

Brine-mineral reactions in evaporite basins: Implications for the composition of ancient oceans

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ABSTRACT

The chemical evolution of several European Mesozoic and Tertiary evaporite basins was reconstructed by using mineral associations, primary fluid-inclusion analyses, and numerical simulations of evaporation scenarios. The solute proportion recorded in the fluid inclusions can be explained by the evaporation of present-day seawater as a major recharge. The sulfate depletion in the brines is responsible for the type of potash deposit formed, potassium-magnesium sulfates or sylvite. This sulfate depletion can be due either to dolomitization or to the addition of a CaCl_2 -rich solution to the basin. The sulfate depletion occurred in varying intensity in basins of the same age, as well as throughout the evolution of the same basin. Therefore, changes in potash mineralogy and sulfate depletion in fluid inclusions are not conclusive arguments in favor of secular variations in the composition of the ocean, as recently proposed by several authors.

Keywords: evaporites, potash, fluid inclusions, brines, paleo-oceanography.

INTRODUCTION

Whether the chemical composition of the ocean has remained fairly constant or has varied in a secular manner over Phanerozoic time has been the subject of a recent controversy. Most marine evaporite sequences have traditionally been interpreted as being the result of the evaporation of a solution with a composition similar to that of present-day seawater (Braitsch, 1971; Holland et al., 1986). The extraction of inclusion fluids has provided direct evidence of the chemistry of ancient evaporite-forming brines (Petrichenko, 1973; Lazar and Holland, 1988). This information has been used to induce the seawater composition. Thus, the fluid inclusions from the Miocene of the Red Sea are not very different from those expected from the evaporation of present-day seawater (Holland et al., 1986). The inclusions from the Permian Salado (New Mexico) and Wellington (Kansas) formations are close to the same evaporation trend (Horita et al., 1991). However, fluid inclusions from the Devonian Prairie Formation of western Canada (Horita et al., 1996), and the Silurian Michigan basin (Das et al., 1990) differ significantly from this pattern. Moreover, the extraction technique requires a large inclusion size ($>200 \mu\text{m}$). Inclusions of such a large size are limited in number in natural samples, and their compositions have been found, in some cases, to be unrepresentative of the original brine (Roedder et al., 1987; Stein and Krumhansl, 1988).

The origin of potash deposits also constitutes an apparent enigma. The evaporation of present-day seawater leads to the precipitation of magnesium and potassium sulfates, whereas many potash deposits in the Phanerozoic sedimentary record consist of sylvite, and potassium-magnesium sulfates are scarce.

Hardie (1996) indicated a correlation between periods of "ara-

gonite and calcite-rich seas" and periods of sulfate-rich and sulfate-poor evaporite sequences, respectively. Hardie proposed that the major solute concentration in seawater varied secularly over the past 600 m.y. owing to fluctuations in the mid-ocean ridge hydrothermal flux. Furthermore, Kovalevich (1988) and Kovalevich et al. (1998) performed analyses of brines extracted from halite of different ages and localities. They concluded that secular variations in seawater chemistry from Ca -to SO_4 -rich composition occurred during the Phanerozoic.

The conclusions of previous authors are based on the assumption that the solute concentration is not significantly modified by brine-rock reactions in the basin during evaporation. Holland et al. (1996) suggested that diagenetic reactions could alter the brine composition. We present unambiguous evidence that these reactions occurred, accounting for not only the potash mineral composition, but also for the details in the chemical composition of fluid inclusions. The detection of brine-rock reactions is not possible by analyzing isolated samples. Reaction detection is only possible when the brine evolution is reconstructed in detail by using systematic fluid-inclusion analyses throughout complete sequences and numerical simulation of evaporation scenarios. Moreover, this methodology distinguishes which parts of the evaporite sequences, apparently deposited in a marine setting, are in fact formed by recycling previous evaporites in an endorheic basin (Ayora et al., 1994a, 1994b). In the following discussion we do not consider these nonmarine evaporites but focus on those formed by evaporation of seawater as a major input.

