

## On the origin of fluid inclusions in ancient halite – basic interpretation strategies

H. Zimmermann

Department of Earth and Planetary Sciences, Harvard University, 20 Oxford St., Cambridge, MA 02138, USA

In addition to the use of Jaenecke units in the  $\text{NaCl-KCl-MgCl}_2\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ / $\text{NaCl-KCl-MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$  system to classify brine origins, a fast and efficient method is described to identify inclusions of evaporated seawater in (ancient) marine halite. The method is based on the calculation of degrees of evaporation for various elements ( $\text{DE}_{\text{ELEMENT}}$ ) of brines created by different salt forming processes. The  $\text{DE}_{\text{ELEMENT}}$  patterns of the fluid inclusions serve as fingerprints and are characteristic of different brine types of known origin.

### 1. AIMS

Although many efforts have been made to constrain the composition of seawater during the Phanerozoic, it is not yet well defined. [1, 2] suggested secular variations of global seawater composition due to changes in the rate of seawater cycling through Mid Ocean Ridges with a maximum shift of seawater composition during the Cretaceous. The effect of variations in spreading rates on global seawater composition was recalculated by [3] resulting in a far more modest change in global seawater composition. [4] has suggested that the molar  $\text{Mg}/\text{Ca}$ -ratio in global seawater during the Paleozoic might have been twice the present value of 5. It was also pointed out by [3, 5] that the composition of seawater in evaporative settings can be seriously affected by the dolomitization of limestone during evaporative concentration without the need of major changes in global seawater composition.

As long as no complete chemical analyses of non-evaporated seawater inclusions in marine carbonate cements are available, we are limited to analytical data of fluid inclusions, e.g. in halite from marine evaporative settings to test the suggested models for changes in seawater composition during the Phanerozoic.

### 2. METHOD

The most useful information for settling this issue comes from the calculation of Jaenecke units [6-8] and the isothermal projection of fluid inclu-

sion compositions in the  $\text{NaCl-KCl-MgCl}_2\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ / $\text{NaCl-KCl-MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$  system. Though originally established to quantify the precipitation and reaction of potash minerals in  $\text{NaCl}$ -saturated systems (calcium carbonate and calcium sulfate are already taken out), the Jaenecke diagram  $2\text{K-Mg-SO}_4/\text{Ca}$  also gives important information for brines that are less evaporated.

Not all of the micro techniques for single fluid inclusion analysis [9-14] provide the complete set of data required for this thorough approach. In case Jaenecke units are not available, or in addition to that, we need to establish another independent tool for characterizing fluid inclusions of different origin, and this is the calculation of degrees of evaporation for various elements ( $\text{DE}_{\text{ELEMENT}}$ ) of brines related to modern seawater composition.

This paper focuses on the development of suitable interpretation strategies for fluid inclusion compositions in marine halite, whereas a subsequent manuscript [15] will address the application of these methods to fluid inclusions in halite from Tertiary marine evaporites in an effort to define the composition of seawater during the past 40 m.y.

### 3. SEAWATER COMPOSITION DURING THE PHANEROZOIC: MODELS

#### No major changes in seawater composition

Using Jaenecke units non-evaporated seawater of modern composition, at  $25^\circ\text{C}$ , projects in the stability field of bloedite (Figure 1), though its water value of  $m(\text{H}_2\text{O})=70,700$  is well above the

