

## Short Communications

# Bromine Distribution Coefficients for Halite Precipitated from Modern Sea Water under Natural Conditions

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The content of bromine replacing chlorine in its minerals can be used to obtain information on the formation of marine salt deposits under the following presumptions:

1. Knowledge of the bromine contents in coexisting chlorides.
2. Knowledge of the bromine partition coefficients

$$b = \frac{\text{wt.-% Br (mineral)}}{\text{wt.-% Br (solution)}} \text{ or } D = \frac{\text{Br/Cl (mineral)}}{\text{Br/Cl (solution)}}$$

for natural systems at various isotherms.

There is no agreement on the data of partition coefficients for halite crystallized at low  $\text{MgCl}_2$  concentrations (beginning of  $\text{NaCl}$  precipitation from sea water); Table 1, see also discussion by Holser (1966). In order to get reliable data under natural conditions it is necessary to study halite precipitated from concentrated sea water in artificial salt pans. In a first program 12 halite samples and the residual solutions were analyzed from 6 different basins of the salt works Sečovlje near Portorož, Yugoslavia. The bromine distribution coefficient varies in the range  $b_{\text{halite}} = 0.12$  to  $0.14$  (Table 1). The uncertainty of the determinations is  $b = \pm 0.01$ . These values agree with earlier experiments by Valyashko and Petrova (1956), Braitsch and Herrmann (1963), Kühn (1968), and are valid for the first precipitate of halite from sea water of normal composition (Fig. 1).

Discrepancies in values by different authors (e.g. Puchelt *et al.*, 1972) can probably be explained by different growth rates in the experiments (as already Schobert, 1912, has mentioned). The assumption by Puchelt *et al.* (1972) to explain the different values for partition coefficients by various amounts of brine inclusions in halite is not valid. It can be shown that 1 wt.-% brine inclusions in halite would cause an increase of  $b = 0.01$  only. Thus, if  $b = 0.12$  to  $0.14$  would be effected by brine inclusions and  $b = \approx 0.053$  ( $D = 0.014$ ) from Puchelt *et al.* (1972) is the true distribution coefficient, halite investigated in this study should have 6 to 8 wt.-% of included brines. However, such a high content was never observed in halite (after washing the samples with water and ethanol absolute) from the salt pans Sečovlje. The brine inclusions of 12  $\text{NaCl}$  samples are varying from 0.25 to 0.75 wt.-% only. The calculated bromine content based on  $b = 0.12$  to  $0.14 \pm 0.01$  for the first halite precipitated from sea water is 60 to 75 ppm. Actually in many marine salt deposits from various geological ages such bromine

Table 1. Bromine partition coefficients from various authors for the initial crystallization of NaCl in different systems and in modern sea water

References	Systems	$b$	$D$	°C
Boeke (1908) <sup>a</sup>	Na <sup>+</sup>   Cl <sup>-</sup> , Br <sup>-</sup> +H <sub>2</sub> O	0.045 <sup>e</sup> 0.10 <sup>e</sup>	0.012 <sup>e</sup> 0.022 <sup>e</sup>	25 45
Bloch and Schnerb (1953/54)	sea water (Mediterranean Sea)	0.066 <sup>e</sup>	0.016 <sup>e</sup>	27.5
Valyashko and Petrova, see Valyashko (1956)	sea water	0.14 <sup>e</sup>	0.034 <sup>e</sup>	no value reported
Braitsch and Herrmann (1962), (1963)	Na <sup>+</sup> , Mg <sup>++</sup>   Cl <sup>-</sup> , Br <sup>-</sup> + H <sub>2</sub> O (≈3wt.-% MgCl <sub>2</sub> )	0.14±0.01	0.038	25
D'Ans (1967) <sup>b</sup>	not described	≈ 0.054 <sup>e</sup>	≈ 0.014 <sup>e</sup>	no value reported
Kühn (1968)	Na <sup>+</sup>   Cl <sup>-</sup> , Br <sup>-</sup> +H <sub>2</sub> O	0.13–0.14	0.033–0.036 <sup>e</sup>	30
Puchelt <i>et al.</i> (1972) <sup>c</sup>	Na <sup>+</sup>   Cl <sup>-</sup> , Br <sup>-</sup> +H <sub>2</sub> O	≈ 0.053 <sup>e</sup>	0.014	40
Herrmann and Schneider (1972) <sup>d</sup>	sea water (Mediterranean Sea)	0.12–0.14 ± 0.01 <sup>f</sup>	0.030–0.034	33–42

