

# Geochemistry of Bromine in Some Salt Rocks of the Prairie Evaporite Formation of Saskatchewan

by  
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## ABSTRACT

*During the crystallization of salts from sea water, bromine does not combine with other elements to form bromides, but occurs in solid solution in chlorides. The significance of the distribution of bromine ions in solid phases of chlorides and the solutions from which they crystallize, and the uses of bromine content as a genetic and prospecting criterion, have long been known.*

*The bromine content of the lowest halites overlying anhydrite, from two cores of the Devonian Prairie Evaporite Formation of Saskatchewan is higher (0.011 and 0.0088 weight percent bromine per 100 NaCl) than that of the first halite to crystallize from present day sea water when evaporated in a container with no additional solutions entering during evaporation. It is also higher than the bromine content of the lowest halites from the German Permian, which also are variable in different parts of the basin of deposition according to local conditions. Bromine weight percentage curves for the Saskatchewan cores show fluctuations in bromine content, from the lowest halite upwards, without a progressive trend for an increase in bromine. Particularly noticeable is a reduction in bromine content above the lowest halite to values comparable to those of some of the lowest halites of the German Zechstein.*

*These results suggest that the bromine content of the Devonian seas of Saskatchewan may have been the same as that of the Permian seas of Germany, and of present day sea water. The bromine values determined correspond to those of the zone of normal halite, and are significantly lower than those of the zone of normal sylvinite and mixed potash salts. However, in one of the cores there are large crystals of carnallite, which probably are secondary.*

*The contention that the Saskatchewan halite is a primary precipitate from marine brines is substantiated by the presence of "hopper" crystals, which generally are interpreted to be the result of growth on the surface of the sea.*

## INTRODUCTION

The significance of the distribution of bromine ions in solid phases of chlorides in relation to the solutions from which they crystallize, as well as the uses of bromine content as a genetic criterion and as an aid in prospecting, have long been known (1).

The object of the present study is to determine the bromine content in halite from the Middle Devonian Prairie Evaporite Formation in Saskatchewan, Canada, and to compare the results with determinations made from halite, in other systems, in other parts of the world. The principles underlying the distribution of bromine in chlorides, and the method of making bromine determinations are outlined.

Two cores have so far been analyzed. The one, which will be referred to as the Winsal Osler core (3-28-39-4-W3), was obtained from a well drilled approximately 22 miles

north-northeast of Saskatoon. The other, here called the Tidewater Bryce Lake core (1-14-25-16-W2), is situated approximately 130 miles southeast of Saskatoon.

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### BROMINE IN CHLORIDES

Bromine does not form bromides during the crystallization of salts from sea water, but occurs in solid solution in chlorides. The quantity of bromine in a chloride bears a definite relationship to the bromine content of the brine from which that chloride crystallized. This definite relationship is expressed by a distribution coefficient, which is constant for a particular chloride at the low bromine concentrations encountered in natural brines. The effect of temperature on the distribution coefficient is negligible (2). Different chlorides have different, but definite, distribution coefficients and where two or more chlorides crystallize simultaneously from a brine, the bromine enters each chloride in the same ratio as if only that one chloride were present. Therefore, the bromine contents of these chlorides bear a definite relationship to each other.

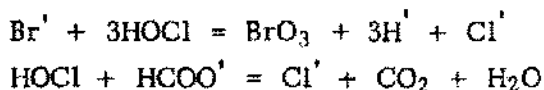
Russian and German workers have expressed bromine distribution coefficients for chlorides in slightly different ways and thus use constants which are numerically different. The Russian coefficient is the ratio of the weight percent of bromine in solid chloride, to the weight percent of bromine in the dry residue of the remaining liquid phase (3). On the other hand, the German coefficient is the ratio of the weight percent of bromine in solid chloride to the weight percent of bromine in the remaining liquid phase (4).

