

# Saltworks—Natural Laboratories for Microbiological and Geochemical Investigations During the Evaporation of Seawater

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## ABSTRACT

Saltworks like those of Sečovlje (Portorož, Yugoslavia) can be used as a model for the study of microbiology and geochemistry of evaporite sequences. The physicochemical environment is significantly modified by the presence and activity of microorganisms. Under natural conditions precipitation takes place for  $\text{CaCO}_3$  from 6.2 times, for  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  from 2 times, and for NaCl from 1.3 times oversaturated solutions with respect to stable equilibrium conditions. The sediment microzones with relating redox-gradients which are developing in the algal mats on evaporation pan floors in the saltworks have a strong influence on the mobilization and fixation of iron as well as on the production of white solar salt.

Temperature gradients were measured in seawater concentrated up to  $\text{CaCO}_3$  and NaCl saturation. The temperature in the surface of the NaCl saturated seawater was  $2^\circ\text{--}4^\circ\text{C}$  higher in comparison to the  $\text{CaCO}_3$  saturated seawater. At noontide the air temperature was  $3^\circ\text{--}9^\circ\text{C}$  lower than the temperature of the NaCl saturated solution on the surface. In a depth of 10 cm below the solution surface, no distinct temperature difference between  $\text{CaCO}_3$  and NaCl saturated solution was measured.

New Br partition coefficients for the first halite crystallized from evaporated modern seawater in the salt pans of Sečovlje are presented. The bromide content in the halite corresponds to an average coefficient of  $b_{\text{halite}} = 0.14 \pm 0.02$ .

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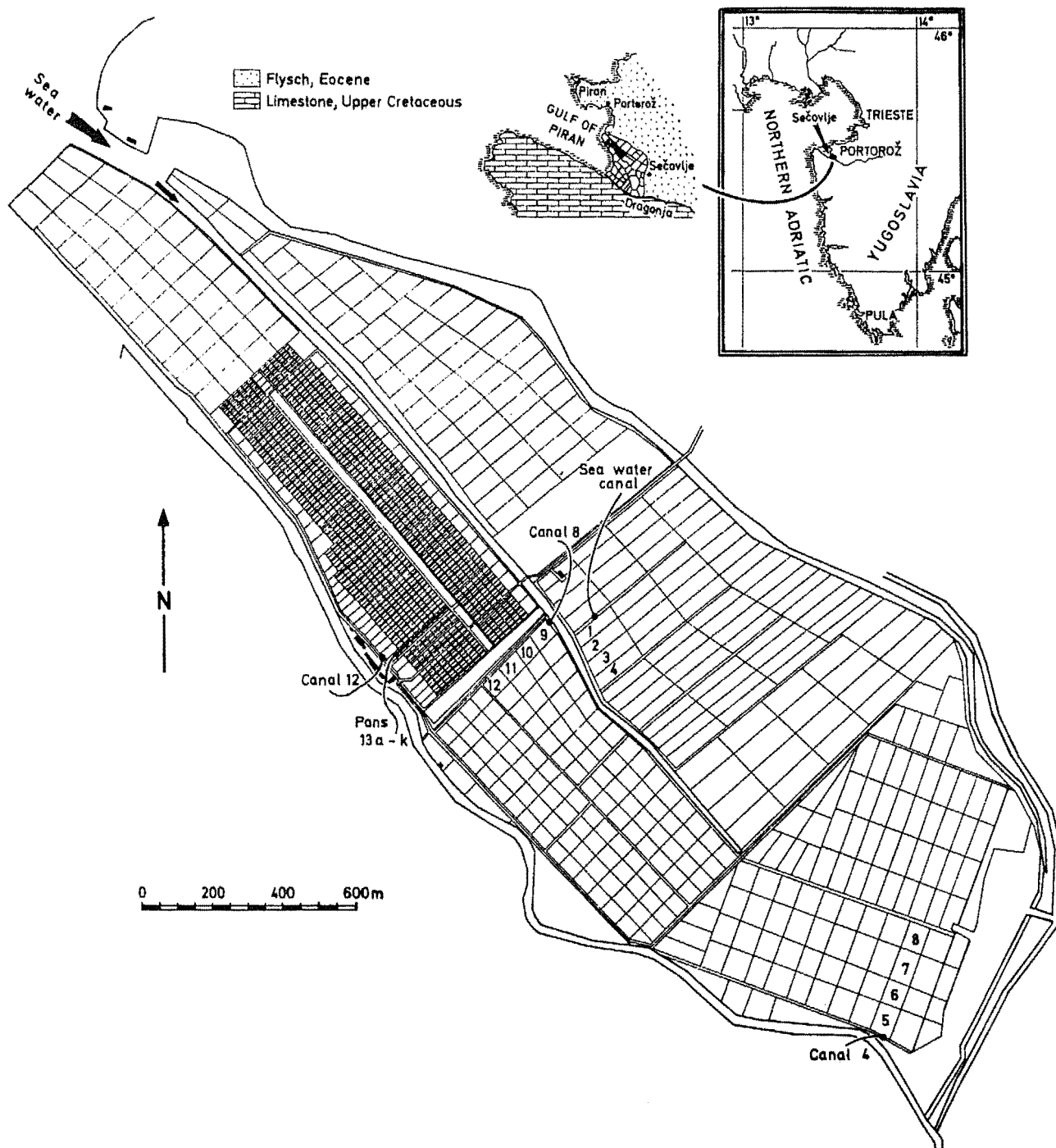
## INTRODUCTION

Within the last 100 years scientific investigations have been carried out in salt mines, salt lakes, saltworks (salinas) and in laboratory experiments. The reason for these studies was to develop genetic models for fossil salt deposits. Unfortunately, there is no modern example of a suitable scale for investigations on the conditions of formation of marine salt deposits. Evaporite formation under natural conditions in salt lakes with more or less continental influences has been much more intensively studied than the evaporite formation from seawater in saltworks (salinas) (saltworks, e.g.; Usiglio, 1849 (1924), v.d. Meer Mohr, 1972; Herrmann et al. 1973; Davis, 1974; salt lakes, e.g. Dzents Litovskiy, 1957; Irion, 1970, 1973; source of information: Lefond, 1969).

