ($\delta^{34}S_k + \Delta^{34}S$). The value of Q_L/Q_{SW} can be inferred from the mineral association. The value of c_B is related to Q_L/Q_{SW} and is calculated solving the mass balance and mineral-solution equilibrium equations and from the fluid inclusion analysis. The value of c_{SW} is assumed to be equal to the present ocean.

Results: the isotopic composition of upper-Eocene seawater sulphate

The procedure described above is illustrated with a case in Fig. 1. A first stage in the evolution of the basin corresponds to the formation of a marginal selenitic sequence. Considering the range of $\delta^{34}S$ and $\delta^{18}O$ analytical values of selenites and the range of Q_L/Q_{SW} values leading to the formation of gypsum at steady state ($0.290 > Q_L/Q_{SW} > 0.115$), equation (2) yields a range of values for seawater sulphate of $\delta^{34}S_{SW} = +20.0$ to $+21.3‰$ and $\delta^{18}O_{SW} = +8.1$ to $+11.6‰$. A borehole from the potash depocenter shows a basal anhydrite and lower halite units. The potash unit and an upper halite unit have been discarded in the present study because they show clear evidence of having been formed in a basin disconnected from the ocean. The $\delta^{34}S$ and $\delta^{18}O$ values of the two lowermost samples from the basal anhydrite unit can only be explained if bacterial sulphate reduction is assumed. The sharp decrease in the $\delta^{34}S$ and particularly the $\delta^{18}O$ values, recorded at the end of the basal anhydrite unit, illustrates a limited reservoir effect produced by the increase in restriction leading to the halite precipitation. Therefore, no isotopic composition of seawater sulphate can be inferred from anhydrite analyses. The constant isotopic values through the lower halite unit and equation (2) lead to a seawater composition of $\delta^{34}S_{SW} = +19.5$ to $+20.5‰$ and $\delta^{18}O_{SW} = +8.3$ to $+9.3‰$.

The experimental δ values obtained for sulphates from the Southern Pyrenean basin (potash and upper halite units excluded) range from $+20$ to $+24‰$ for sulphur and from $+9$ to $+13‰$ for oxygen. However, the intersection of ranges of seawater composition calculated by the above method for marginal selenites and the lower halite unit, significantly constrains the isotopic values of sulphate in the upper Eocene seawater as: $\delta^{34}S_{SW} = +20.0$ to $+20.5‰$ and $\delta^{18}O_{SW} = +8.3$ to $+9.3‰$.

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