MATERIALS AND METHODS

Five marine evaporite sequences were selected for discussion, including two sylvite-bearing, one potassium-magnesium sulfate-bearing, and two barren sequences. The Lorca basin (Spain) was a marginal basin of the western Mediterranean during the late Miocene. The lower part of this sequence is marine and made up of halite with minor sulfate (Ayora et al., 1994a; García-Veigas et al., 1994). No potash minerals are present. The Central Sicilian basin was one of the central Mediterranean late Miocene (Messinian) basins. The sequence has two halite units separated by a kainite ($\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$) unit (García-Veigas et al., 1996). Only the lower halite unit is considered in this paper. The South Pyrenean foreland basin (Spain) was an elongated east-trending trough. Two main depocenters, Catalonia and Navarre, existed during the late Eocene. Only the lower part of the sequence is marine and is made up of sulfates, halite, sylvite, and carnallite (Ayora et al., 1994b). The Lorraine basin (France) forms part of the larger German basin of Late Triassic age. The sequence consists of halite, sulfates, and carbonates, potash salts being absent (Fanlo and Ayora, 1998).

Evaporite samples were systematically taken throughout the sequences, and conventional petrographic studies were carried out. Primary fluid inclusions from growth bands in halite crystals (hopper type, chevron, and plates) were selected for microanalysis. The electrolyte composition of the fluid inclusions was determined by direct X-ray microanalysis of frozen fluid inclusions, following the methodology described in Ayora et al. (1994a). This method allows the quantitative analysis of a representative group of inclusions with sizes ex-

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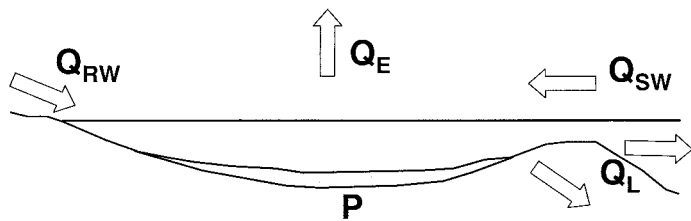


Figure 1. Conceptual model of input and output flows in hydrologically open basin. Legend: Q_{SW} = seawater inflow (liters per time unit); Q_{RW} = continental water inflow (rivers and groundwater); Q_L = outflow by reflux and leakage to aquifers; Q_E = evaporation outflow; P = precipitated minerals.

ceeding $15 \mu\text{m}$ in the same crystal. The Na, Mg, K, Cl, and S (expressed as SO_4) contents were measured in each fluid inclusion. Detection limits increased as the atomic number decreased. Thus, the detection limit was 0.01 mol/kg for Ca and K, 0.05 mol/kg for SO_4 , and 0.3 and 0.6 mol/kg for Mg and Na, respectively. Although the precision varied for each element and analytical process, it never exceeded 10%. The consistency of the results was ensured by fulfilling the charge-balance and the halite-saturation criteria.

The brine evolution and the amount of mineral formed in different scenarios were calculated by using the conceptual model of a hydrologically open basin (Fig. 1). The main principles supporting the calculations are the conservation of the volume of the brine and the conservation of the mass of each solute:

$$\frac{dV}{dt} = Q_{SW} + Q_{RW} - Q_L - Q_E \quad \text{and}$$

$$\frac{d(Vc_i)}{dt} = Q_{SW}c_{SW} + Q_{RW}c_{RW} - Q_Lc_i - P,$$

where c_i is the concentration (moles per liter of solution) of the i th solute in a basin filled with V liters of water; and P is the mass of solute precipitated as minerals. The composition of seawater, c_{SW} , was considered constant and was taken from an average of present-day seawater (Holland et al., 1986). In marine basins, Q_{SW} is higher than Q_{RW} , and c_{SW} is one order of magnitude higher than c_{RW} . Therefore, the term $Q_{RW}c_{RW}$ was not considered in the following discussion. The last term in the second equation is the total amount of solute (moles per time unit) precipitated in mineral phases, and this term was calculated by assuming thermodynamic equilibrium between the minerals and the brine.

The basin was assumed to have evolved with a constant water volume. Thus, the evaporated and leaked volume of water was replaced by an equal volume of inflow water, Q_I , which in our case was entirely made up of seawater ($Q_L + Q_E = Q_I = Q_{SW}$), and complete mixing was assumed to occur. As discussed in detail in Sanford and Wood (1991), the only reasonable mechanism for accumulating a significant thickness of an evaporite rock is the basin evolution under a steady-state regime—i.e., constant volume and solute concentration of the basinal brine. Changes from one mineral association to another are due to varying degrees in the restriction of the basin. Restriction can be easily described by the leakage ratio, Q_L/Q_I . This ratio ranges in value from 0 in a completely closed basin, to 1 for the open ocean. A steady state will develop after some time for a given Q_L/Q_I value. A mineral association and a brine composition will result for each steady state. Therefore, the fluid-inclusion analyses are very useful in accurately determining the degree of restriction of the basin.

