# Stoichiometric saturation tests of $NaCl_{1-X}Br_X$ and $KCl_{1-X}Br_X$

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**Abstract**—Stoichiometric saturation is examined as a possible control on Br contents of halite and sylvite during precipitation from binary salt solutions of NaCl-NaBr and KCl-KBr, respectively. Experimental data at 25°C, assumed to represent stoichiometric saturation, were used to predict mole fractions of NaBr in halite and KBr in sylvite in thermodynamic equilibrium with fluids as a function of aqueous activity ratios of $Br^-:Cl^-$. The predictions are based on the additional assumption that the aqueous activity product of the major salt component in the precipitated salt was independent of the trace Br content in the salt lattice. The extension of the predictions to diagenetic pressures and temperatures is discussed.

The predicted equilibrium Br content of halite at initial halite saturation of evaporating seawater is in close agreement with that computed from the distribution coefficient of LUTZ (1975), measured in slow-growth single crystal experiments. Fluid recrystallization of halite and sylvite at near-surface temperatures is predicted to generally deplete the Br contents in the solids. Bulk Br contents in halite in cap-rock of Gulf Coast salt domes generally agree with those predicted by the recrystallization of halite in the presence of evaporative-concentrated seawater. At a constant solution composition, increasing temperature results in increasing the equilibrium Br content of halite, making less efficient Br depletion in halite by recrystallization.

## INTRODUCTION

GEOCHEMISTS USE bromide (Br) as a genetic indicator for subsurface brines because of its chemically inert character (RITTENHOUSE, 1967). For example, brines produced by the evaporation of sea water have characteristic ratios of Br to other constituents. In some cases Br data on brines associated with deeply buried evaporites can be used to reconstruct the brine composition at the time of evaporite deposition (CARPENTER, 1978; CARPENTER and TROUT, 1978). The low Br:Cl ratios in brines produced by dissolution of halite together with other characteristic ratios can sometimes be used to estimate the contribution of dissolved halite to the total dissolved solids in a subsurface brine.

STOESSELL and MOORE (1983) noted that Br concentrations and relationships in subsurface brines might be altered by the release of Br from halite as a result of recrystallization and suggested that this process may produce significant amounts of Br-rich brines. The purpose of this report is to present a basis for predicting the distribution of bromide between brines and halite and sylvite during recrystallization and the effects of recrystallization on the interpretation of Br concentrations and relationships in subsurface brines.

Experimental determinations of the empirical Br distribution coefficient in halite precipitating from concentrated brines have produced a wide range of values (see HERRMANN, 1980, for a discussion). These data indicate that increasing aqueous Mg concentrations, decreasing rates of precipitation, and subsequent recrystallization can act to lower the Br salt content. In general, the Br content in freshly precipitated halite does not appear to be in thermodynamic equilibrium with the associated fluid.

Less experimental data are available for sylvite. However, the distribution coefficient of Br in sylvite is lowered by increasing the Mg content of the solution from which the salt precipitated (BRAITSCH and HERRMANN, 1963). In addition, the distribution coefficients measured for sylvite precipitating from Mg-rich solutions by BLOCH and SCHNERB (1953/54) vary by a factor of two. These observations and inconsistencies suggest a lack of thermodynamic equilibrium in the Br content of freshly precipitated sylvite.

The concept of *stoichiometric saturation* is used in this report to explain the fluid control on the precipitation of halite and sylvite. Stoichiometric saturation implies the solid reacts with a fluid as though it has a fixed "stoichiometric" composition (THORSTENSON and PLUMMER, 1977). The fluid maintains equilibrium with this bulk composition but not necessarily with the components making-up the solid. The latter equilibria are necessary for thermodynamic equilibrium for a fluid with a solid of variable composition.

The existence of this metastable solid is due to rapid precipitation of the bulk solid and the much slower equilibration occurring between the fluid and the components making up the solid. Recrystallization, by slow dissolution and reprecipitation, changes the solid and fluid composition in the direction of thermodynamic equilibrium. These two competing processes: rapid precipitation followed by slower recrystallization probably occur in most mineral precipitates, *e.g.,* extreme cases being opal to quartz, aragonite to calcite, and disordered dolomite to ordered dolomite. For a solid solution, if the rates of the two processes are significantly different then the bulk solid will initially be controlled by stoichiometric saturation. Future research may show that clay minerals forming at low temperatures are examples of solid solutions controlled by stoichiometric saturation.

