

Bromine and Rubidium as Indicators of Environment During Sylvite and Carnallite Deposition of the Upper Rhine Valley Evaporites

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ABSTRACT

Concentration, density and temperature of the brine at the time of sylvite and carnallite deposition may be estimated from the bromine content of the sylvite and carnallite at the base of a potash deposit, if the following conditions are fulfilled:

- a. the evaporite sequence belongs to the $MgSO_4$ -free type*
- b. sylvite and carnallite are preserved in the primary state*
- c. the samples are taken immediately at the base of the sylvite or carnallite seam*
- d. the bromine content of the original brine is known or determinable.*

In the Upper Rhine Valley evaporites a distinct thermal and concentrational gradient within the basin and with time could be established. In addition the extraordinarily high rubidium content at the base of the carnallite seam in contrast to the normal rubidium contents in the sylvite at the base of the sylvite seam indicates dissolution of carnallite in the outer part and redeposition in the central part of the basin, confirming earlier suggestions of other workers. More work is in progress, to obtain indications of concentrational stratification within the lagoon. It seems possible to prove periodical inflows of less concentrated brines, which overlay a concentrated brine, saturated in halite and sylvite.

INTRODUCTION

The Upper Rhine Valley Evaporites represent a typical and well known example (Görgery, 1909, Sturmfels, 1943, Baar & Kühn, 1963, Braitsch & Herrmann, 1964, a, b) of the modified marine class of evaporites, characterized by the complete absence of magnesium-sulfates and magnesium-sulfate bearing double salts, and by the occurrence of primary sylvite. The possible origin of modified marine sea water is discussed elsewhere (Braitsch 1962, 189-193). The large Alsace basin lies to the west of the Rhine, and a small accessory basin, the Buggingen basin, lies to the east of the Rhine. The lower potash seam is 4-5 m thick and consists of four major units, defined by Sturmfels (1943) as B through E (the individual sylvite bearing beds in every unit being indicated by small letters a, b, c... from bottom to top) and a foot wall unit A, which contains only one individual sylvite bed Ac at the top. For the purpose of reference I shall use Sturmfel's! nomenclature. This paper deals only with the three lower most individual sylvite beds Ac, Ba, Bb (immediately underneath the worked part of the potash seam) and with the roof of bed E, which for safety reasons is not mined.

BROMINE THERMOMETRY

The author, in conjunction with Dr. H. Herrmann, has just completed a geochemical study with the aim of determining the temperature within the salt lake at the time of primary sylvite

crystallization. The method, designed earlier by the present author (Braitsch, 1962), rests on the bromine content of the primary sylvite, at the beginning of sylvite deposition, in potash seams of the MgSO_4 -free type. The following conditions must be fulfilled:

1. The minerals must be preserved essentially unaltered chemically. The simultaneous precipitation of the chlorides must be proved by checking for a paragenetic bromine ratio $\frac{\text{wt} - \% \text{ Br (sylvite)}}{\text{wt} - \% \text{ Br (halite)}}$, which must amount to 10 ± 1 .
3. The K/Mg ratio in the brine has to correspond with this ratio in the modified marine sea water. This perhaps is the major uncertainty of the method, and unfortunately up to now no reliable criterion for checking the K/Mg ratio is available. Further comments are given in section 3.

Assuming these conditions to be fulfilled, the temperature can be derived from the bromine content of primary sylvite. The bromine content of sylvite is proportional to the bromine content of the brine, which can be calculated from the equation

$$p = p_0 \left(\frac{a}{a_0} \right)^{-(1 - qb)}$$

as already shown in a similar form by Boeke (1908). This equation is identical with Rayleigh's distillation equation (Rayleigh, 1896, eq. 18)

$$p = \text{wt} - \% \text{ Br (solution)}$$

a = quantity of solution (gram), at the moment being considered, having started with an initial amount of a_0 (gram) at the beginning of the evaporite stage. Starting with 1000 g initial modified sea water a_0 , at 25° , the following quantities remain at the beginning of the indicated evaporite stages: halite 117 g, sylvite 15.3 g, carnallite 12.4 g, bischofite 7.6 g; a comprises the original brine plus influx minus reflux; for the present purpose these individual contributions need not be distinguished.

