

Effects of Fusion, Rates of Crystallization and Leaching on Bromide and Rubidium Solid Solutions in Halite, Sylvite and Carnallite

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ABSTRACT

Carnallite and sylvite commonly are associated in potash deposits and in a number of instances sylvite appears to have been derived from carnallite by leaching of magnesium chloride.

Bromine and rubidium occur in solid solution in both carnallite and sylvite and have proved useful in interpreting the relationships between these minerals. In this study, controlled experiments were conducted to determine bromine and rubidium in artificial sylvite derived from carnallite by leaching of magnesium chloride in pure water, at room temperature.

Carnallite samples with bromide and rubidium in the ranges 100 to 2500 ppm and 100 to 7000 ppm, respectively, gave sylvite residues with approximately 0.5 times the bromide and 1.3 times the rubidium of the parent carnallites; bromide and rubidium in sylvite being expressed in ppm. These experimental results do not correspond exactly with predictions based on published solubility data and partition coefficients.

While the composition of a solution, its temperature and to a minor extent its pressure are known to affect the partitioning of bromide and rubidium between solution and solid, it is usually assumed that the rate of crystallization has little effect. It was found experimentally that under otherwise similar conditions, sylvite crystallized slowly has only about 0.8 times the bromine of sylvite crystallized rapidly.

Similarly, it is usually assumed that recrystallization of salts in the absence of a liquid phase will not result in changed trace element contents. This assumption is supported by the observation that

fusion of halite and sylvite does not significantly change their contents of bromide.

INTRODUCTION

The distribution of trace elements such as bromine and rubidium, in the salts of evaporite deposits, has been used in a variety of interpretations. These interpretations usually include the assumption that rates of crystallization have little effect on partitioning of an element between solution and crystal. Similarly, it is usually assumed that any recrystallization of salts in the absence of a liquid phase will not change the amount of an element in solid solution in a crystal. In this study, experiments were conducted to validate these assumptions.

Carnallite and sylvite commonly are associated in potash deposits and in a number of instances sylvite appears to have been derived from carnallite by leaching of magnesium chloride (Borchert and Muir, 1964, p. 171).

Bromine and rubidium occur in solid solution in both carnallite and sylvite and have been useful in interpreting the relationships between these minerals. The solubility data for the system $KCl-MgCl_2-H_2O$ and the partition coefficients for bromine and rubidium in both carnallite and sylvite are available. From these data, it is possible to calculate the bromine and rubidium to be expected in sylvite derived from carnallite under given conditions. However, there seems to be an absence of published data on controlled experiments performed to determine directly the redistribution of bromine and rubidium during these transformations. Such experiments are reported in this paper.

The distribution of bromine and rubidium in sylvite and carnallite of the Middle Devonian Prairie Evaporite of Saskatchewan is considered with reference to the new experimental data.

Table 1. Effect of Fusion on Bromine in Halite and Sylvite

Mineral	Number of Samples	Average Bromine Content ppm	
		Before fusion	After fusion
NaCl	5	170	171
NaCl	5	171	172
NaCl	6	216	215
KCl	10	856	858

Bromine was determined in halite and sylvite crystals before and after melting in a furnace and there was no significant change in the amount of bromine present.

Salts in the Prairie Evaporite may have undergone recrystallization in the dry state (Clark and Schwerdtner, 1966) and it is usually assumed that such recrystallization does not affect the trace element content of the salts. This assumption may be substantiated by the fusion experiments, since if no bromine is lost on fusion and subsequent crystallization it seems unlikely that bromine would be lost during any process of recrystallization in the dry state.

Crystallization of salts in natural environments may occur relatively rapidly, as a result of brine cooling, or relatively slowly, as a result of evaporation at approximately constant temperature.

An experiment was conducted to determine the effect of rate of crystallization on bromine solid solution in sylvite. It was found that under otherwise similar conditions, sylvite crystallized slowly has only about 0.8 times the amount of bromine of sylvite crystallized rapidly.

Procedure followed.

