Geochemical evolution of Suria evaporite sequence: implications for the chemistry of the Eocene ocean

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Evaporite sequences have been used, sometimes without concern for their origin, as an important source of data in determining ancient ocean compositions. The studies and interpretations of the origin of these sequences, performed by our research group in different evaporitic basins, have allowed us to develop and refine a methodology. This has proven to be a useful tool in the reconstruction of ocean chemistry and of the isotopic composition of the sulphate dissolved in the ocean during past geological times (Ayora *et al.*, 1994a, 1995).

In this contribution we present the results and interpretations from the Catalan depocenter of the South Pyrenean foreland basin, and compare the results with those published for the Navarra depocenter in Ayora *et al.* (1994a, 1995).

Methodology

The Na, Mg, K, Cl, Ca and SO_4 contents were measured in primary fluid inclusions by direct X-ray microanalysis of frozen inclusions (Cryo-SEM-EDS), according to the methodology described in Ayora *et al.* (1994a). This method allows the quantitative analyses of a representative group of inclusions in the same crystal with sizes >15 μm. Though values of precision error varied for each element and analytical process, they were always <10%. The consistency of the results was checked against the charge balance and the NaCl saturation index.

Isotopic values ($\delta^{34}S$ and $\delta^{18}O$) were systematically measured in sulphates throughout two boreholes recovered from both basins.

The brine evolution, the number of minerals formed, and the sulphate isotopic composition in both depocenters were calculated using a numerical model based on an hydrologically open basin, and on thermodynamic equilibrium and mass balance principles. The model reproduces evaporation scenarios and the parameters are adjusted by the empirical information. The model enables the quantification of the degree of restriction of an evaporitic basin. The main principles supporting the calculations are the conservation of the volume of the brine and the conservation of the mass of each solute (see Ayora *et al.* (1994a) for a detailed explanation).

Geological setting of the Suria sequence

During the Eocene, the South Pyrenean Foreland Basin was an elongated east–west trough, connected initially to the open sea along its north-western edge. The evolution of the basin is related to the uplift of the Pyrenees. It is filled by marine (deltaic and reefal) to continental (lacustrine and alluvial) sediments. An evaporite sequence (sulphate, halite unit, and potash facies) was deposited during the Upper Eocene, in the transition between marine and continental facies. Two main evaporite depocenters developed in the basin: the Catalan depocenter in the eastern sector; and the Navarra depocenter in the west. The Upper Eocene sediments, located in the centre of the basin between the two depocenters, are covered by the South Pyrenean thrust sheets. Although there are few borehole data from that sector, Busquets *et al.* (1985) have suggested a connection between the two depocenters based on detailed petrographical and geochemical correlation of the evaporite sequences of Catalonia and Navarra.

Discussion and results

The solute evolution obtained for the Suria borehole (Fig. 1) shows four different stages of evolution in

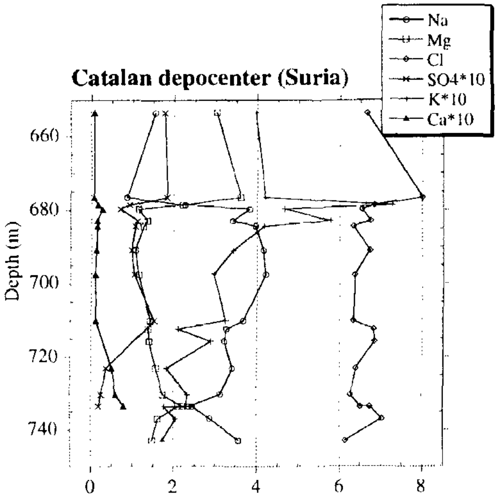

FIG. 1. Evolution of the solute content in fluid inclusion brines.

the basin during the halite deposition. (A) At the onset of halite precipitation the basin is quite restricted and contains more Ca than would be expected from evaporation of actual seawater. The Ca supply could come from the intense dolomitization of the carbonate platforms surrounding the evaporite basin, rather than from global changes in the oceans composition. (B) The Ca concentration decreases as halite precipitation progresses. In the first 40 m of the halite unit, Ca falls under the detection limit (0.02 m) and SO_4 is detected but always depleted with respect to the normal SO_4 concentration. So, there is a constant Ca supply throughout the halite precipitation, which is responsible for SO_4 depletion. (C) The basin becomes more open to seawater inflow as evaporation progresses. This is registered in the Mg content, although minor amounts of polyhalite are formed, Mg has been considered a conservative solute and indicates evaporation of brine. As we move up through the sequence Mg depletes and Na increases. On the contrary, in the Navarra depocenter, the basin becomes more restricted towards the top of the halite unit, with Mg increasing and Na decreasing. (D) The beginnings of the precipitation of the uppermost part of the halite unit are marked in both depocenters by a change in the halite texture and cyclicity. In Navarra, halite is pink in colour and alternates with clay and anhydrite layers. The Catalan side shows a marked change in colour from a white grey to a dark red, including clay layers. This change is also registered in the fluid inclusion compositions with a sharp increase of Mg in both depocenters, this change seems to mark the closure of the basin to the sea and the beginning of potash formation.

This evolution is also registered and confirmed by the isotopic analysis of $\delta^{34}S$ and $\delta^{18}O$, and by Ayora *et al.* (1995). During the halite deposition the δ values are constant and have a marine signature (Claypool *et al.*, 1980) slightly heavier than those registered in Biurrun.

The isopotic values obtained from the halite are used to deduce the sulphate isotopic composition of the Eocene ocean water. The isotopic values deduced from the sulphates interbedded in the halite have less error than those deduced from gypsum (Ayora *et al.*, 1994c). The difference between the sequences in both depocenters could be related to variations in the degree of restriction.

Once the basin is closed to the ocean water, the δ values decrease in the red halite and sylvite-carnallite beds, in both depocenters. After the potash beds there is a continental regime with important contributions of sulphates of triassic signature, which force the $\delta^{34}S$ values to become lighter.

Conclusions

The evaporation of recent seawater explains the major elements trends found in fluid inclusions. However some addition of Ca is required to explain the high Ca and low SO_4 values analysed. This excess of Ca changes throughout evaporation and is attributed to dolomitization and not to global changes in seawater composition.

The comparison between both depocenters shows that the Catalan depocenter (Suria borehole) was deposited in a more open basin than the Navarra evaporites (Biurrun borehole). In this preliminary interpretation this comparison could suggest the sub-basins differentiation in the South Pyrenean basin.

All of these geochemical data are being used to deduce an SO_4 isotopic composition for Eocene seawater. The values obtained for the Navarra depocenter are $\delta^{34}S_{CDT}$= 20.0‰ and $\delta^{18}O_{SMOW}$=8.7‰. The values obtained from the Catalan Depocenter are expected to be slightly heavier because of its less restricted sub-basin.

References

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