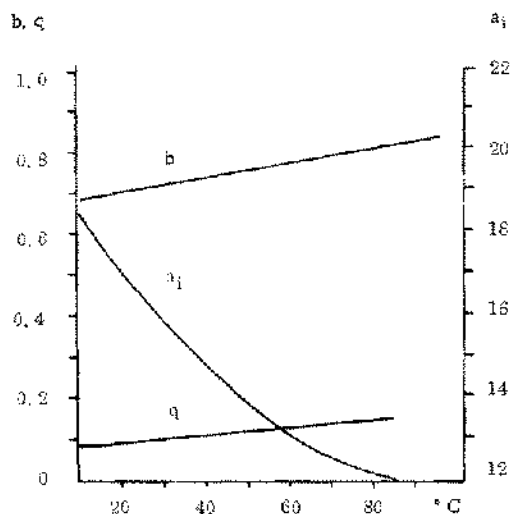
b = partition factor $\frac{\text{wt} - \% \text{ Br (crystals)}}{\text{wt} - \% \text{ Br (solution)}}$, which is just the proportionality constant mentioned

q = fraction of crystals in the total amount of solution removed, consisting of crystals and water vapor; a and q can be derived from the solution equilibria, b has to be determined experimentally (for details see Braitsch, 1962).

In the case of primary sylvite crystallization, the constants b and q are insensitive to temperature. On the other hand, the amount of solution at the beginning of sylvite crystallization strongly depends on temperature, because of the strong temperature coefficient of sylvite solubility (Fig. 1). At low temperatures, the first sylvite contains a low bromine content, for instance about 0.24 wt - % Br (KCl) at 0°C , while at high temperatures the bromine content is high, for instance 0.36 wt - % Br (KCl) at 50°C .

In brief, the results of bromine determinations of 89 exposures in the mine of Buggingen, and of 4 mines of the Alsace, are summarized in Fig. 2. The abscissa refers to the distance from the primary edge of sylvite deposition, in arbitrary units, the units being smaller within the Buggingen side basin. Three facts are clearly established:

1. The bromine content of sylvite, and the corresponding temperature, increases from the first bed to the third from about 10°C to about 50°C .
2. In every bed one observes a distinct concentration gradient from the inner part of the basin to the edge, with distinctly lower bromine contents in sylvite at the edge. In this case, the interpretation of the concentration gradient in terms of an equivalent temperature gradient is open to discussion, and this point will be examined in section 3.
3. In the small Buggingen side basin, the temperature revealed by each bed is slightly higher than in the large Alsace basin.



Temperature Dependency of Constants a , b , q
at the Beginning of Sylvite Crystallization

$$\text{in the Equation } p = p_0 \left(\frac{a}{a_0} \right)^{-(1-qb)}$$

Figure 1. Illustrating temperature dependency of constants a , b , and $-(1-qb)$ from equation $p = p_0 \left(\frac{a}{a_0} \right)^{-(1-qb)}$ at the beginning of sylvite crystallization.