Rapid crystallization was achieved by cooling a saturated solution of potassium chloride from 45°C to 20°C over a period of about one hour. The slow crystallization experiment was conducted, with continuous evaporation, over a 20 day period

Table 2. Effect of Rate of Crystallization on Bromine in Sylvite

Bromine Content of KCl in ppm			
Rapid crystallization		Slow crystallization	
BATCH A	1509	BATCH B	1209
	1483		1201
	1449		1138
	1538		1256
	1506		1241
	1497 average		1209 average
BATCH C	4090	BATCH D	3673
	4281		3453
	4004		3304
	4474		3870
	4248		3794
	4219 average		3619 average

$$\frac{\text{average for B (slow)}}{\text{average for A (fast)}} = .81$$

$$\frac{\text{average for D (slow)}}{\text{average for C (fast)}} = .86$$

at 30°C. In both experiments, the solutions were agitated intermittently to maintain homogeneity.

The effects of the temperature variable on partitioning of bromine in sylvite are minimized by conducting the slow crystallization experiment at the mean temperature of the fast experiment. Since the partition coefficient for bromine in sylvite is reported to be only slightly temperature dependent (Braitsch, 1966, p. 298) errors due to temperature differences are likely to be small under the conditions of the experiments.

Solutions used for rapid and slow crystallization experiments initially should have similar proportions by weight of bromine. Since more potassium chloride is needed to saturate the solutions at the higher temperature these solutions also have slightly more added bromine (Table 3).

Since the bromine content of the sylvite crystals increases with progressive crystallization, it is necessary to compare batches of sylvite crystals of similar weight. Thus, the weights of sylvite produced under conditions of fast crystallization were determined (13gms \pm 1.5gms) and the slow crystallization experiments were allowed to proceed until similar weights of crystals had formed.

Table 3. Bromine in Sylvite Crystallized Slowly and Rapidly

Rate of crystallization	Batch	gm KCl	gm H ₂ O	gm Br	ppm Br in solution
Rapid	Batch A	60.6	150.0	.431	2050
	Batch C	60.6	150.0	.886	4100
Slow	Batch B	55.9	150.0	.422	2050
	Batch D	55.9	150.0	.845	4100

Crystals were removed from solutions by filtration under vacuum and were immediately washed with acetone to remove excess brine. The dried crystals were then ground and thoroughly mixed prior to analyzing for bromine.

The brines were not analyzed for bromine at the beginning and end of these crystallization experiments since the intention was not to specifically determine the partition coefficient for bromine in sylvite, but rather to establish the relative effect of rate of crystallization on the bromine content of sylvites formed under otherwise similar conditions. Experiments to determine the partition coefficient have been made by Braitsch (1962, 1966) and Kühn (1968).

Discussion of results.

The distribution of bromine in sylvite does depend on rate of crystallization as well as on temperature, composition and other conditions. However, the 20 per cent extra bromine which results from rapid crystallization, under given conditions, is not likely to affect significantly interpretations based on bromine content.

It is well known that rapid crystallization tends to favour the inclusion of greater proportions of trace elements in solid solutions (Wells, 1962, p. 176). Buckley (1951, p. 395) reports the results of experiments by Ritzel in which the proportion of an ion in solid solution varies with the speed of crystallization. The quantity of $(\text{NH}_4)^+$ in solid solution in K_2SO_4 was found to increase as the speed of crystallization increased.

Kinsman and Holland (1969, p. 1) show that the distribution of strontium in aragonite depends on the kinetics and mechanism of crystal growth, as well as on other conditions of the solution.

Liquid inclusions tend to be more abundant in rapidly grown crystals than in those grown more

slowly. Since bromine is enriched in the liquid phase, such inclusions could result in anomalously high bromine values. Inclusions are present in both the rapidly and slowly grown halite crystals but it was not possible to estimate if significantly more inclusions are present in the rapidly grown crystals.

BROMINE AND RUBIDIUM REDISTRIBUTION DURING LEACHING OF CARNALLITE TO SYLVITE

Preparation of artificial carnallite.

Carnallite was prepared artificially by cooling a solution (with appropriate composition; $113\text{gmMgCl}_2 \cdot 6\text{H}_2\text{O} + 16.6\text{gmKCl} + 60.3\text{gmH}_2\text{O}$) from 80°C to room temperature (quantities determined from D'Ans, 1933, Table 3).

By appropriate additions of potassium bromide and rubidium chloride to several batches of solution, crops of carnallite crystals with bromine in the range 20 to 2500 ppm and rubidium in the range 100 to 7000 ppm were produced. The carnallite crystals were separated by vacuum filtration and dried. Crystals in each batch were thoroughly mixed to ensure homogeneity.