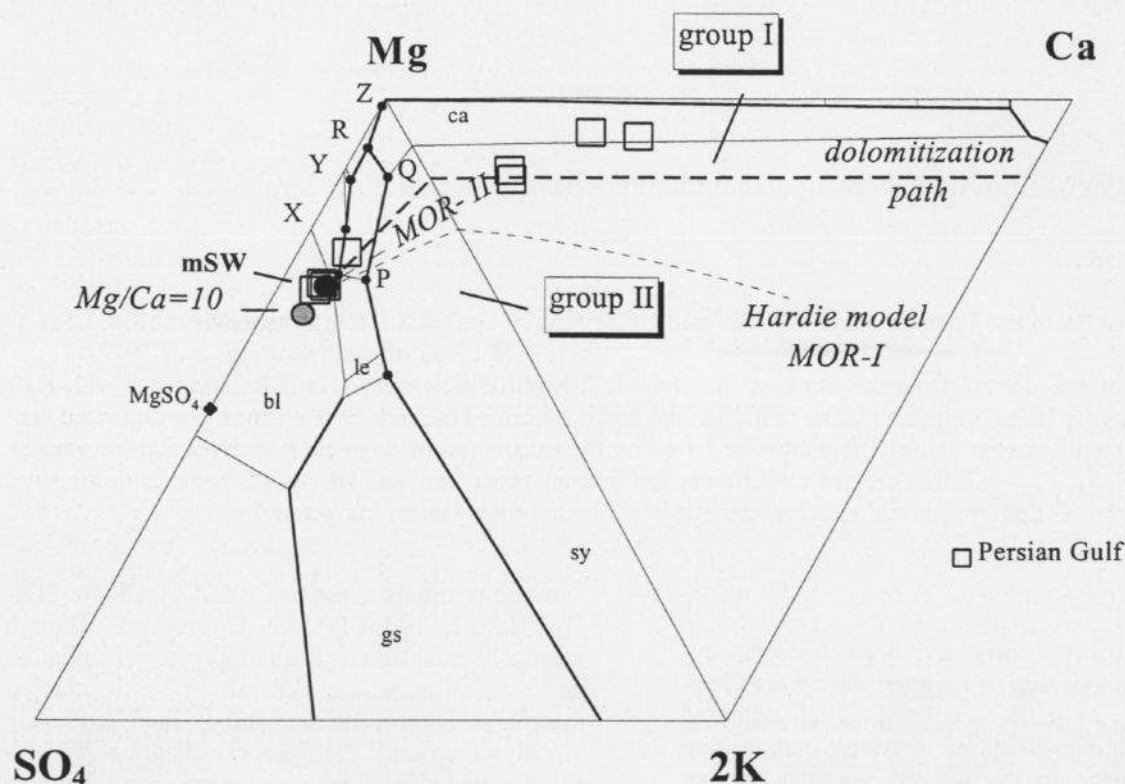


Figure 1. Seawater and fluid inclusion compositions in the Jaenecke diagram at 25 °C.  
mSW=modern seawater, bl=bloedite, ca=carnallite, gs=glaserite, le=leonite, sy=sylvite

saturation surface at  $m(\text{H}_2\text{O})=1,260$ . The  $m(\text{H}_2\text{O})$  value of evaporated seawater starting to precipitate halite is 7,070. The  $2\text{NaCl}$  values of halite saturated seawater at 10 times and 60 times the concentration of modern seawater are 305 and 22. Prior to potash mineral precipitation the relative ratio of Mg, 2K, and  $\text{SO}_4$  of evaporating seawater ( $\text{Mg}=69.0$ ,  $2\text{K}=6.5$ ,  $\text{SO}_4=24.5$ ) remains constant. Therefore all points representing the composition of evaporated seawater prior to potash mineral precipitation fall on the projection point of modern seawater.

If seawater composition has remained constant during the Phanerozoic and if seawater was not affected by processes other than evaporative concentration, fluid inclusions in ancient halite zones should contain evaporated seawater of mod-

ern composition prior to potash mineral precipitation. Their compositions could be characterized by:

$$\begin{aligned}\text{Mg} &= 69.0, 2\text{K} = 6.5, \text{SO}_4 = 24.5 \\ m(\text{H}_2\text{O}) &= 7,070-1,260 \\ 2\text{NaCl} &= 305-22\end{aligned}$$

According to [16] the real degree of evaporation of modern seawater (DE) can be calculated using any element that is not removed during the precipitation of a mineral phase. As an example,  $\text{DE}_{\text{MG}}$ , the degree of evaporation based on the concentration of Mg is given by the equation

$$\text{DE}_{\text{MG}} = (\text{mmol Mg/kg H}_2\text{O})_{\text{BRINE}} / (\text{mmol Mg/kg H}_2\text{O})_{\text{MSW}} \quad (1)$$

Prior to potash mineral precipitation one can use Mg, K, Br, B, Li, and Rb to determine DE. During the evaporation of seawater of modern composition  $DE_{ELEMENT}$  values for Mg, K, Br, B, Li, and Rb are equal and between 10 and 60 during the halite facies.

$$DE_{MG} : DE_B, DE_{LI}, DE_{RB}, DE_{BR}, DE_K = 1 : 1 \\ \wedge DE=10-60$$

This would also apply to fluid inclusions in ancient marine halite if seawater composition had not changed during the Phanerozoic.