We will *assume* stoichiometric saturation controls the initial Br content at 25°C in halite and sylvite pre-
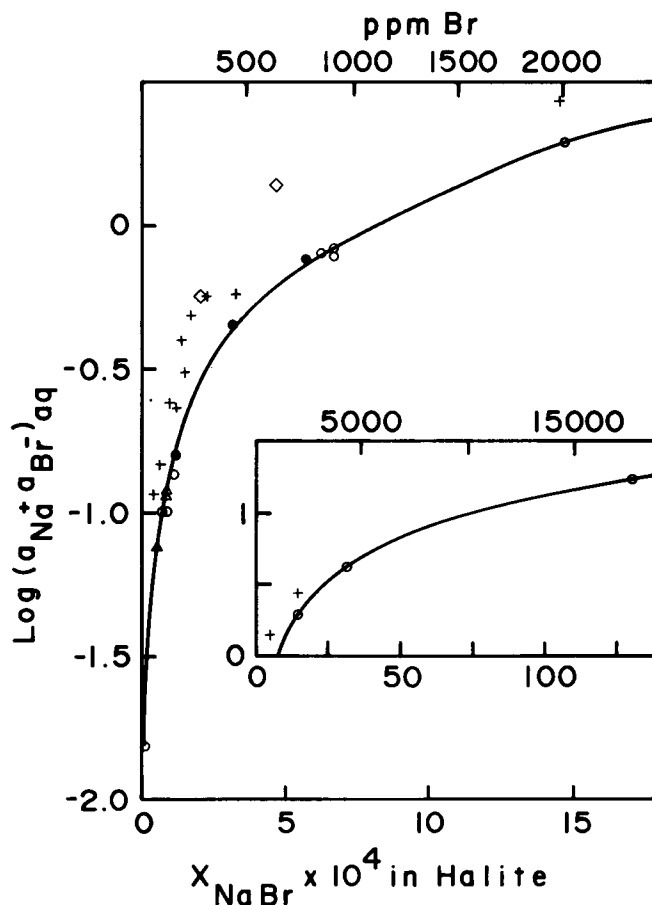
FIGS. 1a and 1b. Aqueous log $(a_{A^+}a_{Br^-})$ versus $X_{ABr}$ in the salt lattice computed from the 25°C experimental data of BRAITSCH and HERRMANN (1963) in which $A^+$ is $Na^+$ and $K^+$ in 1a and 1b, respectively. Curves are fit to data assumed to represent stoichiometric saturation. Solutions plotted on Fig. 1a contain the following salt constituents in which $m$ indicates molality: O, Na-Cl-Br; ●, Na-Cl-Br-K with $1.3 < m_K < 1.4$; △, Na-Cl-Br-Mg with $m_{Mg} = 0.4$; +, Na-Cl-Br-Mg with $1.5 < m_{Mg} < 4.4$; ◇, Na-Cl-Br-Mg-SO$_4$ with 3.3 $< m_{Mg} < 3.8$ and $m_{SO_4} = 0.1$. Solutions plotted on Fig. 1b contain the following salt constituents: O, K-Cl-Br; ●, K-Cl-Br-Na with $m_{Na} = 4.5$; +, K-Cl-Br-Mg with $3.2 < m_{Mg} < 3.9$; ⊕, K-Cl-Br-Mg-Ca with $m_{Mg}$ $= 1.8$ and $1.2 < m_{Ca} < 1.4$.

cipitating from binary salt solutions, and in halite from ternary salt solutions with less than 0.5 molal Mg. This assumption will be used with certain experimental data to predict the distribution of Br between the salts and brines at thermodynamic equilibrium.

### THEORY AND PROCEDURE

Geochemists have generally used the empirical distribution coefficient to predict Br contents in halite or sylvite precipitating from a brine. The distribution coefficient $D_{Br}$ is defined by ratios of Br:Cl as

$$D_{Br} = \frac{(Br/Cl)_{salt}}{(Br/Cl)_{solution}}$$

and is about 0.034 for the first halite precipitating from evaporating seawater (HERRMANN, 1980). The distribution coefficient is a function of both solution and solid compositions. From a practical viewpoint, it is more useful to predict the Br content on the basis of thermodynamic equilibrium than to use an empirical

coefficient. Unfortunately, the Br content of rapidly precipitated halite decreases with recrystallization (HERRMANN, 1980), indicating a lack of thermodynamic equilibrium at precipitation. A similar problem may occur with sylvite. The assumption of stoichiometric saturation, used in this study, allows the prediction of the conditions at thermodynamic equilibrium. This assumption was made to determine if predicted equilibrium conditions are realistic in terms of our knowledge of Br content in these salts.

The general equations necessary for this approach for a two-component solid have been derived by THORSTENSON and PLUMMER (1977). The following hydrolysis reactions need to be considered:

$$ABr_XCl_{(1-X)} = A^+ + XBr^- + (1 - X)Cl^- \quad (1a)$$

$$ABr_{salt} = A^+ + Br^- \quad (1b)$$

$$ACl_{salt} = A^+ + Cl^- \quad (1c)$$
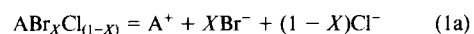
where A is the common cation of the binary salts (ABr and ACl) and $X$ is the mole fraction of ABr in the salt lattice.
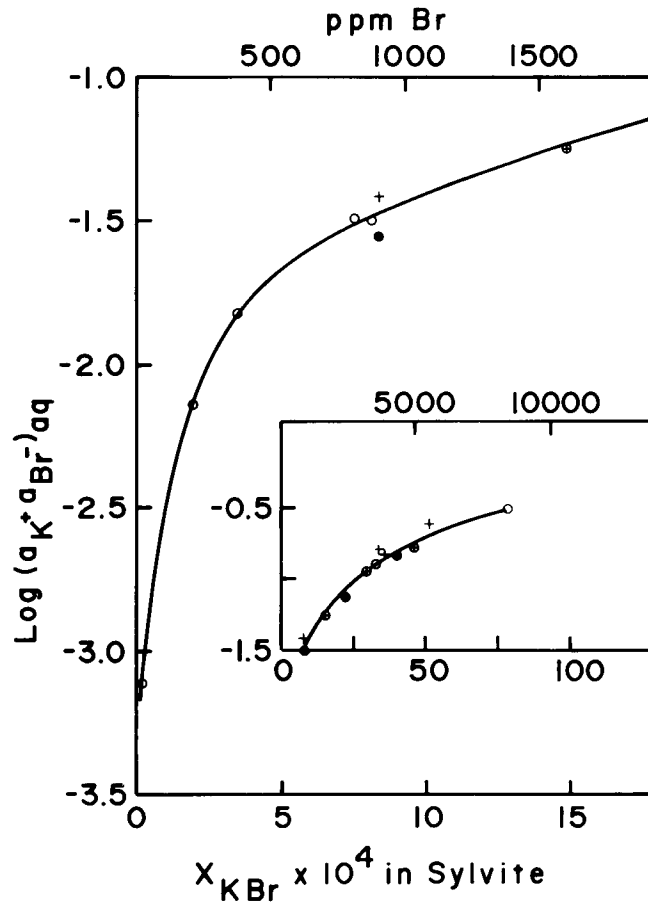
**ppm Br**

FIG. 1 (Continued)