An advantage of marine saltworks is that it is possible to study the different stages of evaporation of seawater from carbonate precipitation to halite crystallization simultaneously within a few hours and under nearly unvarying meteorological conditions. The following results are part of a program in which possible correlations were sought between salt formation in marine saltworks and the formation of fossil salt deposits.

The saltworks of Sečovlje in Yugoslavia, which we studied in 1972 and 1977, are situated in the Gulf of Piran south of Trieste (Italy). The river Dragonja and the Gulf of Piran are bordered in the north by the Eocene flysch series and in the south by Upper Cretaceous limestone (Fig. 1).

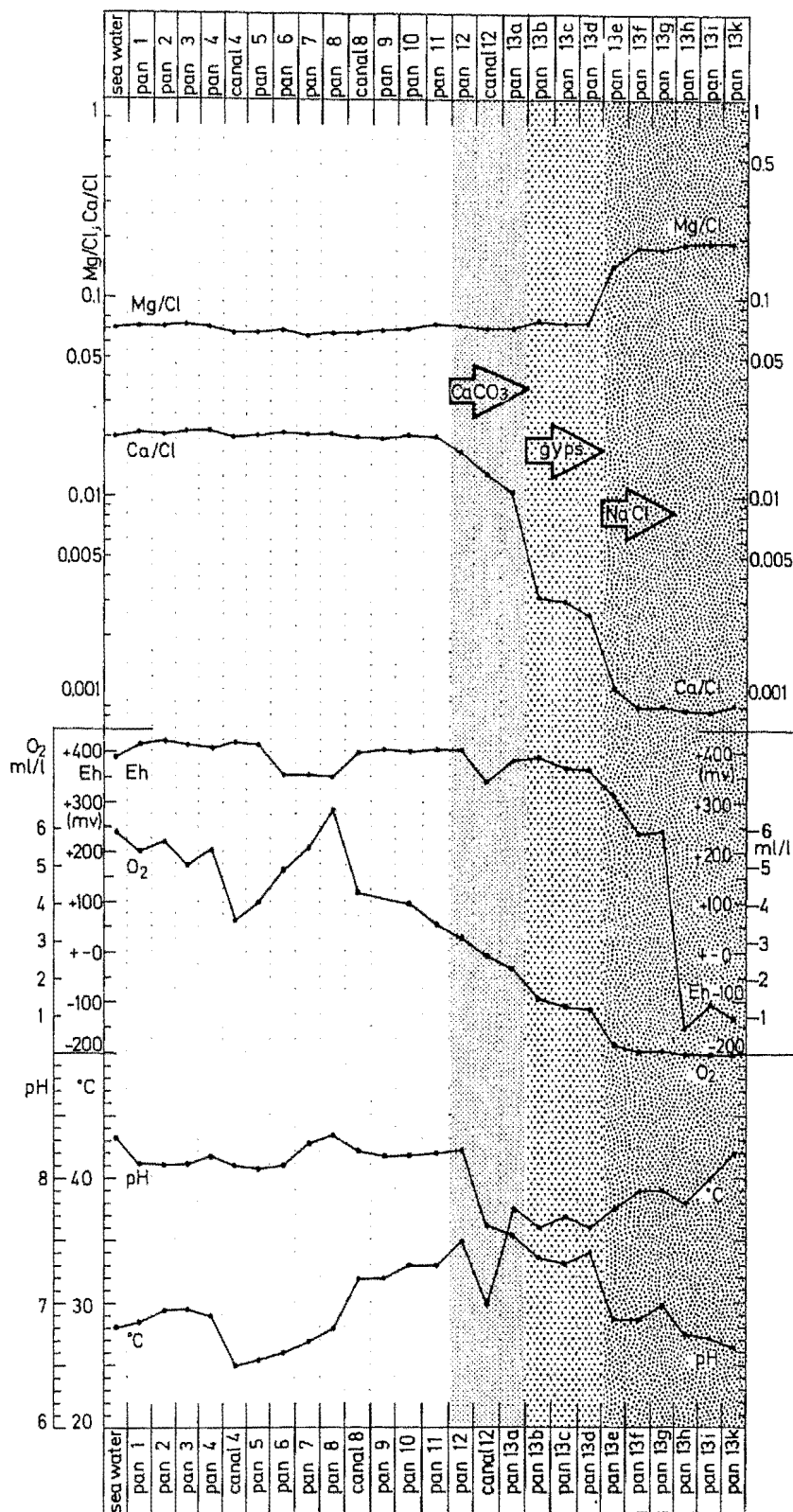
An organized salt production has existed for more than 700 years without any principal change in the technique.



**Figure 1.** Geographical and geological situation and plan of the salt works of Secovlje near Portorož, Yugoslavia. 1–13 = numbers of evaporation pans (see Fig. 2). From Herrmann et al., 1973.

The flysch material (sand, silt and clay) builds the delta of the river Dragonja. It serves as material for the construction of evaporation pans and channels in the saltworks. The evaporation of seawater occurs step by step in 16 pans and in 3 channels until the first halite crystallizes. The first 10

pans are pans for evaporation of seawater without any remarkable precipitation of minerals. From pan 11 to pan 13  $\text{CaCO}_3$  precipitation occurs, from pan 13b to pan 13d  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  precipitation occurs and from pan 13e on NaCl crystallization appears (Fig. 2).