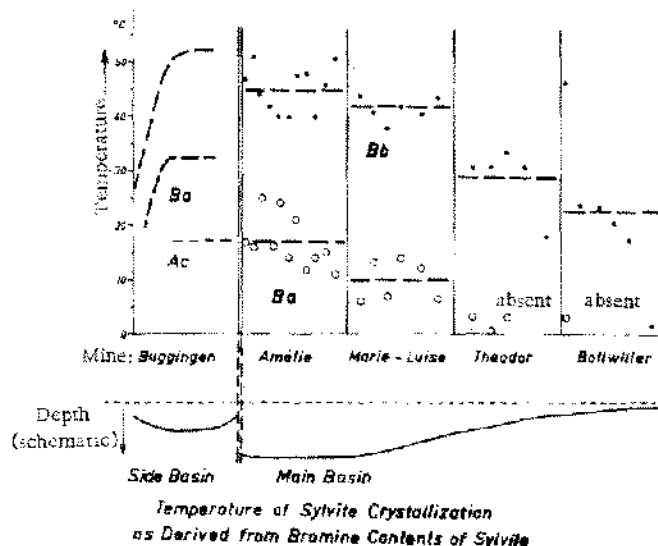


Figure 2. Brine temperature, inferred from the bromine content of sylvite, is shown plotted against the distance from the primary edge of sylvite deposition (arbitrary units). Inferred temperatures increase upward from the first bed to the third, from about 10° C to about 50° C. Also, within each bed, the bromide content of sylvite decreases towards the basin margin. This gradient to the basin margin could be interpreted either as the result of a concentration gradient or a temperature gradient.

An explanation of these observations was offered already in the earlier papers (Braitsch & Herrmann, 1964, a, b), where the increase of temperature was explained in terms of an increase in the density of brines saturated in sylvite plus halite. The observations, therefore, can be understood in terms of a stable density stratification within the salt lake, accompanied by corresponding temperature stratification. As a recent example of such a temperature stratification (a so called thermocline), the Dead Sea may be mentioned in which a temperature difference up to 10°C between surface and bottom brines was observed. The extent of the temperature difference is greatest in the fall and smallest in the late winter. In addition, the temperature increase, inferred from bed to bed, was attributed to a convection mechanism which is closely related to the density increase of the brines as temperatures rose.

THE SIGNIFICANCE OF ANOMALOUS BROMINE RATIOS

However, in bed Ac of all the Alsace samples an anomalous, nonparagenetic bromine ratio between sylvite and halite was observed, namely too low bromine contents in sylvite

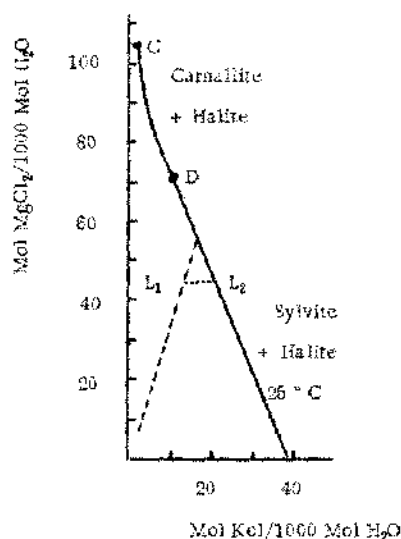
$$\frac{\text{wt} - \% \text{ Br (sylvite)}}{\text{wt} - \% \text{ Br (halite)}} = 7-9 \text{ instead of } 10).$$

In this case the temperature estimation is not possible since the first precondition of the method is not fulfilled. This observation tentatively was explained in the earlier paper (Braitsch & Herrmann, 1964) by recrystallization of sylvite in diluted interstitial solutions. Some quantitative models of this hypothesis were calculated for this paper.

Consider the system in question (Fig. 3) with KCl and MgCl_2 concentrations as coordinates, NaCl-concentrations not being indicated. The crystallization path of the solutions, during the stage of halite precipitation, is shown as a dotted line representing K/Mg ratios of modified sea water. If such a halite saturated solution, for instance corresponding to point L_1 , encounters a sylvite rock, it is able to dissolve sylvite, but not the halite associated with sylvite. The point, representing the composition of the brine in the KCl- MgCl_2 -diagram, shifts to the higher KCl-contents until the KCl-saturation curve is reached at point L_2 . The bromine content of this

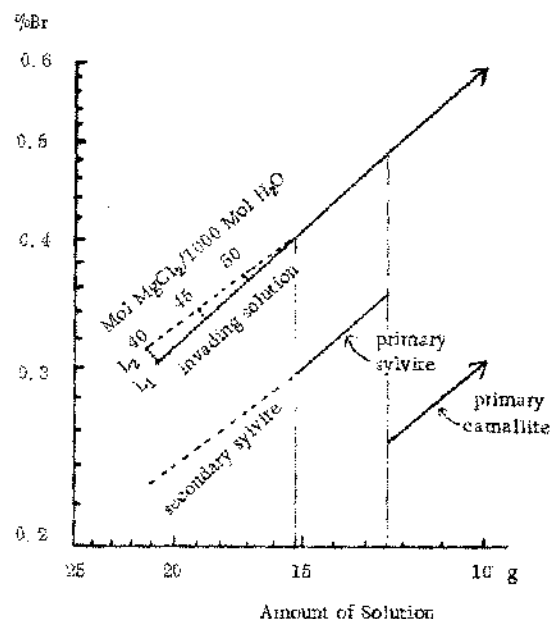
leaching brine is only very slightly increased with respect to the bromine content of point L_1 because of the bromine content of the dissolved sylvite.