Reactions (1b) and (1c) are dissolution reactions for the salt components within the binary salt solid solution. Only the mass law equilibrium condition for Reaction (1a), defined by Eqn. (2a), is satisfied for stoichiometric saturation. The additional mass law equilibrium conditions for Reactions (1b) and (1c), defined by Eqns. (2b) and (2c), hold only at thermodynamic equilibrium.

$$\log K_{sat} = X \log (a_{A^+}a_{Br^-})_{aq,sat} + (1 - X) \log (a_{A^+}a_{Cl^-})_{aq,sat}$$
(2a)

$$\log K_{ABr} = \log (a_{A^+}a_{Br^-})_{aq,eq} - \log (a_{ABr})_{salt}$$
(2b)

$$\log K_{ACl} = \log (a_{A^+}a_{Cl^-})_{aq,eq} - \log (a_{ACl})_{salt}$$
(2c)

where $K$ is an equilibrium constant (dependent only on the standard states of the reaction components), $a$ represents activity, and the activity of the stoichiometric salt is unity in Reaction (1a). The subscripts "sat" and "eq" represent stoichiometric saturation and thermodynamic equilibrium, and the subscripts "ABr" and "ACl" refer to the solid salts.

The derivation of THORSTENSON and PLUMMER (1977, pp. 1211–1212) yields the following relation at thermodynamic equilibrium between a fluid and two-component solid containing Cl and Br:

$$\log \left(\frac{a_{Br^-}}{a_{Cl^-}}\right)_{aq,eq} = \frac{\partial \log K_{sat}}{\partial X}$$
(3)

Eqn. (3) predicts the aqueous activity ratio of Br⁻:Cl⁻ at thermodynamic equilibrium using data obtained at stoichiometric saturation. In our system, the change in log $K_{sat}$ is very minor because the aqueous activity product $(a_{A^+}a_{Cl^-})$ of the

major component remains constant, equal to $K_{ACl}$, within experimental error. In contrast, the dependency of the aqueous activity product $(a_{A^+}a_{Br^-})$ on $X_{ABr}$ is easily measured. For that reason we have to *assume* the change in log $K_{sat}$ is due to changes in the activity product of the trace component. The consequences of this assumption are discussed below.



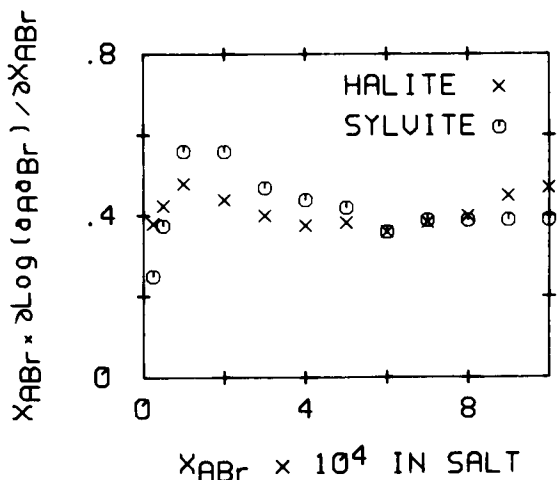FIG. 1c. $X \, \partial \log(a_{A^+}a_{Br^-})_{aq}/\partial X$ versus $X \times 10^4$, computed from the curves on Figs. 1a and 1b.

From Eqn. (2a), at stoichiometric saturation,

$$\frac{\partial \log K_{sat}}{\partial X} = (1 - X)\frac{\partial \log (a_{A^+}a_{Cl^-})_{aq,sat}}{\partial X}$$

$$+ \log\left(\frac{a_{Br^-}}{a_{Cl^-}}\right)_{aq,sat} + X\frac{\partial \log (a_{A^+}a_{Br^-})_{aq,sat}}{\partial X} \quad (4)$$

where the terms on the right side of the equation are at stoichiometric saturation. Substituting into Eqn. (3) and using our assumption of a constant aqueous activity product of $A^+$ and $Cl^-$ yields

$$\log\left(\frac{a_{Br^-}}{a_{Cl^-}}\right)_{aq,eq} = \log\left(\frac{a_{Br^-}}{a_{Cl^-}}\right)_{aq,sat} + X\frac{\partial \log (a_{A^+}a_{Br^-})_{aq,sat}}{\partial X} \quad (5)$$

The term containing the partial derivative in Eqn. (5) can be estimated from finite derivatives of the curves on Figs. 1a and 1b (derived from experimental data of BRAITSCH and HERRMANN, 1963 and explained later). The term varies in magnitude between 0.2 and 0.6 for sylvite and between 0.3 and 0.5 for halite and is plotted at discrete values of $X$ on Fig. 1c for both halite and sylvite. The maximum in both sets of points on Fig. 1c is due to the relative significance of the "decreasing" partial derivative as $X$ is increasing. The minimum in the points for halite at about $X = 0.0006$ may not be correct, resulting from error in drawing the smooth curve on Fig. 1a at the higher values of $X$.

The deleted partial derivative term (from Eqn. (4)) would exactly balance this term at thermodynamic equilibrium. This occurs because a very small change in the log aqueous activity product of the major component is amplified by the coefficient $(1 - X)$. This amplification also occurs, of course, at stoichiometric saturation. Thus, assuming the activity product of $A^+$ and $Cl^-$ is independent of the Br content of the salt lattice is an *important* assumption. The assumption is made because the term cannot be experimentally evaluated. The justification is that the "resulting predicted" conditions for thermodynamic equilibrium are reasonable when compared to the known behavior of Br in halite and sylvite.

The procedure followed in this study utilized Eqn. (5) together with the extensive set of 25°C experimental data of BRAITSCH and HERRMANN (1963). In their experiments, K, Mg, Ca, and $SO_4$ were analyzed graviometrically; Br, by iodinometric titration; Cl, by Mohr titration; and Mg in Ca-free solutions, by complexometric analysis. Na was computed by electrical neutrality, and K was similarly computed when Na was not present in the experiments. Estimates of analytical error were not reported.