**Figure 2.** Some important geochemical data from the various concentrated solutions and brines in the saltworks of Sečovlje (after Herrmann et al., 1973). The differently pointed fields indicate from left to right: concentration of seawater, precipitation of  $\text{CaCO}_3$ , precipitation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , precipitation of  $\text{NaCl}$ .

### THE INORGANIC PRECIPITATION OF $\text{CaCO}_3$ , $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ AND $\text{NaCl}$

Looking at the inorganic calcium carbonate crystallization under natural conditions, we find that a seawater which is about 388% oversaturated with respect to aragonite must be concentrated 4 times prior to an inorganic precipitation of  $\text{CaCO}_3$ . The  $\text{Ca}/\text{Cl}$  ratio (Fig. 2) indicates that the first precipitation of  $\text{CaCO}_3$  happens in pan 12. In natural waters the following mechanisms could be responsible for inhibition of carbonate precipitation: Inorganic complexation and ion pair building of carbonate ions (Garrels et al., 1961) partly with  $\text{Mg}$ -ions (Pytkowicz, 1973) and organic complexation of  $\text{Ca}$ -ions (e.g. Suess, 1970, Pytkowicz, 1973).

With regard to the precipitation of inorganic gypsum in pans 13b to 13d (Fig. 2), we find that the seawater is concentrated here 6.2 times. The additional decrease of the  $\text{Ca}/\text{Cl}$  ratio (Fig. 2) indicates the strengthened withdrawal of  $\text{Ca}$  ions during precipitation of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ . With respect to stable equilibrium conditions in the laboratory under natural conditions a nearly twofold oversaturation is necessary before the first gypsum is precipitated inorganically. It could be that inorganic and organic  $\text{Ca}$  ion complexation is also responsible for this oversaturation.

Looking at the halite crystallization in the pans 13e to 13k, we find that  $\text{NaCl}$  crystallizes partly at the brine surface in the form of "hopper crystals" (upside down pyramids) and partly as regular cubes at the pan bottom (Fig. 5). Taking the  $\text{Mg}/\text{Cl}$  ratio (see Fig. 2; no  $\text{Mg}$ -mineral crystallizes yet) as an indicator for the first halite crystallization, we note that in pan 13e the seawater is concentrated 15.9 times. This means, that under natural conditions, the halite crystallizes from a solution which is oversaturated 1.3 times with respect to stable equilibrium conditions in the laboratory.

In nature, therefore, we find smaller concentration differences between the first carbonate and the first halite crystallization than we expect from stable laboratory conditions. Therefore a smaller volume of water must evaporate between the carbonate and the halite crystallization than we expect from the conditions of stable equilibria. This could have consequences considering the length of time and the conditions of formation of saline evaporitic sediments, especially of those which show closely intercalated beds of carbonate/gypsum or gypsum/halite.

### THE ALGAL MATS

All phases of the evaporation of seawater including the halite precipitation in the saltworks of Sečovlje proceed on stromatolitic algal mats. The algal mats are comparable to the stromatolitic mats which are well known from the Bahamas (e.g. Black, 1933; Monty, 1965, 1972), from the Sebhka sediments of the Persian Gulf (Kinsman and Park,

1976), from Florida (Ginsburg, 1955), and from W-Australia (e.g. Logan and Cebulski, 1970).

The saltworks are also a useful model for geomicrobiological studies since the physico-chemical environment in every pan is well defined. The different types of algal mats and their species composition are a response to and an expression of the existing physico-chemical environment (Golubic et al., 1977). These algal mats have an influence on the salt production of the saltworks as well as for the genetic interpretation of fossil salt deposits. With regard to the saltworks as an ecosystem and its importance for salt production see especially Davis (1974, 1978 and this volume).

The algal mats grow on the sediment and stabilize its surface. This leads to the formation of characteristic sediment microzones with typical redox-gradients (e.g. Kusnezow, 1959, Fenchel and Riedl, 1970). The thickness of these sediment microzones can be measured in millimeters. According to the light demand various photoautotrophic cyanophytes and other algae (chlorophytes, diatoms etc., see e.g. Golubic, 1976) grow on the top of the algal mats producing an oxygen-rich surface layer in the sediment surface. The surface algal mat is clearly divided into a brownish colored uppermost layer (with predominantly cyanophytes as *Entophysalis*, *Lyngbya*) and a lower layer of *Microcoleus chthonoplastes* (Fig. 3).

As a result of the decay of organic material below the redox-discontinuity-layer (RDL) an anaerobic microenvironment appears where hydrogen sulfide ( $\text{H}_2\text{S}$ ) is produced by the activity of sulfate reducing bacteria. If there is enough light, the photosynthetically active purple bacteria which precipitate elementary sulfur within their cells form a *Chromatium* "plate" beneath the RDL. This "plate" is very well visible as a purple red layer (Fig. 3).

### MODEL OF MOBILIZATION OF IRON IN THE ALGAL MAT

Iron, which is bound on clay and other minerals, and which is dissolved also in the pore water, is in solution as  $\text{Fe}^{++}$  underneath the RDL and precipitates as  $\text{Fe}^{+++}$  hydroxide above the RDL. This is possibly due to a mobilization and upward migration as  $\text{Fe}^{++}$  within pore water or by diffusion. Under the RDL,  $\text{Fe}^{++}$  could be fixed as  $\text{FeS}$  or  $\text{FeCO}_3$  (Fig. 4), see e.g., Borchert, 1960; Braun, 1964; James, 1966).

It should be noted that in this high productivity microenvironment of such an algal mat, the redox gradients are very high (more than 500 mV Eh-difference between, above and below the RDL, (Fig. 5).