Three examples were calculated (Table 1), for a temperature at 25°C. In each case, the primary sylvite was assumed to contain 0.29 wt. - % Br/KCl, corresponding to primary sylvite crystallization at 25°C. 15.3 g solution remaining of an original 1000 g modified sea water. Different amounts of this primary sylvite can be dissolved in the invading brine, depending on the degree of saturation, as will be seen for three solutions with different $MgCl_2$ -contents. The results are presented in Fig. 4 with the amount of solution on the abscissa, and the bromine content on the ordinate. The normal halite precipitation stage extends up to 15.3 g of solution. The corresponding bromine content of the solution is given as solid line (L_1).



Modification of the K/Mg - Proportion
by means of Sylvite Dissolution

Figure 3. KCl, $MgCl_2$, NaCl system. NaCl -- concentrations not indicated in figure. Dashed line indicates crystallization path during stage of halite precipitation. Solution of composition L_1 can dissolve sylvite, but not halite, and at point L_2 sylvite saturation is achieved. The bromine content of the brine at L_2 is only slightly increased with respect to that at L_1 .



The Effect of Sylvite Dissolution on the
Bromine Partition (25°C)

Figure 4. Amount of solution, which is related to stage evaporation, plotted against weight percentage bromide. The normal halite precipitation stage extends up to 15.3 grams of solution. The corresponding bromine content of the solution is given by solid line L_1 . The stippled lines correspond to the shift L_1 - L_2 (in Figure 4) for three individual $MgCl_2$ contents. The bromine content of the reprecipitated (secondary) sylvite is shown as the lower dashed line.

From Table 1, and the diagram (Fig. 3), the following conclusions may be drawn:

1. Dissolution of sylvite in brines of an intermediate composition, but already saturated in halite, causes reprecipitation of sylvite at a higher K/Mg ratio in the brine than would be the case with undisturbed primary crystallization. If reprecipitation of sylvite occurs, this reprecipitated sylvite has a lower bromine content in comparison with a primary sylvite. In addition, on cooling, such a brine will precipitate a higher proportion of sylvite to halite than an unchanged brine (see Figs. 10 and 11 in Braitsch, 1962).
2. In as much as halite remains unchanged in an NaCl-saturated brine, the halite associated with the original sylvite retains, to a first approximation, its bromine content. The bromine content of the reprecipitated sylvite, on the other hand, is low. Therefore, the observed nonparagenetic ratio is to be expected -- with sylvite low in bromine compared with halite.

Table 1
Calculated Bromine Distribution resulting from Dissolution
and Reprecipitation of Sylvite
(25°C; MgSO₄ - free Sea - Water)

| Mol MgCl ₂ 1000 Mol H ₂ O | Invading brine L ₁ amount [gram] | sylvite dissolved [gram] | halite precip- itated [gram] | weight-% bromine in invading brine L ₁ % | in KCl-saturated brine L ₂ % | in sylvite reprecip- itated % | %Br (sylvite 2) %Br (sylvite 1) |
|--|---|--------------------------------|---------------------------------------|--|---|--|------------------------------------|
| 56.5 | 15.3 | - | - | .404 | - | - | 10 |
| 50 | 17.0 | .17 | .02 | .364 | .368 | .268 | 9.1 |
| 45 | 18.7 | .40 | .06 | .334 | .344 | .251 | 8.5 |
| 40 | 20.8 | .66 | .18 | .302 | .312 | .226 | 7.6 |

3. The amount of sylvite dissolved is small in comparison with the quantity of the dissolving brine (compare row 2 and 3 in Table 1). This means, that interstitial pore solutions, in many cases, are insufficient as a mechanism owing to their small volume. More efficient, with respect to quantity is the influx of new brines not yet saturated in KCl.