Braitsch and Herrmann's data on precipitation from binary salt solutions together with some ternary salt solutions (for halite) were utilized. The ternary salt solutions did not contain more than 0.45 molal Mg or 1.5 molal K. More complex salt solutions, *e.g.*, seawater evaporated past initial halite precipitation, are likely to contain kinetic interferences from high concentrations of Mg and other ions.

Pitzer's specific ion interaction model (including electrostatic unsymmetric mixing terms) was used to compute activity coefficients (PITZER, 1975, 1979; and HARVIE *et al.*, 1984). At 25°C, we used the parameters tabulated by HARVIE *et al.*, (1984) with the exception of the Br parameters. The single electrolyte Br parameters came from PITZER and MAYORGA (1973). The common-ion Br parameters came from PITZER and KIM (1974) for terms not involving electrostatic un-

symmetric mixing. The common-ion Br parameters used in the electrostatic unsymmetric mixing terms were set equal to the equivalent Cl parameters listed by HARVIE *et al.*

Some error will result by setting parameters containing Br (used in the electrostatic unsymmetric mixing terms) equal to the equivalent Cl terms and mixing sources of the parameters. However, for almost all of the solution data used in this study, assumed to represent stoichiometric saturation, there were no electrostatic unsymmetric mixing terms, *e.g.*, Na-Cl-Br and K-Cl-Br solutions. For these binary salt solutions, the parameters taken from HARVIE *et al.* (1984) are the same as those tabulated in PITZER and MAYORGA (1973) and PITZER and KIM (1974). Indeed, with two exceptions (the $CaSO_4$ and Ca-Mg parameters), the single electrolyte parameters and the common-ion parameters (not used in the unsymmetric electrostatic mixing) taken from HARVIE *et al.* (1984) are identical to those in PITZER and MAYORGA (1973, 1974) and PITZER and KIM (1974).

For estimates of activity coefficients at temperatures above 25°C, the tabulated temperature derivatives of the single salt parameters at 25°C (PITZER, 1979) were used in a linear extrapolation. The common-ion parameters were assumed to be independent of temperature. The tabulated single salt parameters from PITZER (1979) for $CaSO_4$ and $Na_2SO_4$ were substituted for the 25°C parameters (previously used) to be consistent with the temperature derivatives. We recognize that considerable error is possible in these activity coefficient estimates at higher temperatures; however, using ratios of activity coefficients may minimize some of the errors.

The 25°C and 1 bar aqueous log $(a_{Na^+}a_{Cl^-})$ and log $(a_{K^+}a_{Cl^-})$ products are 1.59 and 0.89, respectively, for equilibrium with pure halite and pure sylvite, using standard state data from the Berkeley Data Bank (1/83 SUPCRT update—see HELGESON *et al.*, 1978, 1981) for aqueous species and sylvite and from ROBIE *et al.* (1978) for halite. The aqueous activity products, computed with our application of Pitzer's activity coefficient model and the binary salt experiments of BRAITSCH and HERRMANN (1963) were within 0.01 log units of 1.59 for solutions precipitating halite and were precisely 0.89 for solutions precipitating sylvite. Ternary salt solutions (assumed to represent stoichiometric saturation) precipitating halite had aqueous log $(a_{Na^+}a_{Cl^-})$ products within 0.04 units of 1.59. Based on this good agreement and consistent with our assumption of constant activity products of the major salt components, we used 1.59 and 0.89 for the aqueous log activity products of $a_{Na^+}a_{Cl^-}$ and $a_{K^+}a_{Cl^-}$ in all solutions precipitating these salts. Minor deviations from these values (on the order of 0.1 log units) in more complex and concentrated brines (discussed later) were assumed due to inconsistencies in the parameters used in Pitzer's activity coefficient model.

Aqueous log $(a_{A^+}a_{Br^-})$ products are plotted as a function of $X_{ABr}$ in halite and sylvite, respectively, in

Figs. 1a and 1b. Data from more complex solutions, not assumed to represent stoichiometric saturation, are also plotted on the figures. These data are discussed later. Finite difference derivatives (see Fig. 1c) of the curves on Figs. 1a and 1b were used in Eqn. (5) to derive the equilibrium curves on Figs. 2a and 2b. The slight divergence between the two curves on Fig. 2a for $X$ greater than 0.0006 reflects the minimum on Fig. 1c for halite. As previously mentioned, this minimum may not exist, reflecting errors in drawing the smooth curve on Fig. 1a.

The 25°C and 1 bar activity coefficients $\lambda_{ABr}$ in the salt lattice as a function of $X$ are shown for halite and sylvite in Fig. 3. These were computed using Eqn. (2b), the activity ratios in Figs. 2a and 2b at thermodynamic equilibrium, and assuming the log $(a_{Na^+}a_{Cl^-})$ and log $(a_{K^+}a_{Cl^-})$ products are those for the pure salts. The 25°C and 1 bar log $K$ values for Eqn. (2b) were computed as discussed below and were 2.97 and 1.07, respectively, for NaBr and KBr.

The effects of increasing pressure and temperature at thermodynamic equilibrium on the activity ratio of $Br^-:Cl^-$ can be discussed in terms of an aqueous reaction between the two components within the solid salt.

$$ABr_{salt} + Cl^-_{aq,eq} = ACl_{salt} + Br^-_{aq,eq} \qquad (6)$$

and

$$\log K = \log (a_{Br^-}/a_{Cl^-})_{aq,eq} + \log ((X\lambda)_{ACl}/(X\lambda)_{ABr})_{salt}$$

$$= \log K_{ABr} - \log K_{ACl} \text{ (from Eqns. (2b) and (2c))}$$

where $X_i$ and $\lambda_i$ refer to the mole fraction and activity coefficient, respectively, of the $i$th salt component.