Other phases which could crystallize in this system and contaminate the carnallite are magnesium chloride hydrates and potassium chloride. Carnallite was identified positively by obtaining diffractograms for several samples and all samples were examined optically to establish their purity. In addition, quantitative analyses for potassium, magnesium and chloride were made on some samples.

Leaching of carnallite to sylvite.

Carnallite was treated with distilled water and stirred constantly as magnesium chloride went into solution leaving a solid residue of potassium

chloride. It is important to use enough water to dissolve all the carnallite but not to use too great an excess of water since this would reduce the yield of potassium chloride. The carnallite batches were leached with a slight excess of water to ensure that there would be no undissolved carnallite (28 gms of carnallite were dissolved in 18 gms of water, at room temperature, and 6 gms of potassium chloride remained as a residue). The potassium chloride was rapidly vacuum filtered, washed in absolute ethyl alcohol, dried, and examined for purity.

Four carnallite and two sylvite samples were analyzed for potassium, magnesium and chloride as a check on their purity. The weight percentages of potassium, magnesium and chloride in the natural carnallites were within 0.5 per cent of those for

pure carnallite. However, the artificially grown carnallites had an excess of potassium and of chloride which suggests that these samples contain some sylvite.

The samples of carnallite and of derived sylvite were analyzed for bromine and rubidium and the results are represented in Figures 1 and 2.

Results.

Artificially prepared carnallite samples with bromide and rubidium in the ranges 100-2500 ppm and 100 to 7000 ppm, respectively, gave sylvite residues with 0.75 times the bromide and 1.3 times the rubidium of the parent carnallites from which they were derived.