Since only bed Ac in the Alsace shows this anomalously low bromine ratio between sylvite and halite, a specific and detailed explanation of the environmental conditions leading to this anomalous ratio at present is not feasible.

A more general conclusion, on the other hand, may be derived from Table 1. If the amount of influx is higher than required for the dissolution of the younger sylvite, then the reprecipitation of sylvite is preceded by the deposition of halite. In this case, a normal bromine ratio between this halite and sylvite will be found, but graphically determined temperatures are erroneously low because the K/Mg-ratio at the beginning of sylvite reprecipitation has been increased by means of earlier sylvite dissolution.

Therefore, regardless of the details, the anomalously low bromine ratios between sylvite and halite, in the Alsace bed Ac, point to a significant reworking of earlier sylvite deposits. In addition, the distinct drop of the bromine content in sylvite towards the marginal parts of each investigated sylvite bed, might primarily indicate a higher K/Mg-ratio, rather than lower temperatures. The increase of the bromine content from bed to bed on the other hand, is understandable only in terms of a temperature increase.

Another, and much more common, anomalous partition ratio of bromine between sylvite and halite, in all the sylvite beds of the worked part of the potash seam, should be mentioned. In this case, the bromine content in sylvite is too high $\frac{\text{wt. - \% Br (sylvite)}}{\text{wt. - \% Br (halite)}} = 11-13$ instead of 70. This case, already observed and explained by Baar & Kühn (1962), and Braitsch & Herrmann (1964), is easily understood in terms of influx of new brines, which overlie more concentrated bottom brines. Halite crystallizes predominantly from the surface brines, while most of the sylvite crystallizes later from the more concentrated bottom brines. An independent proof for this assumption is offered by the increase of bromine within the individual halite beds from bottom to top, whereas the bromine content in the sylvite beds, in a first approximation, remains constant.

RUBIDIUM CONTENTS OF CARNALLITE AND SYLVITE

The problem of reworking mentioned above is important from a geological, as well as a paleogeographical, point of view. Therefore, an independent indicator is desirable. Rubidium content is of some use in this respect. Earlier studies by R. Kühn (1963) showed an anomalously high rubidium content in a carnallite sample from the mine Amelie in the Alsace. His value, although higher than all values of this report, was roughly confirmed by a set of rubidium determinations in a complete section through bed E (in the sense of Sturmfels, 1943) taken from the area of maximum carnallite thickness in the Alsace basin.

The results are shown in Fig. 5, together with the carnallite content (carnallite content determined by Dr. H. Eghbali). The rubidium content of pure carnallite, in the lower part of the

carnallite section, decreases slightly and then remains roughly constant at about 0.1% Rb/Carnallite. In addition, the rubidium content of the footwall sylvite beds, and of the sylvite intercalations in carnallite, are shown. They are about one order of magnitude lower than the rubidium contents of carnallite.

The average values, and the ranges of the rubidium concentrations observed in different horizons of bed E, are assembled in Table 2. In addition, a few determinations from the two beds Ba and Bb, immediately underneath the worked part of the potash seam, are included for comparison. Two points are remarkable:

1. The average rubidium content at the beginning of sylvite crystallization, represented by bed Ba and Bb, is roughly half the rubidium content at the transition to the carnallite deposition (bed E).
2. The average rubidium content of the sylvite beds immediately underneath the carnallite beds is roughly half the rubidium content of sylvite intercalations within the carnallite bed.