<sup>a</sup> If bromine is determined by a distillation method with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titration the values are normally too low (see Schobert, 1912).

<sup>b</sup> Without any description of the conditions of crystallization, bromine contents and composition of the solutions, temperatures, analytical methods etc.

<sup>c</sup> It is very difficult to get identical conditions for the crystal growth rates in thermostates and in natural salt seas and salt pans.

<sup>d</sup> Crystallization under natural conditions in the salt works at Sečovlje near Portorož, Yugoslavia.

<sup>e</sup> For this table data of several authors have been converted into  $b$  or  $D$ .

<sup>f</sup> The original values were corrected for brine inclusions and for the MgCl<sub>2</sub> concentration at the beginning of NaCl precipitation from sea water because the partition coefficient for bromine in halite is a function of the MgCl<sub>2</sub> content in marine systems (Braitsch and Herrmann, 1963).

contents can be found (e.g. Braitsch, 1971; Wardlaw, 1964). Values which are distinctly lower or higher (the total range is about 2 to 200 ppm Br for pure halite rock; see e.g. Holser, 1966) cannot be explained by primary precipitation. They are the results of recrystallization, metamorphism, and so called descendent processes in the development of marine salt deposits.

The following bromine partition coefficients were obtained for coexisting halite-sylvite and halite-carnallite from systems high in MgCl<sub>2</sub> as concentrated sea water at 25° C; halite:  $b = 0.073 \pm 0.004$  ( $D = 0.026$ ), sylvite:  $b = 0.73 \pm 0.04$  ( $D = 0.31$ ), carnallite:  $b = 0.52 \pm 0.03$  ( $D = 0.30$ ) Braitsch and Herrmann (1962), (1963), see also Kühn (1968). These data agree with observations on the absolute and relative bromine distribution in many primary mineral associations from marine salt deposits (e.g. Braitsch, 1971; Braitsch and Herrmann, 1964). The coefficient for sylvite precipitated from systems containing no MgCl<sub>2</sub> ( $b = 0.81 \pm 0.05$ ;  $D = 0.21$ ), as mentioned by Puchelt *et al.* (1972) after data from Braitsch and Herrmann (1963), cannot be used to explain the formation of sylvite rocks in marine salt deposits.

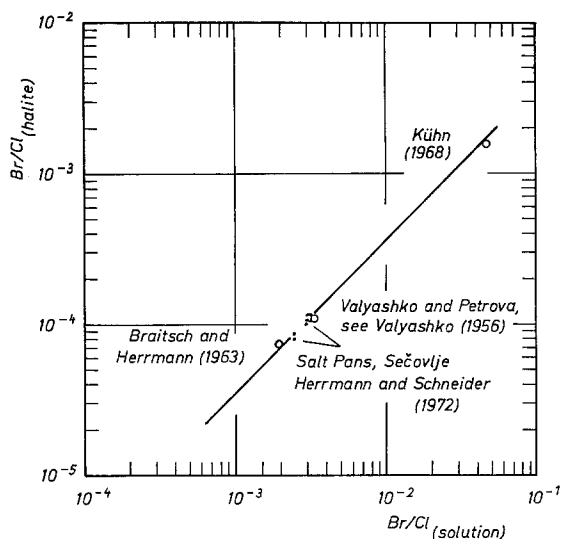


Fig. 1. Bromine distribution between NaCl and the residual solutions from sea water; salt pans Sečovlje near Portorož, Yugoslavia (see also footnote f, Table 1)

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