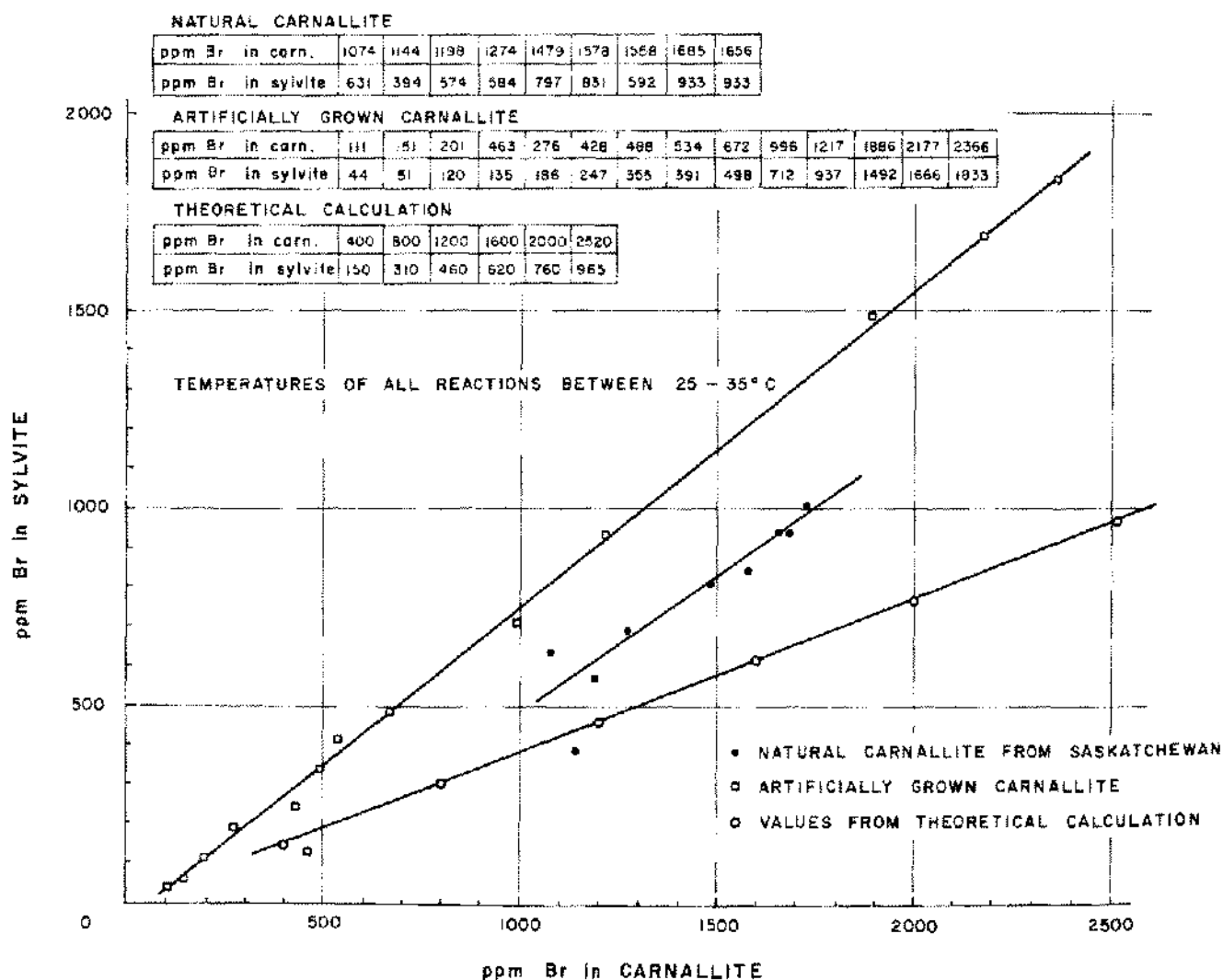


Figure 1. Relation between bromine in carnallite and bromine in sylvite derived from carnallite by fresh-water leaching.