Log $K$ values of Reaction (6) at different pressure temperature $(PT)$ points of diagenetic interest are listed in Table 1 for halite and for sylvite. The standard state thermodynamic data required to compute log $K$ as a function of $P$ and $T$ are based on the Berkeley Data Bank (1/83 SUPCRT update—see HELGESON et al., 1978, 1981) for NaCl, KCl, aqueous Br⁻ and Cl⁻. The necessary data for KBr and NaBr, with the exception of heat capacity power coefficients, are from WAGMAN et al. (1981). Heat capacity data are from KELLEY (1960; KBr) and GARDNER and TAYLOR (1964; NaBr).

Temperature changes, unlike pressure changes, have a significant effect on the equilibrium constant of Reaction (6), as shown in Table 1. An increased Br content in halite is favored by the decrease in the log $K$ of Reaction (6) with increasing temperature. The opposite is true for sylvite because the log $K$ increases with increasing temperature. $\lambda_{ABr}$ in both halite and sylvite should decrease (from that shown on Fig. 3), with increasing temperature as relative energy differences decrease between Br and Cl in the salt lattice. Presumably, since $\lambda_{ACl}$ in both halite and sylvite are already near unity, temperature changes will have a lesser effect on its value. The changes in the log $K$ and the activity coefficient of ABr work together in halite to promote
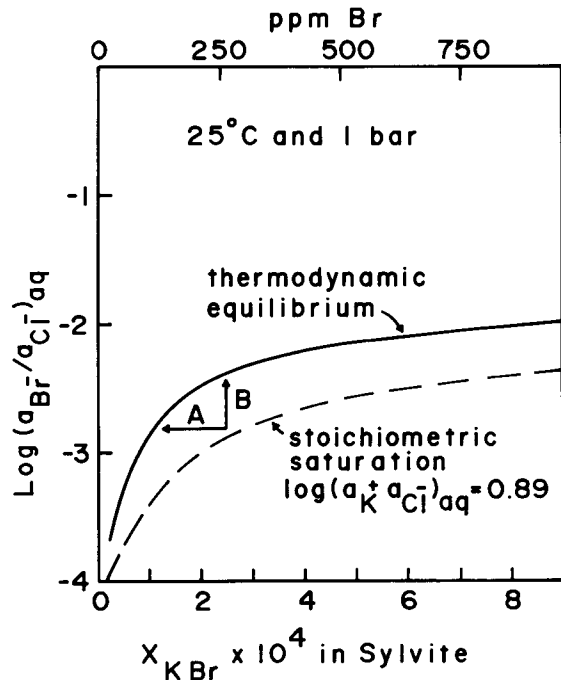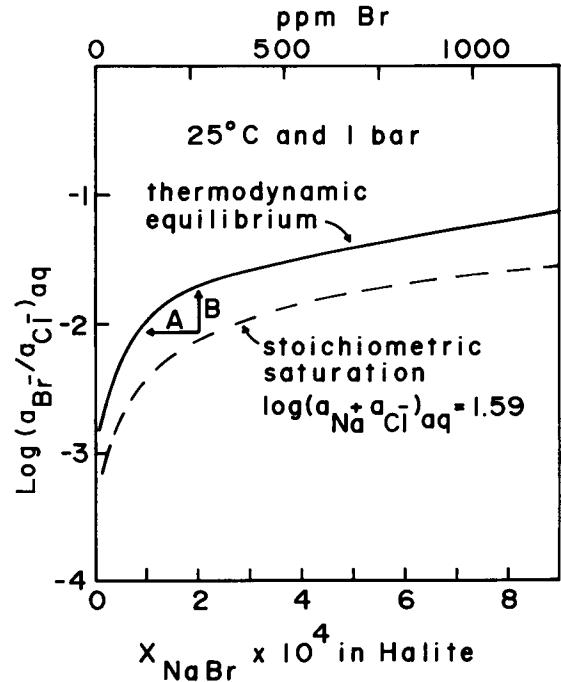




FIGS. 2a and 2b. Computed thermodynamic equilibrium curves for 25°C Br partitioning with halite and sylvite, respectively, in 2a and 2b with a brine. A and B represent trend lines for salt recrystallization for a fluid- and salt-dominated system, respectively. Dashed curves represent stoichiometric saturation.

more Br in the salt lattice and against each other in sylvite with increasing temperature.

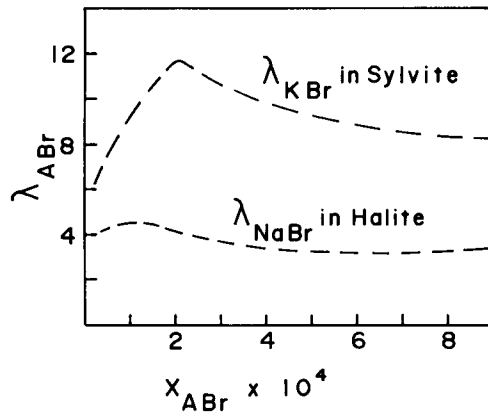The change in $a_{Br^-}/a_{Cl^-}$ with temperature can be estimated by neglecting the "unknown" temperature de-

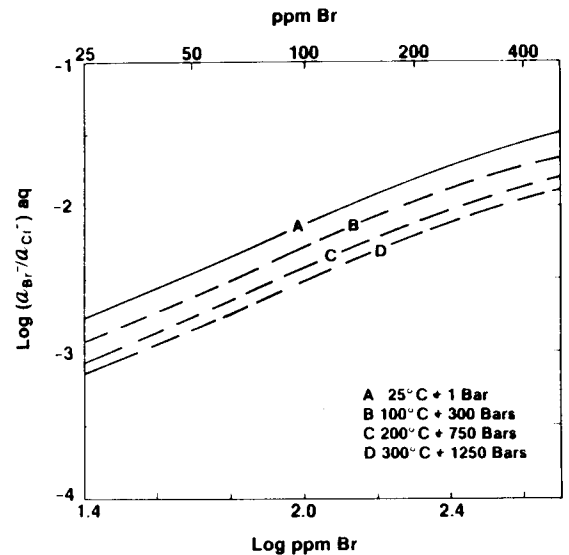FIG. 3. Computed activity coefficients of ABr in halite and sylvite.