Other genetic models of  $\text{Fe}^{++}/\text{Fe}^{+++}$  distribution within sediments are valuable for pelagic marine sediments as described by Franke and Paul (1980) for Devonian red beds.

In cross sections of algal mats the  $\text{Fe}^{++}$  iron precipitate is

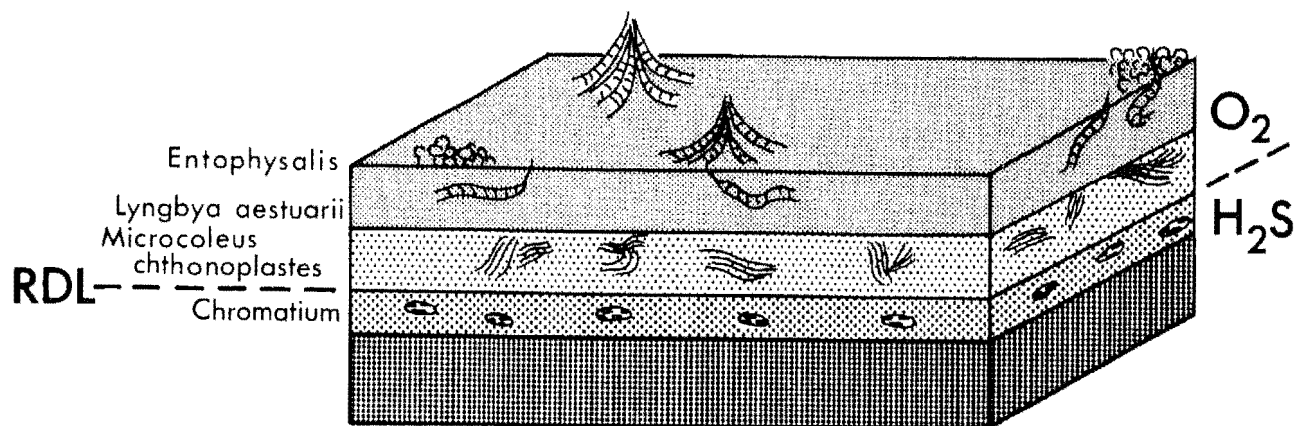


Figure 3. Characteristic sediment microzonation of a stromatolitic algal mat. RDL = Redox-Discontinuity-Layer (= border between aerobic and anaerobic environment). Thickness of the living algal mat above the RDL, approximately 1–3 mm. On the surface, "tufts" of *Lyngbya aestuarii*.

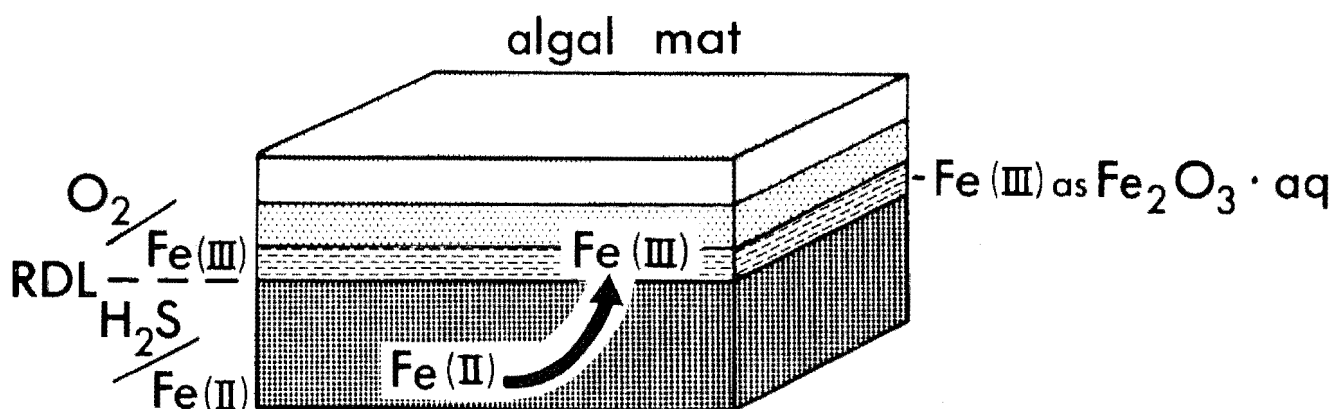


Figure 4. Possible model for the mobilization of iron in a stromatolitic algal mat. RDL = Redox-Discontinuity-Layer (= border between aerobic and anaerobic environment). Thickness of the layers above the RDL approximately 1–3 mm. The layer above the RDL ( $\text{Fe}^{\text{III}}$ ) is rusty red in color.

very good visible directly above the RDL as a rusty red layer. This iron hydroxide leaks out of the sediment on furrows and edges in the form of small streamlets.

Whether any iron bacteria (e.g. Hanert in Puchelt et al., 1973) take part in the precipitation of iron hydroxides has not yet been studied. Further and more detailed investigations on the algal mats of the saltworks are in progress.