RESULTS AND DISCUSSION

A brine was simulated to evaporate, with present-day seawater as the only recharge into the system. Given the lack of significant amounts

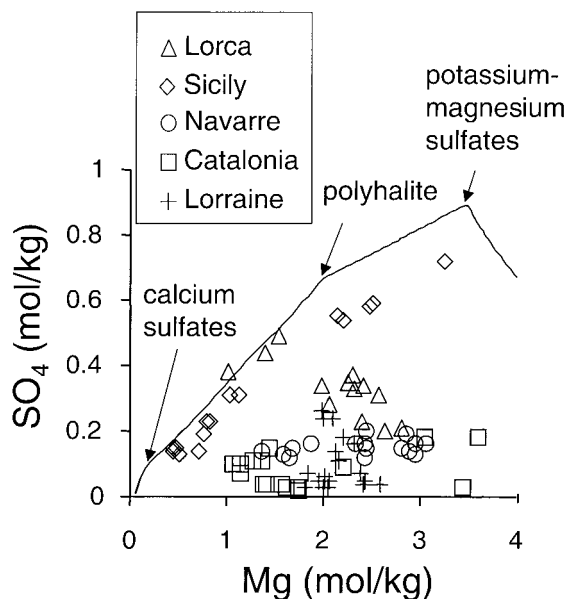


Figure 2. Calculated evolution of SO_4 content with respect to Mg (moles per kilogram of water) for evaporation of present-day seawater. Symbols plot means of analyses from primary fluid inclusions in halite.

of Mg minerals in the sequences, Mg was considered almost constant and was used as a reasonable indicator of the degree of evaporation until the stage of precipitation of magnesium sulfates and chlorides. The evolution of solute contents was plotted against Mg (Figs. 2 and 3).

The most relevant feature is that the SO_4 content recorded in the fluid inclusions is variable and much lower than expected (Fig. 2). In addition, the predicted values for Cl were lower than observed, whereas those for Na were higher (Fig. 3). Two main hypotheses have been suggested to account for the depleted values of SO_4 in the analyses: (1) bacterial sulfate reduction, and (2) addition of Ca into the basin and removal of SO_4 by precipitating calcium sulfates. Bacterial sulfate reduction is excluded, given that the predicted solute proportions are very different from those observed in the fluid inclusions (Ayora et al., 1994b). Moreover, the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of the sulfates interbedded in the sequences are fairly constant and do not match the ratio

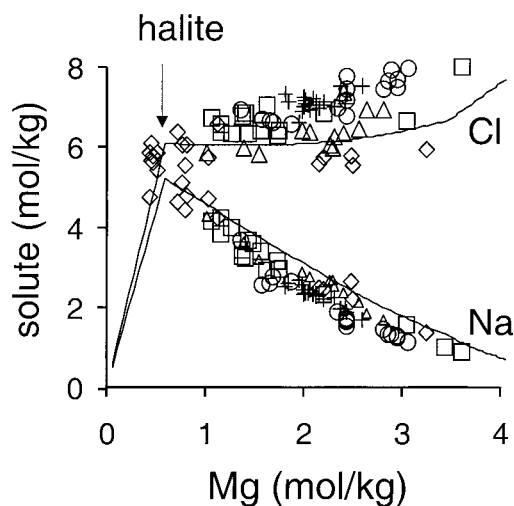


Figure 3. Calculated evolution of Cl and Na content with respect to Mg (moles per kilogram of water) for evaporation of present-day seawater. Symbols as in Figure 1.

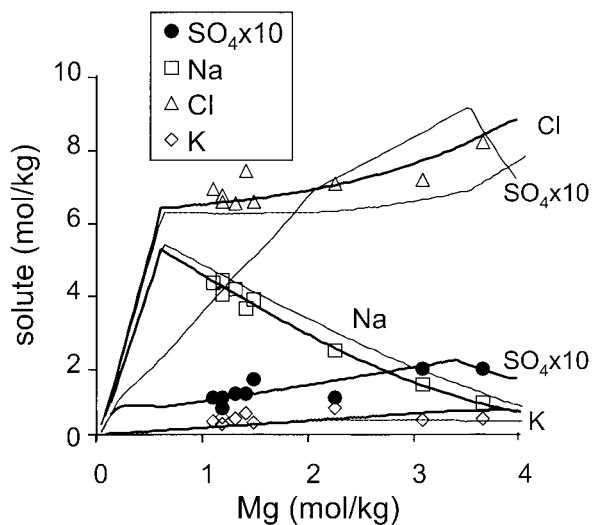


Figure 4. Calculated evolution of solute content with respect to Mg for different scenarios: present-day seawater recharge (thin lines) and fraction (0.017) of recharge being made up of 1M CaCl₂ brine (thick lines). Dolomitization trend (0.016 mol Mg/kg of water replaced by Ca), which is very close to that of CaCl₂, was not drawn. Symbols plot means of fluid-inclusion analyses from upper part of Catalonia sequence. Both predicted and analyzed contents of Ca are below detection limit (0.01M) and were not drawn.

of isotopic enrichment expected from sulfate reduction (Ayora et al., 1995).