FIG. 4. Estimated thermodynamic equilibrium curves for Br partitioning between halite and a brine at several $PT$ points of diagenetic interest. See the text for an explanation of assumption used in the procedure.

pendence of $\lambda_{ABr}$ and $\lambda_{ACl}$ in the salt lattice. Begin with a salt-dominated (excess salt present) system at equilibrium. Raising the temperature will significantly change the solution composition but not the salt composition. The change in the log $(a_{Br^-}/a_{Cl^-})$ can be set equal to the shift in the log $K$ of Eqn. (6). The dashed curves on Fig. 4 for halite were plotted using this procedure. This was not done for sylvite, because the larger values of $\lambda_{KBr}$ (see Fig. 3) imply the possibility of greater error in neglecting its temperature dependence. The curves on Fig. 4 are speculative, particularly at temperatures above 100°C, and are presented to show trends. They imply that during diagenesis in a "solution-dominated" system, i.e., nearly constant log $(a_{Br^-}/a_{Cl^-})$, the thermodynamic equilibrium Br content increases in the halite lattice with increasing temperatures.

## RESULTS

Log $(a_{Na^+}a_{Br^-})$ products are plotted on Fig. 1a for solutions from which halite precipitated, exps. 1–26 and 31–32 at 25°C for BRAITSCH and HERRMANN (1963). Information on solution composition are listed in the captions of both Fig. 1a and Fig. 1b which is discussed later. Data from the binary and ternary salt solutions of exps. 1–16 fall upon a smooth curve, assumed to represent stoichiometric saturation. The other data are from solutions having more than 1.5 molal Mg. The discrepancies could be due to a reaction kinetic control or inaccuracies in the common-ion parameters for Br and Cl in Pitzer's specific ion inter-

action model. The latter possibility is supported by the computed decrease in the log $(a_{Na^+}a_{Cl^-})$ product from 1.59 to between 1.40 and 1.50 for exps. 23–26 and 31. Solution compositions in these experiments contained more than 3 molal Mg.

Log $(a_{K^+}a_{Br^-})$ products are plotted on Fig. 1b for solutions from which sylvite precipitated, exps. 33–46 and 51–53 at 25°C of BRAITSCH and HERRMANN (1963). As in the case of halite, data from the binary salt solutions (exps. 33–39) fall upon a smooth curve, assumed to represent stoichiometric saturation. The other solutions contained more than 4.4 molal Na or 3.2 molal Mg or a combination of more than 1.2 molal Ca and 1.8 molal Mg. Again, the slight discrepancies could be due to a reaction kinetic control or inaccuracies in the common-ion parameters for Br and Cl in Pitzer's specific ion interaction model. The latter possibility is also supported by a computed decrease in the log $(a_{K^+}a_{Cl^-})$ product from 0.89 to between 0.82 and 0.84 for the solutions containing both Mg and Ca (exps. 51–53).

PLUMMER (1985, written commun.) suggests another possibility of explaining inconsistent results in the more complex and concentrated solutions (shown on Figs. 1a and 1b). The salt lattice could contain additional ions such as Mg which would have an effect on the stoichiometric saturation of the solid phase. However, sensitivity tests of the common-ion parameters in Pitzer's model indicate inaccuracies in these parameters could account for the inconsistencies.

The computed relationship between the log activity ratio of Br⁻:Cl⁻ and $X_{ABr}$ at thermodynamic equilibrium are shown on Figs. 2a and 2b, respectively, for halite and sylvite at 25°C. Curves representing stoichiometric saturation are also plotted on the figures.

Table 1. Values of the log K for Reaction (6) for some PT points of diagenetic interest.

| °C | bars | log K halite | log K sylvite | °C | bars | log K halite | log K sylvite |
|----|------|------|---------|----|------|------|---------|
| 25 | 1 | 1.38 | 0.18 | 150 | 500 | 1.13 | 0.30 |
| 60 | 1 | 1.30 | 0.22 | 200 | 750 | 1.07 | 0.33 |
| 60 | 150 | 1.29 | 0.22 | 250 | 1000 | 1.02 | 0.37 |
| 100 | 1 | 1.22 | 0.27 | 300 | 1250 | 0.99 | 0.41 |
| 100 | 300 | 1.21 | 0.26 | | | | |

Solution compositions plotted on Figs. 1a and 1b which did not fall on the smooth curves, lie to the right (larger $X_{ABr}$) of the equilibrium curves on Figs. 2a and 2b. Regardless if stoichiometric saturation or reaction kinetics controls the initial Br content in the precipitated salt, recrystallization will deplete the Br content in the salt lattice as the brine and salt come to thermodynamic equilibrium. The recrystallization path will trend more parallel to the $x$ axis (on Figs. 2a and 2b) in a fluid-dominated (usually open) system and more parallel to the $y$ axis in a salt-dominated (usually closed) system.

Initial halite precipitation from evaporating seawater occurs in a brine with nearly 0.6 molal Mg. The control on the Br content in halite could be stoichiometric saturation or reaction kinetics. Assuming it is stoichiometric saturation, the predicted Br content (from Fig. 2a) in halite at 25°C would be 78 ppm with an equilibrium value of 27 ppm. These values are based on a brine composition estimated by Carpenter using the procedures outlined by CARPENTER (1978). The brine has a log $(a_{Br-}/a_{Cl-})$ ratio of $-2.69$. HERRMANN et al. (1973) estimate (from field studies) 60 to 75 ppm Br in the first halite precipitating from evaporating seawater. The general agreement with the predicted value implies stoichiometric saturation may control Br partitioning at initial halite saturation in evaporating seawater.