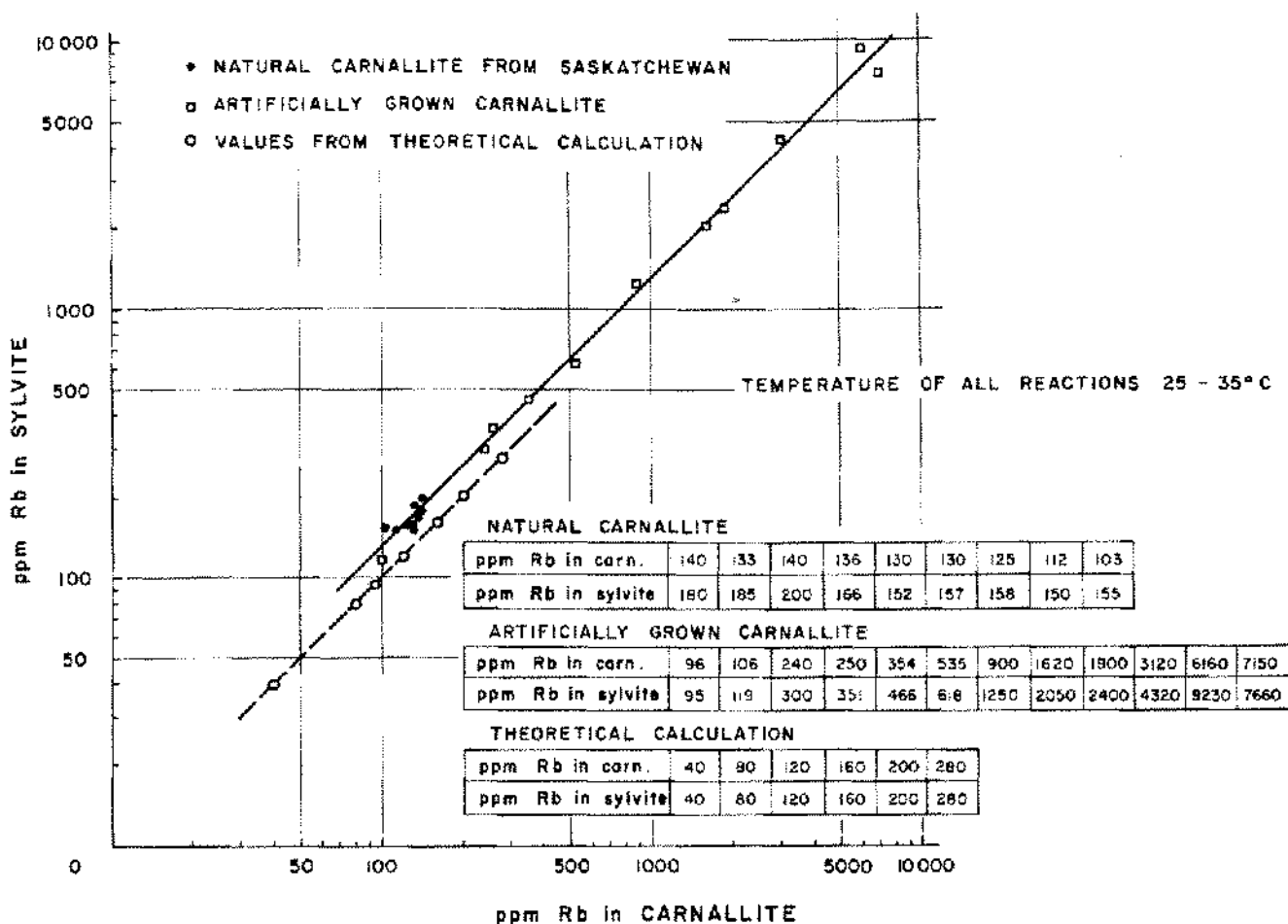


Figure 2. Relation between rubidium in carnallite and rubidium in sylvite derived from carnallite by fresh-water leaching.

Several samples of carnallite from the Prairie Evaporite Formation, Saskatchewan, were leached and the sylvite derived had 0.55 times the bromide and 1.3 times the rubidium of the parent carnallite. Since the natural carnallites are purer than the artificially prepared samples, these results may be taken as more reliable than those from the experiments with artificially grown carnallite crystals. Kühn (personal communication 1969) has conducted similar experiments and found that carnallite with 42 ppm rubidium yielded sylvite with 50 ppm rubidium, a result close to those reported here. Kühn (1965) earlier reported that the amount of rubidium in sylvite derived from carnallite decreased as the time of reaction increased and as the time the sylvite crystals maintained contact with the altering solutions increased. However, the sylvite always had more rubidium than the parent carnallite from which it was derived.

Based on D'Ans' (1933) solubility data and partition coefficients determined experimentally by Braitsch (1962, p. 106-107, 1966, p. 298), Braitsch and Hermann (1963), Kühn (1963, p. 111) and Kühn and Ritter (in Kühn, 1968), Wardlaw (1968, p. 1289) calculated the amounts of bromine and rubidium to be expected in sylvite derived from carnallite by leaching in fresh-water. These calculated results are plotted along with the experimentally determined results in Figures 1 and 2. Both the bromine and rubidium in the derived sylvite is substantially less in the case of the calculated results than for the direct experimental results. A number of factors may contribute to this difference. In the calculations, the assumption is made that the solution is homogeneous. In fact, the reaction of carnallite to sylvite is very rapid and the sylvite grains nucleate and grow adjacent to carnallite surfaces. Even with stirring during

solution of the carnallite, the solution may not be homogeneous. Also, the rapid nature of sylvite crystallization would tend to the inclusion of greater proportions of rubidium and bromine than would be the case with slower crystal growth. In addition, small brine inclusions in crystals would tend to increase the relative amount of bromine in a sample since bromine is enriched in the liquid phase.

The rapidly formed sylvite crystals in such leaching experiments are invariably fine grained (Fig. 3), whereas natural sylvites in the Prairie Evaporite, although thought to be derived from carnallite, are

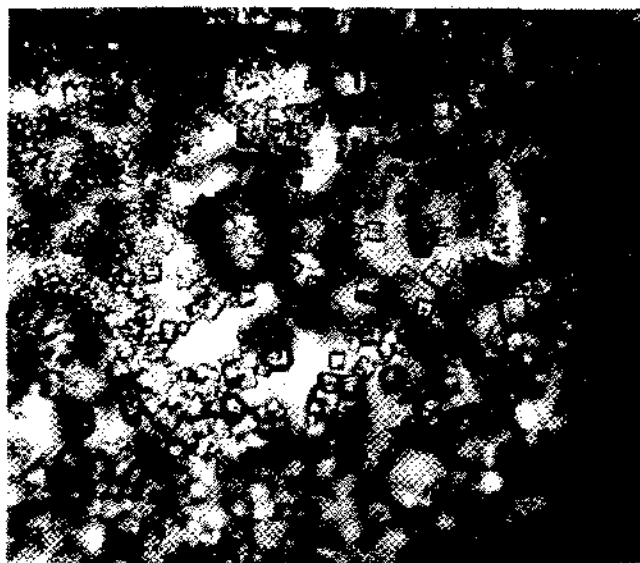


Figure 3. Cubes of sylvite forming from carnallite during fresh-water leaching. Magnification $\times 40$, plane polarised light.