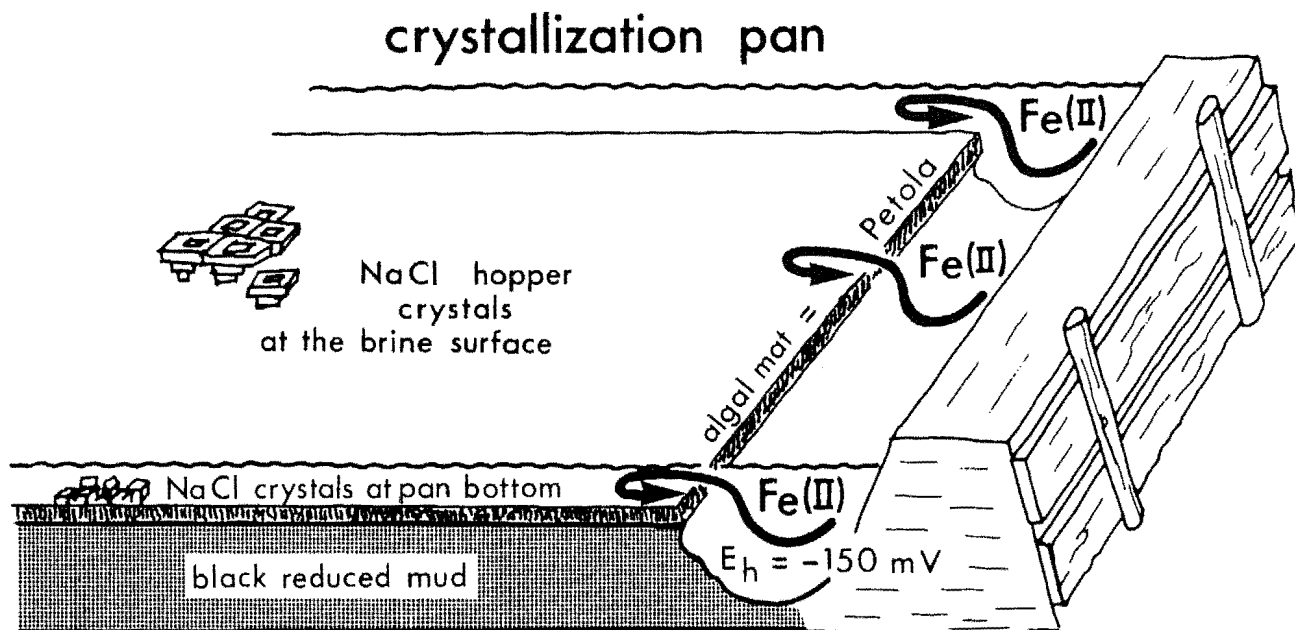
Such a microbially induced mobilization of iron from flat shelf areas or from Sebhka plains might be a supply of the iron content in sylvinites and carnallites in evaporitic basins of fossil salt deposits.

#### THE INFLUENCE OF MICROBIAL PROCESSES ON THE SALT PRODUCTION

The brine in the NaCl crystallization pans must be agitated frequently to prevent a salt crust formation on the brine

surface which would hinder further evaporation. Therefore the salineros (workers in the salinas) stir up the brine frequently in the crystallization pans, thereby bringing the microbially reduced and reducing mud from the surrounding channel into the brine with the crystallizing salt (Fig. 5).

The Petola-mat is built by *Microcoleus chthonoplastes* (in this extreme environment the only surviving cyanophyte) which is intergrown with crystals of carbonate, gypsum and halite. This Petola is broken through in the surrounding channels. The underlying reduced and reducing black mud is therefore exposed and causes a reducing environment in the brine ( $-150 \text{ mV Eh}$ , see Herrmann et al., 1973) so long as the salineros stir it up. Therefore the iron dissolved in the brine is held in solution as  $\text{Fe}^{++}$ , so hindering a red or brown coloration of the solar salt. (Inexperienced younger salineros who do not mix the reducing mud with the brine always produce a reddish colored salt).



**Figure 5.** NaCl crystallization pan with stable algal mat (*Petola*) above the reduced mud. In the surrounding channel (width and depth about 10 cm) the algal mat is broken through. On the brine surface "hopper"-crystals grow in form of small upside-down pyramids; on the bottom grow well developed NaCl cubes. Thickness of the *Petola*: 0.5–1 mm.

The salt is piled up in the crystallization pans, loaded on carts and finally stored in great stockpiles. While the reducing solution is further drained and the salt gets white. The white color of the solar salt is therefore ultimately caused indirectly by microbial activity. This process has been used by the salineros for more than 700 years without their having any knowledge of the geobiological reasons.

The studies in saltworks can give answers to many questions about the interrelationships between inorganic and organic (geomicrobiological) processes during the formation of salt deposits (see also Davis, 1974, 1978 and this volume) and the diagenesis of sediments.

Purely inorganic processes, which are of highest importance for the science of salt deposits were also investigated in saltworks. Two examples are given as follows:

#### EXAMPLE 1—TEMPERATURE GRADIENTS IN DIFFERENT STAGES OF CONCENTRATED SEAWATER

Horizontal and vertical temperature changes can be measured during evaporation of salt solutions under natural conditions (e.g. Dzons-Litovskiy, 1957; Gregg, 1973; Kalecsinszky, 1901; Lew, 1977; Sonnenfeld et al., 1976). For reconstructions of the temperature distribution in salt basins of the geological past information must be available about a different heating of several concentrated seawater solutions in the case of the same climatic conditions. Such

an effect depends on several possible reasons like absorption of solar radiation and others (e.g. Harbeck Jr., 1955; Hoare, 1966; Shirlcliffe, 1964; Turner, 1967). One of the reasons seems to be also the specific heat which decreases with increasing NaCl-, KCl- and MgCl<sub>2</sub>-concentrations in aqueous salt solutions.