The equilibrium value is not known; however, halite precipitated at 40°C in very slow-growth single crystal experiments, without aqueous Mg, had a distribution coefficient of 0.0145 (LUTZ, 1975; PUCHELT et al., 1972) which corresponds to 30 ppm Br in halite at initial halite saturation of evaporating seawater. These slow-growth experiments should represent a close ap-

proach to true thermodynamic equilibrium with regard to Br partioning. The predicted value (mentioned above) was 27 ppm Br at 25°C. The expected effect of a 15°C temperature increase will be a minor increase in the amount of Br in halite, as shown on Fig. 4 at a log $(a_{Br-}/a_{Cl-})$ ratio of $-2.69$. Thus, the temperature increase will move the predicted value of 27 ppm towards the experimental value of 30 ppm, improving an already excellent agreement.

## DISCUSSION

A significant increase in the Br content of a brine coexisting with halite may occur during recrystallization to thermodynamic equilibrium. The largest increases will occur at the lowest fluid:rock ratios, corresponding to salt-fluid systems having the lowest porosities.

Calculated increases in the Br content of a brine due to halite recrystallization are presented in Table 2 using two end-member brine compositions: a seawater sample which has reached halite saturation by halite dissolution (5.6 moles of halite containing 100 ppm Br) and a brine produced by evaporating Black Sea water past initial halite saturation (ZHEREBTSOVA and VOLKOVA, 1966, sample 3). Halite saturation for the seawater sample was determined using the constraint that the activities computed using Pitzer's method gave a log $(a_{Na+}a_{Cl-})$ product of 1.59. The sample had 266,690 ppm total dissolved solids and an estimated density of 1.21 g/cm³. The Black Sea brine had 270,430 ppm total dissolved salts and a density of 1.227 g/cm³.

For each fluid, recrystallization was considered for halite having 75, 100, and 125 ppm Br. The compu-

TABLE 2. Fluid* recrystallization of halite to thermodynamic equilibrium at 25°C.

| fluid | Br molality increase | $\frac{cm^3 \text{ halite}}{cm^3 \text{ fluid}}$ initial ppm Br in halite | | | ppm Br halite | ppm Br aqueous |
|---|---|---|---|---|---|---|
| | | 75 | 100 | 125 | | |
| 1 | 0 | =>0 | =>0 | =>0 | 4 | 74 |
| | 0.001 | 0.48 | 0.35 | 0.28 | 7 | 133 |
| | 0.005 | 2.9 | 2.0 | 1.5 | 19 | 367 |
| | 0.010 | 8.0 | 5.0 | 3.6 | 34 | 660 |
| | 0.015 | 19 | 9.6 | 6.5 | 49 | 952 |
| | 0.020 | 55 | 18 | 11 | 63 | 1246 |
| | 0.0245 | =>∞ | 32 | 16 | 75 | 1509 |
| | 0.025 | | 34 | 17 | 76 | 1538 |
| | 0.030 | | 98 | 28 | 90 | 1831 |
| | 0.034 | | =>∞ | 45 | 100 | 2064 |
| | 0.035 | | | 50 | 102 | 2123 |
| | 0.040 | | | 120 | 114 | 2415 |
| | 0.0445 | | | =>∞ | 125 | 2678 |
| 2 | 0 | =>0 | =>0 | =>0 | 49 | 823 |
| | 0.001 | 1.4 | 0.69 | 0.45 | 52 | 881 |
| | 0.005 | 15 | 4.6 | 2.7 | 64 | 1114 |
| | 0.0085 | =>∞ | 11 | 5.6 | 75 | 1317 |
| | 0.010 | | 16 | 7.2 | 79 | 1405 |
| | 0.015 | | 83 | 16 | 94 | 1697 |
| | 0.017 | | =>∞ | 23 | 100 | 1814 |
| | 0.020 | | | 39 | 108 | 1986 |
| | 0.025 | | | 280 | 122 | 2277 |
| | 0.026 | | | =>∞ | 125 | 2335 |

*Fluids: (1) Seawater saturated with NaCl through dissolution of 5.6 moles of halite/kg H₂O (100 ppm Br in salt) and (2) evaporated Black Sea water (Zherebtsova and Volkova, 1966, sample 3).

tations were made by exchanging molal amounts of Br for Cl in the solution, determining the resulting $\log(a_{Br^-}/a_{Cl^-})$ ratio with Pitzer's method, and using this value with the 25°C curve on Fig. 4 to estimate the equilibrium Br content in halite. The volume ratio of halite:fluid was then computed using the difference between the initial and final amounts of Br in the halite, the molal increase of aqueous Br, the total dissolved solids in the fluid, and the appropriate densities of the fluid and salt.

The results involving the brine sample of Black Sea water should be regarded as estimates because of the high concentrations of Mg (0.9 molal) and other components, e.g., sulfate, not normally found in high concentrations in subsurface brines. The computed log $(a_{Na^+}a_{Cl^-})$ product is 1.53, significantly different from the expected value of 1.59. As previously discussed, such discrepancies are probably due to inaccuracies in the common ion parameters used in our application of Pitzer's specific ion interaction method. Such inaccuracies will produce errors in the $\log(a_{Br^-}/a_{Cl^-})$ ratio used in Fig. 2a to determine the equilibrium Br content in halite.

The important point made in Table 2 is the large increases in Br content, in excess of a 1000 ppm, which can result from recrystallization at low temperatures. For the general conditions used in the examples, a salt:fluid volume ratio of 10 can provide excess Br ranging from 100 to a 1000 ppm. Recrystallization by interstitial brine prior to its expulsion from the salt appears to be a viable mechanism for increasing aqueous Br concentrations. Alternatively, the recrystallization could take place in an open system in which the fluid interacts with salt diapirs or bedded salts.