much coarser grained. Sylvite grains in the latter case are large and have processes extending preferentially along carnallite twin planes (Fig. 4) and grain boundaries. The carnallite grains appear to have been partially replaced by sylvite, locally on a volume for volume basis, and do not have the rounded forms typical of partially dissolved carnallite grains observed in leaching experiments (Fig. 3). Grain relationships between carnallite and sylvite are clearly quite different in the rapid experimental reactions and in the naturally occurring rocks. In the rocks, it is possible that original grain relationships between carnallite and sylvite have been modified by subsequent recrystal-



Figure 4. Sylvite (black) occurring in relation to carnallite twin planes. Magnification $\times 40$, nicols crossed. Location 12-22-30-25W2 Saskatchewan at 3856 feet.

lization, perhaps without a liquid phase, such as suggested by Clark and Schwerdtner (1966, p. 102); or, replacement of carnallite by sylvite may have occurred by some slower reaction.

DISTRIBUTION OF BROMINE AND RUBIDIUM IN SYLVITE AND CARNALLITE OF PRAIRIE EVAPORITE

In the lower part of the Middle Devonian Prairie Evaporite of Saskatchewan, halite is interlayered with thin anhydrite-carbonate laminae. In the upper part of the formation, members with sylvite and, or, carnallite occur and have been numbered from oldest to youngest Members 1, 2, 3A and 3B (Wardlaw, 1968). These members are separated by units of halite with only traces of carnallite and sylvite. Table 4 summarizes the average bromine and rubidium contents for carnallite and sylvite in each member. The averages are based on a total of 383 analyses from 12 cores and these data have been illustrated graphically elsewhere (Wardlaw, 1968, Plate 1).

In the leaching experiments, carnallite from the Prairie Evaporite yielded sylvite with 0.55 times the bromide of the parent carnallite. Table 4 shows the Members 3A and 3B contain sylvite with 0.54 and 0.53 times the bromine of associated carnallite in the same member. These results support the conclusion that the sylvite in Members 3A and 3B was

Table 4. Bromine and Rubidium in Carnallite and Sylvite of Prairie Evaporite

MEMBERS	YOUNGEST	Bromine		Br in Syl	Br in Carn	Rubidium		Rb in Syl	Rb in Carn
		Carnallite	Sylvite			Carnallite	Sylvite		
	3B	810(11)	427(49)	0.53		290(7)	97(50)	0.33	
	3A	1300(24)	702(22)	0.54		255(26)	60(21)	0.24	
	2	1510(49)	1165(12)	0.77		141(44)	18(11)	0.13	
	1	1754(11)	1553(15)	0.88		79(13)	7(18)	0.09	
	OLDEST								

Bromine and rubidium in carnallite and sylvite members of the Prairie Evaporite. Average values in ppm presented with numbers of analyses shown in brackets. Data displayed graphically in Wardlaw (1968, Plate 1).

derived from carnallite. In Members 1 and 2, the bromine in sylvite to bromine in carnallite ratio is somewhat larger.

The experimental results show that sylvite derived from carnallite has about 1.3 times the rubidium of the parent carnallite. From Table 4, it can be seen that the ratio of rubidium in carnallite to rubidium in sylvite increases from 0.09 in Member 1 to 0.33 in Member 3B, ratios considerably smaller than would be expected for sylvite derived from carnallite.

As well as considering the ratios of bromine and rubidium in the sylvite and carnallite of particular zones, it is useful to compare the trends in vertical profile with those of an "ideal" evaporite model.

"Ideal" evaporite model.

Progressive evaporation of magnesium sulphate deficient sea water, in a closed system, results, eventually, in the deposition of sylvite and then of carnallite. The top portion of Figure 5 illustrates the ideal distribution of bromine and rubidium to be expected in sylvite and carnallite (after Braitsch, 1962, p. 76, p. 107; 1966, p. 299).