Four horizontal temperature profiles are plotted in Figure 6 for the surface and a depth of 10 cm below the surface of the solutions. The concentration of seawater corresponds to two different stages of evaporation: 1) CaCO<sub>3</sub> saturation; 2) beginning of NaCl saturation. The two solutions were evaporated in different pans. The depths of the CaCO<sub>3</sub> saturated solution was measured with 15 cm, and of the NaCl saturated brine with 10 cm. Figure 6 shows that the temperature in the surface layer of the NaCl saturated seawater is 2°–4°C higher in comparison to the CaCO<sub>3</sub> saturated seawater. At noon the air temperature is 3°–9°C lower than the temperature of the NaCl saturated solution on the surface. During the night no temperature difference between air and solution was measured. Also, at the depth of 10 cm below the solution surface, no distinct temperature difference between CaCO<sub>3</sub> and NaCl saturated solution was measured. The increasing solution temperature with increasing seawater concentration is limited to the surface of the brine. The maximum air and solution temperatures correspond to a minimum of relative air humidity. August 9, 1977 was a rainy day and therefore the absence of a relative air humidity minimum (Fig. 6).

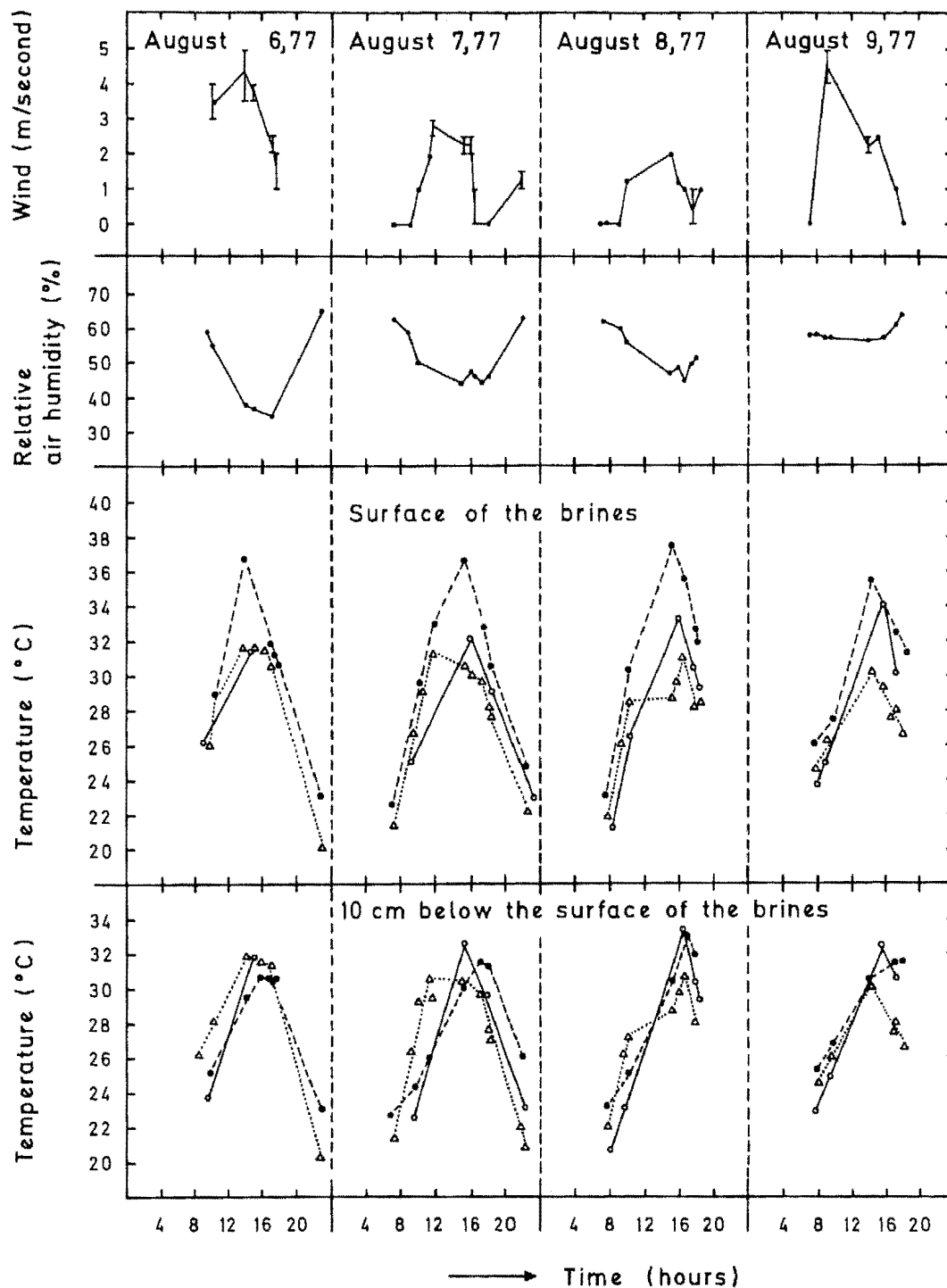


Figure 6. Horizontal temperature gradients in seawater concentrated up to  $\text{CaCO}_3$  and  $\text{NaCl}$  saturation.