### Changes in seawater chemistry due to variations in spreading rates of Mid Ocean Ridges

The validity of the proposed changes in seawater composition predicted by [1,2] can be tested with the help of the Jaenecke-plot. If Hardie's predictions were correct, fluid inclusion compositions in ancient halite (prior to potash mineral precipitation) that were not seriously affected by diagenesis should follow the dotted line (MOR-I) in Figure 1. In this case the  $DE_{ELEMENT}$  pattern proves not to be not very useful, since both K and Mg concentrations of seawater are changing. Verifying the variation of seawater composition due to changes in spreading rates estimated by [3] turns out to be more difficult, because the calculated trend (MOR-II, Figure 1) is to some extent similar to the effects on seawater composition caused by the dolomitization of limestones (see below).

### Changes in Mg/Ca-ratios of seawater

If the sum of the concentration of calcium and magnesium was the same as today, seawater with a molar Mg/Ca-ratio of 10 plots on the grey filled circle in the Jaenecke-diagram (Figure 1), showing a trend opposite to that caused by dolomitization and changes in spreading rates. If the molar Mg/Ca-ratios of initial seawater changed between 5 and 10 and assuming no other fractionation except the evaporative concentration of seawater, fluid inclusions in Phanerozoic halite zones should plot between the grey circle and modern seawater composition (Figure 1).

### Seawater modified by the dolomitization of limestones

If during the Phanerozoic dolomitization associated with evaporative concentration was an important process it gets extremely difficult to constrain the initial contemporaneous seawater composition. Assuming that the initial seawater composition was similar to the modern one, the dolomitization of limestones would affect seawater chemistry in the following way: While magnesium is removed from modern seawater to form dolomite, an equal amount of calcium is released from the reacting limestone. The excess calcium combines with dissolved seawater sulfate to form gypsum, the net balance of the whole process being an equimolar removal of magnesium and sulfate. The composition of seawater changed by this process (dashed line, Figure 1) plots along a line towards the 2K-Mg side of the Jaenecke-diagram, moving directly away from the projection point of  $MgSO_4$ . If magnesium is depleted by more than 35 % of that in modern seawater, there is not enough seawater sulfate to precipitate all of the released calcium, and  $CaCl_2$  will build up in the evaporating brine. The modified seawater compositions then plot along a line towards the 2K-Ca side of the Jaenecke diagram (Figure 1). Sabkha and algal flat groundwater analyses from the Persian Gulf, a modern marine setting with extensive dolomitization of carbonates [17], confirm the predicted trend. In magnesium depleted seawater compositions are characterized by:

$$\text{Plot on dolomitization path} \\ m(H_2O) < 7,000-14,000 \\ 2NaCl < 600$$

Initial seawater with higher Mg/Ca-ratios or modified due to changes in spreading rates according to [3] and affected by dolomitization would also lead to seawater compositions along the dashed line in Figure 1. In this case for a given composition of modified seawater the extent of dolomitization relative to the initial seawater composition would be different compared to modern seawater as a starting point.



The evaporation paths of seawater deficient in magnesium can also be modeled on the base of the HMW model [18]. With the exception of lower values for  $DE_{MG}$ , the  $DE_{ELEMENT}$  pattern for evaporated and by dolomitization modified seawater is the same as that of the initial seawater:

$$DE_{MG} : DE_B, DE_{Li}, DE_{RB}, DE_{BR}, DE_K = <1 : 1 \\ \wedge DE=10-60$$

If Mg/Ca-ratios in seawater varied between 5 and 10 during the Phanerozoic and given that in most evaporite basins the dolomitization of limestones with evaporative concentration was important, fluid inclusion compositions in ancient marine halite should follow the predicted dolomitization path.  $DE_{ELEMENT}$  patterns can be applied based on the, admittedly not yet well constrained, assumption, that there were no major changes in the Br, B, Rb, Sr, and Li contents of seawater during the Phanerozoic.