The quantity of bromide in a chloride, or of rubidium in a potassium salt, bears a definite relationship to the trace element content of the parent brine. This relationship is expressed as a partition coefficient which can be defined as:

$$\frac{\text{weight percent trace element in the solid phase of a salt}}{\text{weight percent trace element in the liquid phase from which the salt crystallized.}}$$

The partition coefficient for sylvite in the system discussed is approximately 0.7 and it follows from the above definition that as sylvite crystallization progresses the brine will become enriched in bromine and that successive crystals of sylvite will contain increasing amounts of bromine, as depicted in Figure 5.

As the partition coefficient for rubidium in sylvite is greater than unity (approximately 2), it might be thought, from the definition of the partition coefficient, that progressive crystallization of sylvite from a brine would lead to impoverishment of rubidium in the brine, and therefore in successive crystals of sylvite. However, as Braitsch (1966, p.298) has indicated, whether progressive crystallization will result in enrichment or impoverishment of a trace element in solution depends not only on the partition coefficient, but also on the fraction of crystals formed and of water evaporated. This relationship has been summarized by Wardlaw (1968, p. 1287).

Figure 5 illustrates that rubidium, like bromine, increases from oldest to youngest sylvite in a primary sequence.

The partition coefficient for bromine in carnallite is approximately 0.5 and bromine increases from oldest to youngest carnallite in a primary sequence. The reverse is the case for rubidium in carnallite, where the partition coefficient is very large (22 ± 1 at 25°C , Kühn, 1963, p. 111).

Thus, in vertical profile, there is a direct correlation between rubidium and bromine in sylvite but an inverse correlation between rubidium and