Alternatively, two processes could result in an excess of Ca and in the subsequent depletion in dissolved sulfate: (1) the addition of Ca from a source external to the basin and (2) dolomitization. The addition of external Ca was modeled by means of the inflow of small amounts of a hypothetical 1M CaCl₂ solution. Although such a solution is uncommon in natural environments, its use in modeling does not constitute a conceptual problem. Thus, diagenetic, evolved meteoric and hydrothermal solutions have been reported to have a high salinity in the Na-Ca-Cl system (Hanor, 1987; Frape and Fritz, 1987; Lowenstein et al., 1989; Hardie, 1990; Zak, 1997). Because evaporation took place under conditions of halite saturation in the studied sequences, the excess of NaCl in the solution was consumed by halite formation, and only CaCl₂ merits further consideration. Besides the expected decrease in SO₄, the addition of CaCl₂ also causes an increase in Cl in the basin. The addition of Cl enhances the formation of halite, resulting in a corresponding decrease in Na. Therefore, after the addition of a given amount of CaCl₂, the predicted values match the SO₄, Cl, and Na analyzed in fluid inclusions (Fig. 4).

Dolomitization of limestones is a process commonly described in restricted marine environments and evaporite basins (Machel and Mountjoy, 1986). This process was modeled by replacing a constant fraction of Mg by Ca during evaporation. An identical result was also obtained by modifying the Mg/Ca ratio in the seawater recharge. The addition of Ca induces anhydrite to precipitate and dissolved SO₄ to decrease. Moreover, the consumption of Mg causes the Cl and Na concentrations to shift to the left in the plots with respect to Mg. As a result, by selecting the appropriate amount of dolomitization, the match between the predicted and analyzed SO₄, Cl, and Na contents may be achieved (Fig. 4). Dolomitized carbonates (marginal reefs and basinal marls) are present in the studied basins. Their isotopic composition suggests dolomitization by hypersaline fluids. However, the volumes of dolomite required to explain the sulfate depletion of each particular basin are not exposed. The evolutions of the solutes predicted by the addition of CaCl₂ and by dolomitization were very similar.

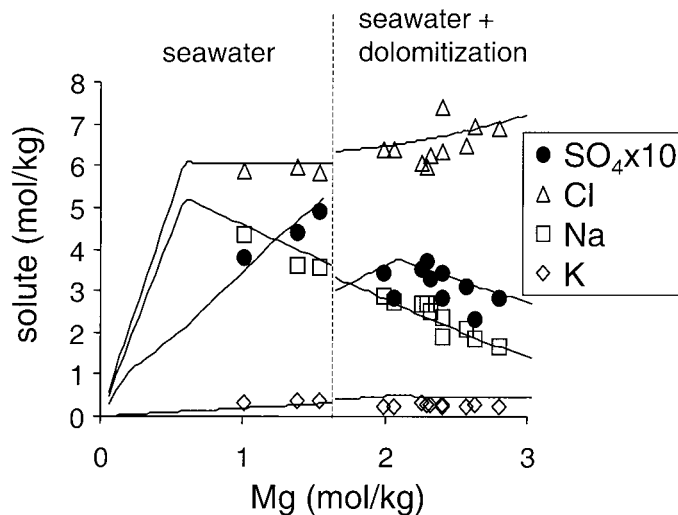


Figure 5. Calculated evolution of solute content with respect to Mg for two subsequent scenarios: initially, evaporation with recharge of present-day seawater; later, constant amount of 0.011 mol Mg/kg of water is replaced by Ca (dolomitization) throughout evaporation. Symbols plot means of fluid-inclusion analyses from Lorca sequence. Ca contents are below detection limit and were not drawn.

Therefore, the analytical data compiled did not reveal which of the two processes was responsible for the sulfate depletion observed. Additional Ca and loss of Mg could be produced by ion exchange in silicates interbedded with the halite. Calculations indicate, however, that the amount of mass involved in this process is negligible.