#### 4. BRINES FROM OTHER SALT FORMING PROCESSES

For establishing that evaporated seawater compositions suggested by the different models for Phanerozoic seawater chemistry can be distinguished clearly from brines originating from several other salt forming processes, it is useful to split brine compositions plotted in the Jaenecke diagram into 2 groups:

Fluid inclusions of group I plot in the upper part of the Jaenecke diagram above the dolomitization path towards the Mg-Ca side of the diagram and can originate from the following salt forming processes, which can be distinguished only by  $m(H_2O)$ -values and/or trace element concentrations:

- (1) strongly evaporated seawater of modern or in magnesium depleted composition precipitating potash minerals
- (2) reaction brines that have dissolved primarily from seawater precipitated potash mineral assemblages

- (3) strongly evaporated brines (process 1) or reaction brines (process 2) mixed with more dilute waters of either marine or non-marine origin.
- (4) brines from mineral/brine reactions which are not in equilibrium with primary mineral assemblages from evaporated seawater (either group I or II, see below)

In summary, fluid inclusions of group I are characterized by:

$$\text{Plot above dolomitization path} \\ \wedge DE_{MG}/DE_K > 1 \\ \wedge DE_{MG, BR} > 60 \text{ (except mixing)}$$

Fluid inclusions of group II plot below the dolomitization path towards the 2K-SO<sub>4</sub> side of the Jaenecke diagram in the stability fields of bloedite, leonite, glaserite, and sylvite and can be identified by the following criteria:

$$\text{Plot below dolomitization path} \\ \wedge DE_{MG}/DE_K < 1 \\ \wedge DE_K > 60 \text{ (except mixing)}$$

Like fluid inclusions of group I (4), group II inclusions represent brines interacting with mineral assemblages that are not in equilibrium with evaporated seawater. Usually this type of brine is related to secondary, mostly post-sedimentary processes, where additional brine mixing cannot be excluded. Most halite that contains group II inclusions is found in healed fractures and can usually be distinguished clearly from primary evaporites precipitated from seawater by simple petrographic criteria (eg. large clear crystals, occurrence of blue halite or sylvite). The latter salt forming processes are discussed more in detail in an extended version of this paper that will be printed separately [19].

#### 5. CONCLUSIONS

- (1) Brine inclusions from several salt forming processes (potash mineral precipitation, recycling of evaporites, or brine mixing) can be distinguished clearly from fluid inclusions containing evaporated seawater prior to potash mineral precipitation.

- (2) Besides the Jaenecke units of the NaCl-KCl-MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O/NaCl-KCl-MgCl<sub>2</sub>-CaCl<sub>2</sub>-H<sub>2</sub>O system, DE<sub>ELEMENT</sub> patterns of fluid inclusions are an efficient and independent tool for identifying fluid inclusion of evaporated seawater prior to potash mineral precipitation.
- (3) Both methods prove to be complementary and essential for the successful distinction between the different models of Phanerozoic seawater compositions using fluid inclusions in ancient marine halite.
- (4) The following interpretation strategy is recommended: Check with Jaenecke diagrams whether fluid inclusion compositions in ancient halite plot on the projection points of modern seawater, on seawater compositions with higher Mg/Ca-ratios, or along the path of predicted by the Hardie model. If they do not, select fluid inclusion compositions with DE<60 using the DE<sub>ELEMENT</sub> pattern approach. Plot these selected fluid inclusion compositions in the Jaenecke diagram and check whether they plot along the dolomitization path. In any case, doublecheck with petrographic features and stratigraphic position of the samples, whether it is reasonable to assume evaporated seawater prior to potash mineral precipitation as brine source. If fluid inclusion compositions indicate Mg-depletion of seawater, estimate the degree of magnesium and sulfate depletion.
- (5) Although these results are encouraging, it should always be kept in mind that conclusions based on fluid inclusions in marine halite are limited to the composition of seawater in the evaporite basin; this does not necessarily reflect the composition of contemporaneous global seawater.

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# Salt Extraction

Solution mining

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