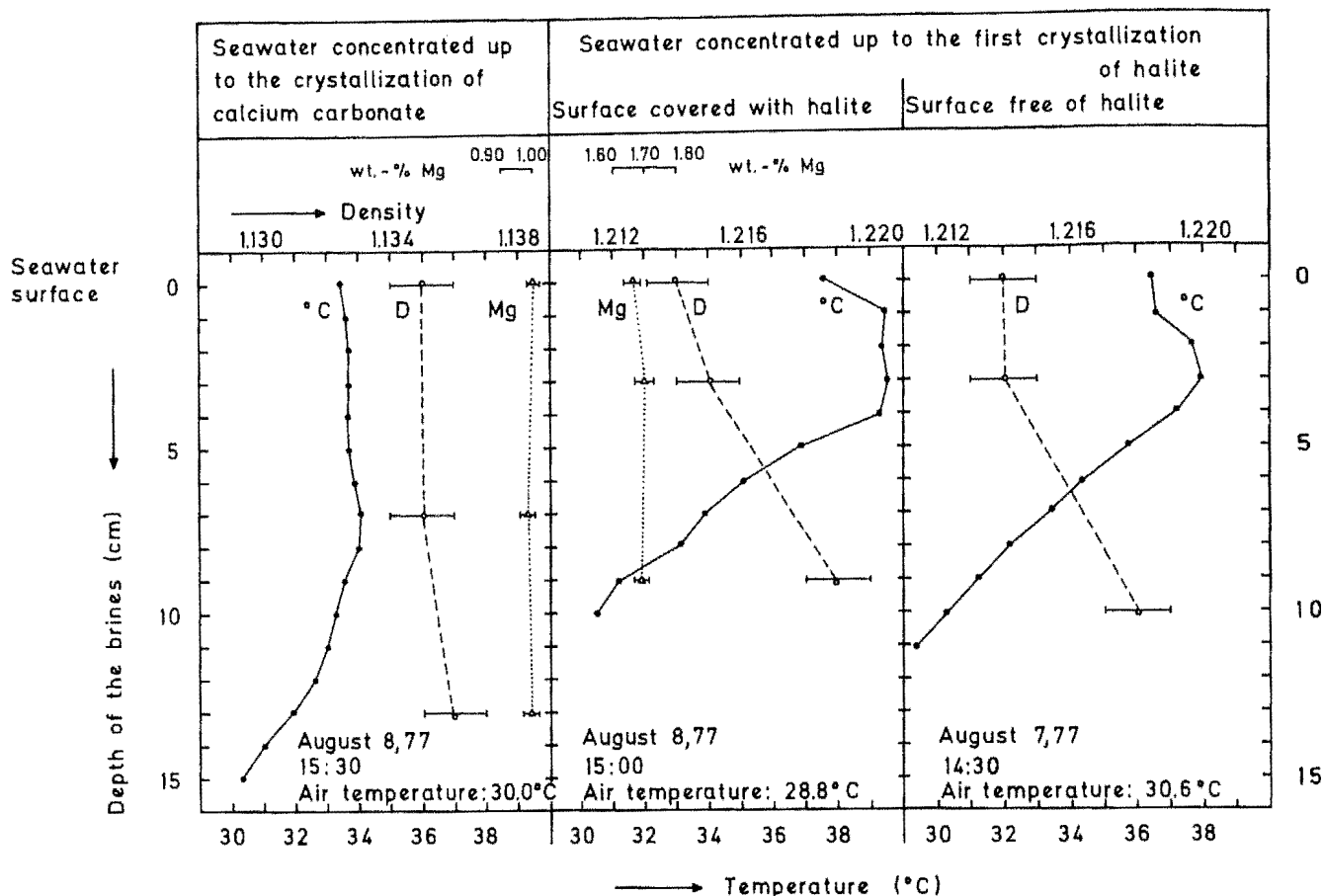


Figure 7. Vertical temperature gradients in seawater concentrated up to  $\text{CaCO}_3$  and  $\text{NaCl}$  saturation.

Similar results are demonstrated by vertical temperature profiles (Fig. 7). While thermoclines are developed in 1–4 cm depth of the  $\text{NaCl}$  saturated solution, no typical temperature maximum could be measured in the  $\text{CaCO}_3$  saturated solution. The temperature of the  $\text{CaCO}_3$  saturated solution was 4°–5°C lower than the  $\text{NaCl}$  saturated brine. Thermoclines are described from many salt lakes and lagoons. Different reasons for their explanation are possible: e.g. layers of different densities in the solution, crystallizing of minerals, and muddy material suspended in the brines. In Figure 7 no differences in the chemical composition (e.g. Mg concentration) and the brine density are the reason for the thermoclines in the  $\text{NaCl}$  saturated solution. The increasing density values in the lower part of the solution are dependent on a cooling effect of the brine.

Gradients of temperature and density in the Oligocene salt lagoon of the upper Rhine Valley were reconstructed 15 years ago by application of the Br-thermometry (Braitsch, 1962, 1966, 1971; Braitsch and Herrmann, 1964, 1965; Herrmann, 1977). The temperature increases vertically from the bed Bar to Bbr in the central part of the salt lagoon from about 20° to about 50°  $\pm$  10°C. A horizontal increase of about 10°C in temperature for each potash bed was also

found from the shore to the center of the lagoon. These results seem to be understandable, considering the temperature inhomogenities which occur in recent natural salt brines. The increasing salt concentration in the salt lagoon of the upper Rhine Valley was certainly accompanied by a decrease of the specific heat of the solution. Maybe this effect is one of the different possible reasons for the increasing solution temperatures with increasing salt concentration. The more concentrated, and therefore also warmer, solutions migrated from the shore to the center of the lagoon. Because KCl has a very strong positive temperature coefficient of solubility, sylvite crystallizes as a result of the cooling which occurs as the saturated solutions sink from the surface into the lower parts of the lagoon.