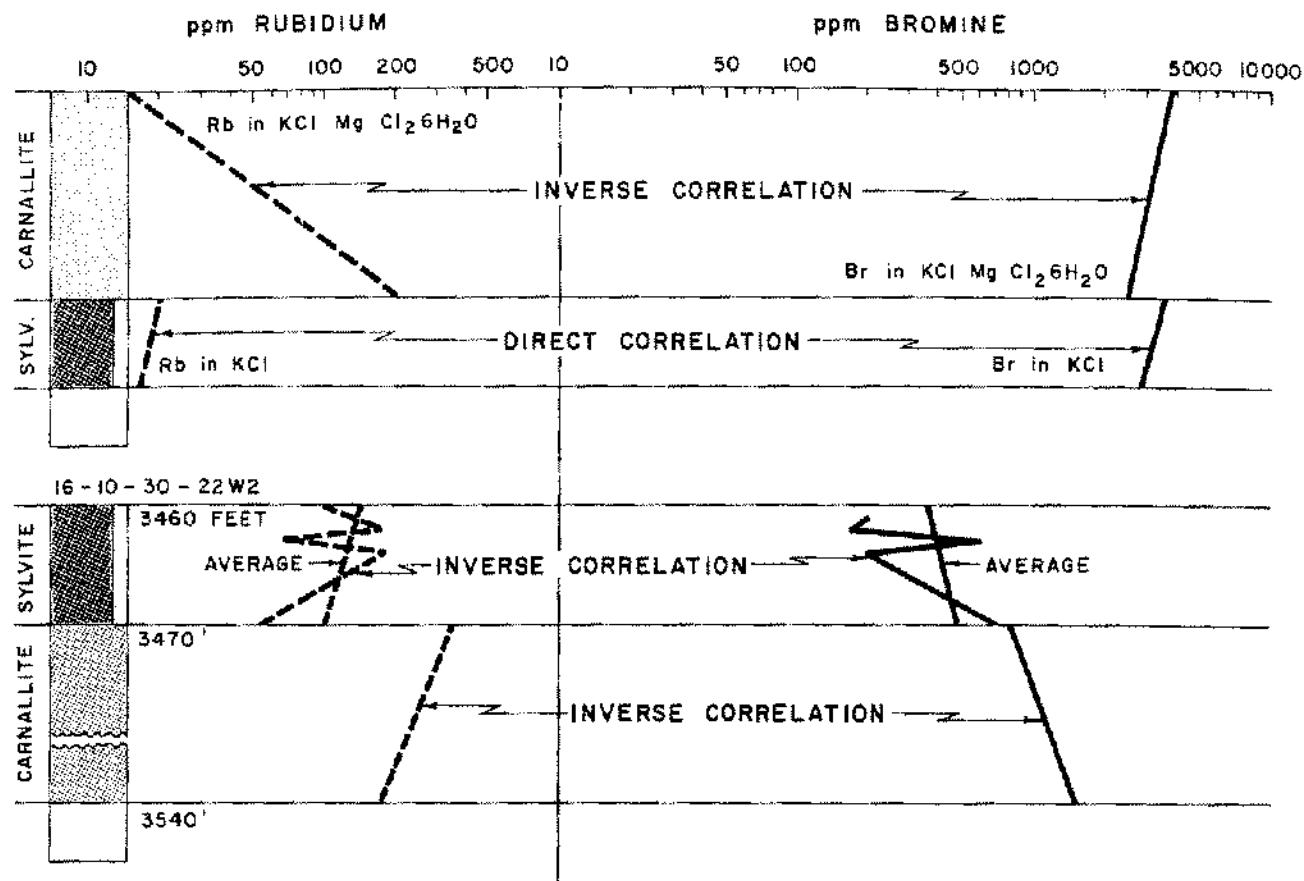


Figure 5. Upper portion illustrates the ideal distribution of bromine and rubidium to be expected in sylvite and carnallite formed by progressive evaporation of magnesium sulphate deficient seawater in a closed system (after Braitsch, 1962, p. 76, p. 107; 1966, p. 299). Lower portion illustrates a typical situation from the Prairie Evaporite Formation (from Wardlaw, 1968, Plate 1).

bromine in carnallite, as depicted in the upper part of Figure 5.

Comparison of Prairie Evaporite with "ideal" model.

From the oldest carnallite-sylvite member (1) to the youngest (3B), certain trends are evident (Table 4). These trends may be summarized as follows. From the oldest to the youngest members;

- (1) bromine in carnallite decreases,
- (2) bromine in sylvite decreases,
- (3) rubidium in carnallite increases, and
- (4) rubidium in sylvite increases.

These trends are depicted for a specific core in the lower portion of Figure 5 (generalized from Wardlaw 1968, Plate 1) and may be compared with the ideal profile described above.

Major sylvite occurrences tend to overlie carnallite in the Prairie Evaporite, the reverse of the

ideal sequence. Bromine and rubidium in carnallite have an inverse correlation as in the ideal situation, but unlike the latter, bromine decreases in profile from oldest to youngest carnallite (although, locally, in a given potash zone, bromine in carnallite may increase upward in profile).

Bromine and rubidium trends in sylvite differ from the ideal in having an inverse correlation and in having bromine decreasing from oldest to youngest sylvites.

Table 4 and Figure 5 (lower portion) show that rubidium and bromine trends for sylvite conform with those for carnallite, which suggests some relationship between these minerals.

Sylvite in the Prairie Evaporite contains as much as ten times the maximum amount of rubidium possible in a primary salt. This is most satisfactorily explained if sylvite was derived from carnallite, since carnallite tends to have a relatively

large rubidium content which can be inherited by sylvite on leaching, as demonstrated in the experiments reported here. Although the rubidium content of much of the Prairie Evaporite sylvite is too large for a primary salt, it is small in relation to the associated carnallite from which it is thought to have been derived. On the other hand, the bromine content of the Prairie Evaporite sylvite is very close to the value which would be expected were it derived from the associated carnallite. The derivation of sylvite from carnallite may be supported also by the inverse correlation which generally exists between bromine and rubidium in sylvites of the Prairie Evaporite. It has already been noted (Fig. 5) that there is a direct correlation between rubidium and bromine in an ideal sylvite profile and an inverse correlation between the same elements in carnallite. The inverse correlation of bromine and rubidium in a Prairie Evaporite sylvite profile is like the relationship for carnallite, but not for sylvite, in the ideal profile. A possible explanation is that the sylvite was derived from carnallite and that the sylvite inherited the major rubidium and bromine trends which existed in the carnallite before replacement.

In conclusion, the results of the laboratory experiments on leaching of carnallite to sylvite conform approximately with results which can be calculated from previously determined partition coefficients from bromine and rubidium, and provide a useful basis for interpreting the distribution of these elements in natural rocks. Such experiments should be extended to include the effects of leaching by solutions other than fresh water.

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