THEORETICAL RUBIDIUM DISTRIBUTION AND DISCUSSION

To interpret these facts, theoretical models of the rubidium partition were calculated. The partition factors of rubidium between the solution and the solids were experimentally determined at 25°C and at 83°C. This work is not yet finished and true partition equilibria are not yet confirmed, but a highly interesting fact is already clearly indicated, namely a large negative temperature coefficient at the partition factor for the rubidium uptake of carnallite. At 25°C the partition factor

$$b = \frac{\text{wt. - \% Rb (Carnallite)}}{\text{wt. - \% Rb (solution)}}$$

equals 22 ± 1 and at 83°C only 10 ± 1 . The partition factor for the rubidium uptake of sylvite, on the other hand, seems to remain nearly constant at about 2. Unfortunately, the experimental error in this case is not yet established. McIntyre's (1963, table 5) results in the system KCl-RbCl-H₂O show a distinct increase of rubidium uptake by sylvite with rising temperature. This question will be studied in more detail later. But the data available are sufficient to interpret the geochemical facts, at least qualitatively.

A theoretical model using the rubidium content of present day sea water (Bolter & al., 1964) for 25°C is shown in Fig. 6. During sylvite deposition, the rubidium content should increase only by a factor of 1.2, namely from 17 to 20 ppm. The observed values were 60 and 120 ppm respectively. The absolute values as well as the degree of increase are much higher than predicted. This clearly points out that we don't have a normal continuous evaporation process. The same discrepancy between calculated and observed values is found in the carnallite region. The decrease of the rubidium content in the carnallite region is only slight, and in the upper part of bed E_k an anomalous increase was observed. The high absolute rubidium content most likely has to be interpreted -- as have been pointed out earlier by R. Kühn (1963) -- as a reprecipitation of carnallite, which has been dissolved in marginal parts of the basin or in an adjacent basin. At least two major phases of dissolution and reprecipitation within horizon E itself are indicated, namely at the base of bed E_b, and at the base of bed E_k. In addition, a similar explanation probably applies to the very slight drop of the rubidium content within the carnallite region. The anomalous increase of the rubidium content immediately at the base of the carnallite bed (Fig. 5) could be a result of secondary carnallite crystallization, but in this case other explanations are also possible.

Therefore, the rubidium contents confirm the suggestion of reworking, or second cycle, salt deposition. During the sylvite deposition an even more specific assumption is required, namely the dissolution of carnallite in marginal parts, or in adjacent basins, because the dissolution of sylvite would not increase, but decrease, the rubidium content of sylvite. This situation arises because the product qb in equation (1) is less than 1 for the sylvite deposition stage.

* I am greatly indebted to Dr. R. Goguel, who developed the method of rubidium analysis by atomic absorption spectrophotometry as well as of the preparation of crystals. In addition, the diligent and skillful assistance of W. Ohmacht is highly appreciated. The values obtained will be checked by an independent method in the near future. The work was made possible by the Deutsche Forschungsgemeinschaft in providing the PERKIN-ELMER atomic absorption spectrophotometer.

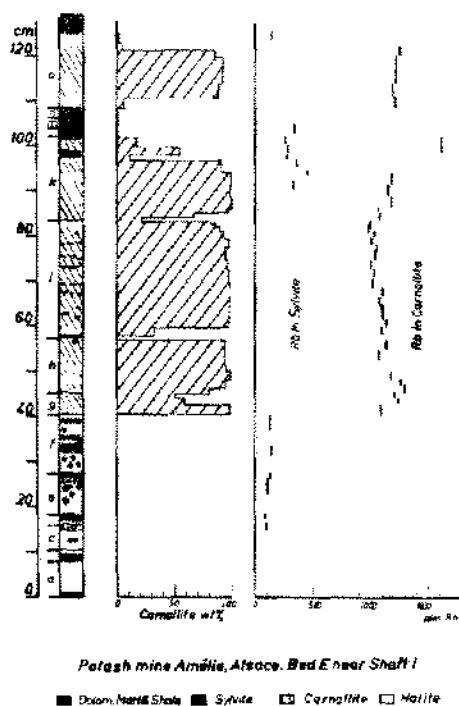


Figure 5. Rubidium content of sylvite and carnallite from the mine Amélie in the Alsace.