#### EXAMPLE 2—BROMIDE DISTRIBUTION BETWEEN HALITE AND $\text{NaCl}$ -SATURATED SEAWATER

Important information on the genesis of salt mineral associations and for the exploration of salt deposits depend on the bromide concentration and distribution in chloride minerals. The bromide distribution coefficients



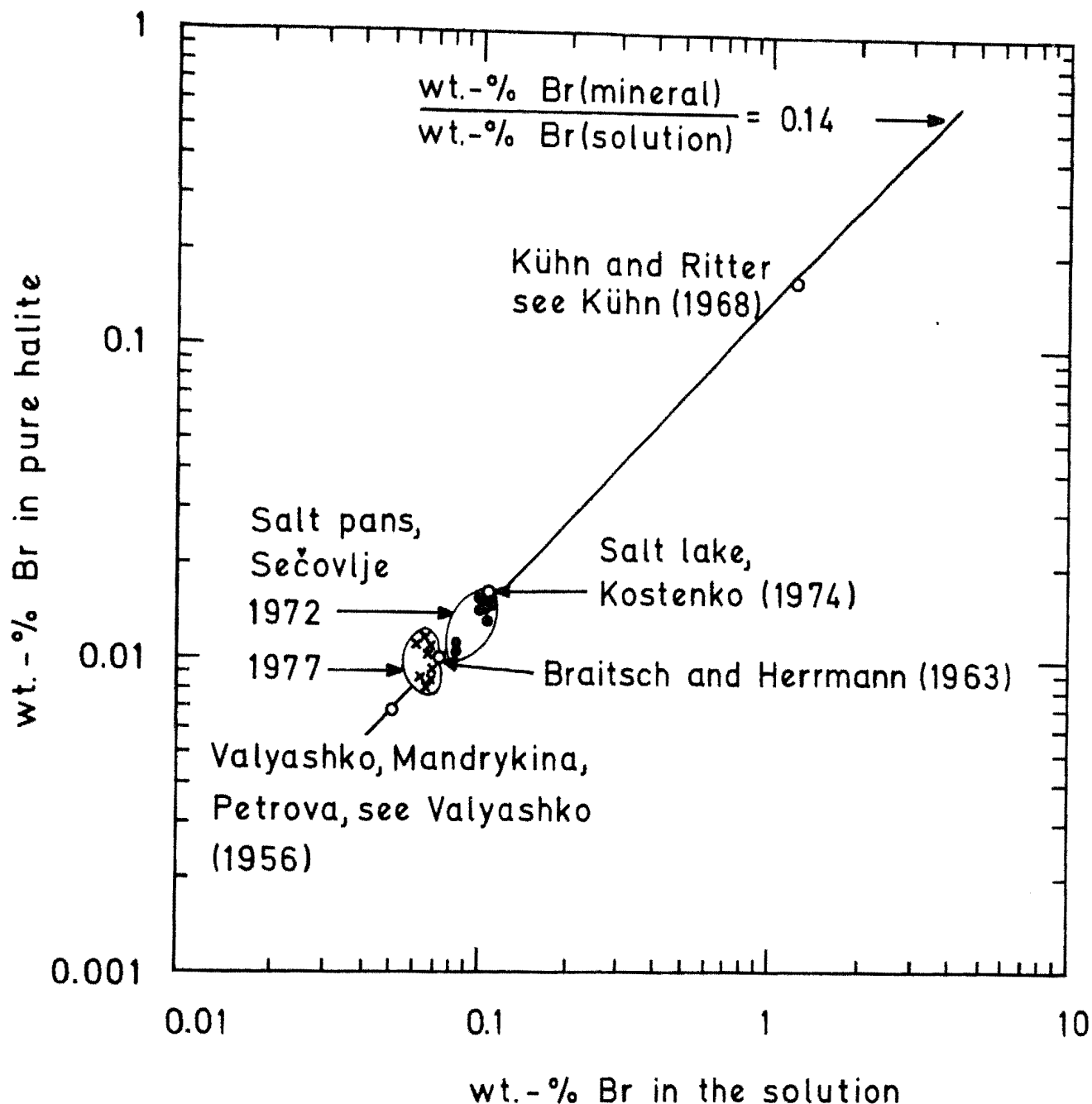


Figure 8. Bromide distribution between seawater and the first crystallized halite.

$b = \frac{\text{wt.-% Br (mineral)}}{\text{wt.-% Br (solution)}}$  are well known for all important chloride minerals in salt deposits. There was no agreement only in the the data of partition coefficient for the beginning of halite crystallization from seawater. Distribution coefficients determined by laboratory experiments with halite growth rates comparable to natural conditions (e.g. Braitsch and Herrmann, 1963; Kühn and Ritter, by Kühn, 1968) and by the examination of halite crystallized in salt lakes (e.g. Valyashko, Mandrykina, Petrova, by Valyashko, 1956; Anochina and Kolosov, 1967; Kostenko, 1974) varies in the

range  $b_{\text{halite}} = 0.14 \pm 0.02$  (Fig. 8). In contrast Puchelt et al. (1972) and Lutz (1975) published a partition coefficient about 3 times lower ( $b_{\text{halite}} = 0.053$ ) for a NaCl single crystal growth in aqueous solutions. This value contrasts to all geochemical and petrographic criterias for primary and secondary halite in potash and salt deposits. Therefore a critical examination of this problem was necessary (Herrmann, 1972, 1977; Herrmann et al., 1973). New Br partition coefficients for the first halite crystallized from evaporated modern seawater in the salt pans of Sečovlje are presented in Figure 8. The bromide content in the halite cor-

responds to an average value of  $b_{\text{halite}} = 0.14 \pm 0.02$ . The influence of the growth rates of NaCl of the Br partition coefficient for halite is demonstrated by the 1977 results (Fig. 8). Halite which crystallizes faster on the surface of the solution in the salt pans has a higher Br partition coefficient than the NaCl which crystallizes more slowly at the bottom. The difference between all the results shown in Figure 8 and the values published by Puchelt et al. (1972) and Lutz (1975) can be explained by different growth rates in the laboratory experiments of Puchelt et al. (1972) and the halite crystallization under natural conditions. This effect is well known and already mentioned by Schobert (1912).

It is proposed that in arriving at conclusions about evaporite forming processes in the past, results from salt deposits, recent evaporite formation and laboratory experiments should be considered. Example 2 (Br partition coefficient) demonstrates the problems which result in the case of generalization of unspecific laboratory experiments used for the explanation of evaporite forming processes.

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