To match the solute content in fluid inclusions, a different amount of dolomitization or CaCl₂-rich brine inflow was needed for each sequence studied and, in some cases, for different parts of the same sequence. Lorca provides a good example: the lower part matches the evolution of present-day seawater, whereas the rest of the sequence needs additional Ca to explain the sulfate depletion observed (Fig. 5).

The solute content in fluid inclusions is also consistent with the mineral associations observed. Thus, halite and minor anhydrite form most of the evaporite sequences studied. The depletion of sulfate accounts for the undersaturation of brine in glauberite and for the absence of this mineral in all the sequences studied. For similar reasons, polyhalite formed later or failed to precipitate as a primary mineral. In the basins where a high degree of evaporation was reached, the type of potash minerals also agrees with the fluid-inclusion composition. The solute proportion is closer to seawater evaporation in the case of Sicily (Fig. 2), where potassium-magnesium sulfates consistently form most of the potash deposits. The degree of sulfate depletion is significant in the south Pyrenean basin (Navarre and Catalonia) where the potash beds consist of sylvite.

The evaporation rate of a brine with the degree of concentration corresponding to halite precipitation was reported to be 2 m/yr for Lake Asal in Djibouti (Fontes et al., 1979). However, the actual rate of accumulation and preservation of evaporites was estimated in recent halite-forming pans to be between one-fourth and one-third of the precipitation (Neev and Emery, 1967; Eugster, 1980). Therefore, a broad estimation of the longest time span required for the accumulation of each of the sequences studied was obtained with an evaporation rate of 0.25 m/yr. Depending on the degree of restriction (Q_L/Q_1), several hypothetical basins of 1 m depth should be evaporated in order to form the sequence thickness measured (mainly halite and anhydrite). Thus, the higher the Q_L/Q_1 value, the more solute is leaked from the basin, and a higher number of basins are required to evaporate. The highest Q_L/Q_1 value was selected, for each basin studied, as this value repro-

TABLE 1. CHARACTERISTICS OF THE STUDIED BASINS

Evaporite sequence	Age	Thickness (m)	$\frac{Q_{CaCl_2}}{Q_{sw}}$	Dolomitization Mg→Ca	Evaporated basins	Time (yr)
Lorca (upper)	Late Miocene	82	0.010	0.011	7 200	54 400
Lorca (lower)	Miocene	50	0.000	0.000	6 400	
Sicily	Late Miocene	214	0.005	0.005	44 500	178 000
Navarre	Late Eocene	20	0.015	0.016	2 200	8 800
Catalonia (upper)	Late Eocene	35	0.016	0.017	4 300	30 800
Catalonia (lower)	Eocene	32	0.021	0.020	3 400	
Lorraine	Late Triassic	75	0.019–12	0.019–14	8 000	32 000

Note: The fourth and fifth columns include the volume fraction of a hypothetical 1 M CaCl₂ solution in the seawater recharge, and the molar fraction of Mg in the brine replaced by Ca (dolomitization).

The sixth and seventh columns include the maximum number of hypothetical basins (1 m deep) evaporated to form the thickness of the sequences, and the time required for this evaporation, respectively.

duced the least concentrated brines analyzed in fluid inclusions, and led to the longest time span estimation (Table 1).

CONCLUSIONS

The mineral associations and the solute content analyzed in primary fluid inclusions can be predicted from the evaporation of present-day seawater as a major recharge. The different minerals of the potash deposits are correlated with varying degrees of sulfate depletion in the primary fluid inclusions. Thus, slight sulfate depletion with respect to present-day seawater led to a potassium-magnesium sulfate association (Sicily), whereas significant sulfate depletion correlated with sylvite (Navarre and Catalonia). The depletion in sulfate can easily be explained either by dolomitization or by the addition of a CaCl₂-rich brine to the basin, both processes leading to very similar solute proportions.

Two basins of the same age, Sicily and Lorca (late Miocene), displayed very different amounts of sulfate depletion. Two subbasins from the same basin, Navarre and Catalonia (late Eocene south Pyrenean basin), showed different amounts of sulfate depletion. Finally, the same basin underwent varying degrees of sulfate depletion during its evolution, as evidenced by the early and the more advanced stages of the evolution in the Catalonia and Lorca basins. The residence time of sulfate in the ocean is estimated to be 7.9×10^6 yr (Holland et al., 1986). This is more than one order of magnitude larger than the maximum time span required to form these sequences. Therefore, secular variations in the composition of the ocean cannot account for the observations described. Although variations in the composition of the ocean cannot be entirely ruled out, the arguments supplied to date from evaporite sequences (potash minerals and fluid-inclusion chemistry) are not conclusive.

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