THEORETICAL RUBIDIUM DISTRIBUTION MgSO₄-free Sea-Water

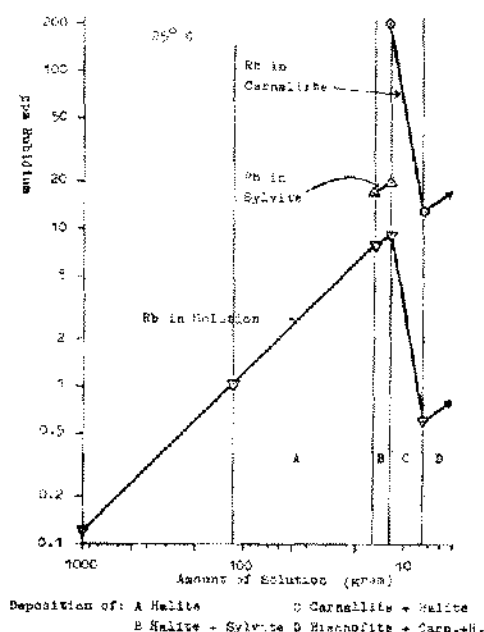


Figure 6. Theoretical model using the rubidium content of present day sea water illustrates the relationship between rubidium in brine and rubidium in sylvite and carnallite crystallizing from brine. The model is for MgSO₄ free sea water at 25° C.

Table 2
Rubidium Content (ppm) in Sylvite and Carnallite
(Upper Rhine Valley Evaporites)

| Bed STURMFELS | av. | Sylvite range | Z | av. | Carnallite range | Z |
|------------------|-----|------------------|----|-------------|---------------------|----|
| E o | | | | 1360 | 1170 1670 | 6 |
| E k-o | 216 | 252 183 | 5 | 1620 | 1620 | 2 |
| | | | | 1100 | 1180 1000 | 5 |
| E i | | | | 1060 | 990 1150 | 17 |
| E h | | | | 1200 | 1090 1310 | 5 |
| E g | | | | 1190 | 1250 1090 | 3 |
| E c-f | 117 | 141 93 | 6 | not present | | |
| B a + B b | 57 | 67 47 | 12 | not present | | |

Additional work on 5 more carnallite sections of minor thickness is in progress to check the results obtained on the standard section. Furthermore, the experimental determination of the rubidium partition factors will be refined and extended to intermediate temperatures. This might eventually result in a special geothermometer. Because of the strong temperature dependency of the partition factor for rubidium in carnallite, this geothermometer need not to be based on absolute contents as is the case with the bromine thermometer, but it can be based on the proportion of rubidium in carnallite to rubidium in sylvite, at the primary transition from the sylvite to the carnallite region. This transition corresponds with an invariant point on the crystallization path, and, therefore, it refers to a constant K/Mg ratio, neglecting possible CaCl_2 -contents, or small additional MgSO_4 -contents.

CONCLUSION

In conclusion, the trivial fact should be recalled, that with one parameter, only one variable can be fixed. In this study three parameters were used, i.e., the bromine ratio between sylvite and halite, the absolute bromine content of sylvite and the rubidium contents of sylvite and carnallite. Therefore, in principle, three independent environmental factors should be determinable. The major results include (1) a significant temperature increase at the beginning of the sylvite deposition from about 10 to about 50°C, (2) a significant concentration gradient within the salt lake, which either corresponds to an equivalent temperature gradient or perhaps more probably to a variable K/Mg ratio in the brine, and (3) a significant reworking of sylvite, as well as of carnallite, in marginal parts of the basin, or in adjacent basins. Rubidium appears to be a sensitive indicator of these recycling processes.

Many problems remain:

I shall mention only,

the full significance of the horizontal gradient of the bromine content in the same bed, the reconstruction of the composition of the brine at individual stages of the crystallization path, particularly the fixation of the K/Mg ratio at the beginning of the sylvite precipitation, which perhaps could be investigated by Holser's method of analysis of liquid inclusions, the paleogeographic problems of a shrinking lake area versus a constant brine level.

Regardless of these open questions, one case, in contrast to statements of Borchert (1959) and Borchert & Muir (1964) appears to be clearly established, namely the primary nature, including synsedimentary recycling, of the potash ores.

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