The increase in aqueous Br concentrations due to recrystallization can be recognized by decreases in the ratios of potassium, divalent cations, etc., to bromide. CARPENTER (1978) has outlined the differences in characteristic elemental ratios in brines evolving from evaporating seawater versus those derived from dissolving halite. Brines generated by evaporating seawater plot on a straight line when the sum of the concentration equivalents of divalent cations balanced by Cl are plotted versus Br concentrations.

Compositions of Jurassic oil-field brines in the Mississippi Salt Basin are plotted in this manner on Fig. 5. The general correlation of the data to the seawater evaporation line implies the origin of the brines is related to the precipitation of evaporites such as the underlying Louann Salt of Jurassic age. The spread of points above and below the line can be explained by two diagenetic events: halite recrystallization supplying excess Br and the albitization of the anorthite component of plagioclase, supplying excess Ca.

Although recrystallization will most commonly result in the transfer of Br from salt minerals to the coexisting brine, there are situations in which the transfer may occur in the other direction. The shift in the equilibrium lines in Fig. 4 with increasing temperature pre-
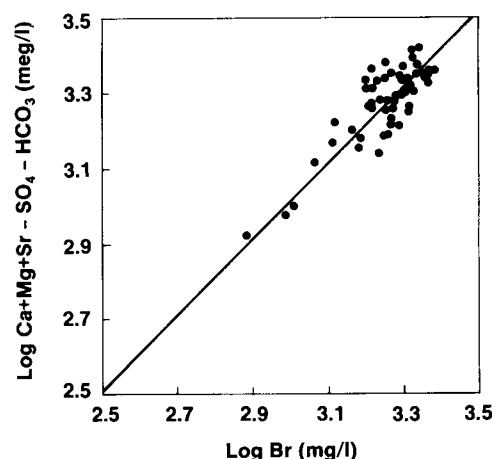


FIG. 5. Relationship between bromide and divalent cations after subtracting sulfate and bicarbonate in Jurassic oil-field brines, Mississippi Salt Basin. Evaporating seawater plots on the solid line. Brines formed by evaporating seawater can be moved to the right of the line by Br enrichment due to low temperature halite recrystallization. Movement to the left of the line can occur by Ca enrichment due to albitization of plagioclase.

dicts recrystallization will be less effective in lowering the Br content of halite with burial, and (depending on the aqueous ratio of $a_{Br^-}:a_{Cl^-}$) might result in an increase in the Br content in halite in a fluid-dominated system.

## APPLICATION TO SPECIFIC BRINES AND EVAPORITES

Halite in the East Texas Oakwood Dome and the North Louisiana Vacherie Dome have average Br contents of 45 and 33 ppm, respectively (DIX and JACKSON, 1983; STIRLING et al., 1983). Recrystallized halite in the caprock of the Oakwood Dome averages 23 ppm Br. The predicted value of 27 ppm Br in halite in equilibrium with evaporating seawater at initial halite saturation is a reasonable estimate, if the measured Br contents represents a low-temperature recrystallization progression towards thermodynamic equilibrium. The scatter in values can be explained by different activity ratios of $Br^-:Cl^-$ in the fluids recrystallizing the halite.

Brines containing 4,500 to 5,900 mg/liter Br are produced from the upper part of the Smackover Formation in the Kerlin Field, southwestern Arkanasas (COLLINS, 1974). The temperature of the brine reservoir is approximately 100°C. Eight samples of halite from the Louann salt taken at depths of 800 to 2,200 feet below these brines contain up to 447 ppm Br, assuming that all of the Br in the bulk salt is in the halite fraction. Log activity ratios of $Br^-:Cl^-$, computed for twelve brine samples reported by Collins, range from $-1.83$ to $-1.72$ with a mean value of $-1.78$. Using the 100°C curve on Fig. 4, the ratios predict Br contents in equilibrated halite of 310 to 460 ppm. These esti-

mates are remarkably close to the observed Br contents of the halite deeper in the section.

The high Br content of the Kerlin halite is probably the result of deposition from brines with very high Br concentrations. The origin of the Br-enriched brines are not known (CARPENTER and TROUT, 1978). However, the origin may be related in part to extensive low-temperature recrystallization of the lower portion of the Louann Salt in some part of the southern Arkansas salt basin.

Recently, LAZAR and HOLLAND (1984) reported high Br concentrations in two fluid inclusions in upper Miocene Red Sea halite. LAZAR (1984, pers. commun.) measured a distribution coefficient of 0.0036 at an assumed equilibration temperature of 51°C. This distribution coefficient is a factor of four lower than that measured by LUTZ (1975) from single crystal growth at 40°C. The solution composition (LAZAR, 1985, pers. commun.—corrected from LAZAR and HOLLAND, 1984) has an ionic strength greater than 13 and more than 3.2 molal Mg. Our application of Pitzer's method to their solution yielded inconsistent results. The aqueous log $(a_{Na^+}a_{Cl^-})$ product was 2.2 versus a predicted value below 1.7 for pure halite in aqueous equilibrium at 50°C. In addition, the high Na, K, and Mg concentrations will produce significant error due to setting the Na-Mg-Br and K-Mg-Br common-ion parameters equal to the equivalent Cl parameters. Application and testing of the model cannot be done in complex solutions of such high ionic strength.

## SUMMARY

"Assumed" stoichiometric saturation data for trace Br partitioning between brines and halite or sylvite have been used to estimate conditions for thermodynamic equilibrium. The predicted equilibrium value of Br in halite at initial halite saturation in evaporating seawater is in excellent agreement with the value predicted from the slow-growth single crystal experiments of LUTZ (1975). At near-surface temperatures, the model predicts significant Br transfer from the salts to the solution during recrystallization towards thermodynamic equilibrium. Less Br depletion in halite occurs during recrystallization at higher temperatures. The predicted results are consistent with bulk Br contents in both Br-depleted and Br-enriched (recrystallized?) halites in Gulf Coast Louann Salt.

Data for trace components in other solids should be examined from the viewpoint of stoichiometric saturation. Such examination may explain some of the inconsistencies in observed distribution coefficients.

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