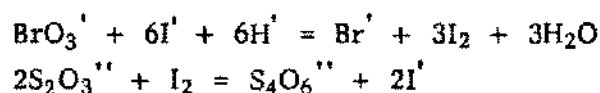
Experiments have shown that the distribution coefficients for all chlorides are always less than one. Consequently, during the progressive evaporation of a brine, although bromine is removed from solution into the chloride crystals, the concentration of bromine in the brine progressively increases, because only part of it enters the chlorides. A definite bromine content in the chloride as well as in the remaining liquid will correspond to each stage of concentration during evaporation and a particular bromine content for chloride crystals can be related to a particular concentration of mother brine. Valyashko, and other workers before him have drawn attention to the usefulness of the bromine content of halite as a guide to detecting horizons of high brine concentration at which potash deposits could be expected (5).

Stressing and recrystallization in the dry condition will not change the bromine content of chlorides. However, resolution of precipitated chlorides by fresh water (or sea water diluted with fresh water), and subsequent crystallization, will result in a lowering of the original bromine content which was determined by the salinity of normal sea water. Many salt minerals have been formed during, or have been affected by, post depositional changes, and the bromine weight percentages in chlorides may provide information valuable in interpreting the genesis of these minerals.

### METHOD OF ANALYSIS

The method used for determining bromine content of halites from the Prairie Evaporite Formation was devised by Van der Meulen, subsequently modified and improved by D'Ans and Hoefer (6). This method is based on the oxidation by hypochlorite, of bromide to bromate. Excess hypochlorite is destroyed by reaction with formic acid. Potassium iodide and hydrochloric acid are then added; the bromate ions are reduced, and iodide is oxidized to iodine, which is quantitatively determined by titration with sodium thiosulphate, using a starch indicator. The chemical reactions can be summarized as follows:





A separate analysis is made to determine the total sodium chloride in the sample, and the bromine content is expressed as a weight percentage of the sodium chloride.

If there are significant amounts of magnesium and potassium chlorides in halite then, in a determination of the weight percentage of bromine in halite, a correction has to be made for the bromine in the other chlorides present.

Potassium and magnesium weight percentages were determined for the samples using a spectrophotometer (Table I). Only the uppermost two samples of halite in the Winsal Osler core contain significant amounts of potassium and magnesium, and here the correction of the bromine weight percent in the halite amounts to less than 8 percent and does not substantially affect the form of the bromine curve (Figure 1).

Sample No.	NaCl (Wt%)	K (Wt%)	Mg (Wt%)	Br (Wt%)	Wt% Br per 100 NaCl
1	98.23	0.009	-	0.0086	0.0088
2	94.90	0.005	-	0.0040	0.0042
3	98.09	0.007	-	0.0041	0.0042
4	95.28	0.009	-	0.0033	0.0037
5	99.83	0.011	-	0.0036	0.0036
6	99.01	0.015	-	0.0044	0.0044
7	97.47	0.084	-	0.0048	0.0049
8	98.69	0.014	-	0.0038	0.0039
9	98.91	0.014	-	0.0040	0.0040
10	98.20	0.011	-	0.0038	0.0039
11	99.75	0.010	-	0.0054	0.0054
12	99.25	0.006	-	0.0031	0.0031
13	99.12	0.005	0.043	0.0111	0.0112
14	97.94	0.012	0.049	0.0080	0.0082
15	99.50	0.016	0.048	0.0111	0.0112
16	99.11	0.006	0.047	0.0157	0.0158
17	99.16	0.006	0.060	0.0111	0.0112
18	98.96	0.006	0.059	0.0124	0.0125
19	97.72	0.018	0.054	0.0156	0.0160
20	98.78	0.027	0.059	0.0082	0.0083
21	98.47	0.022	0.054	0.0070	0.0071
22	97.58	0.250	0.062	0.0076	0.0078
23	98.69	0.140	0.160	0.0143	0.0145

Table I. Chemical data for Bryce Lake core above (samples 1-12) and Winsal Osler core below (samples 13-23). See Figure 1 for graphical plot of bromine weight percentages in halite.

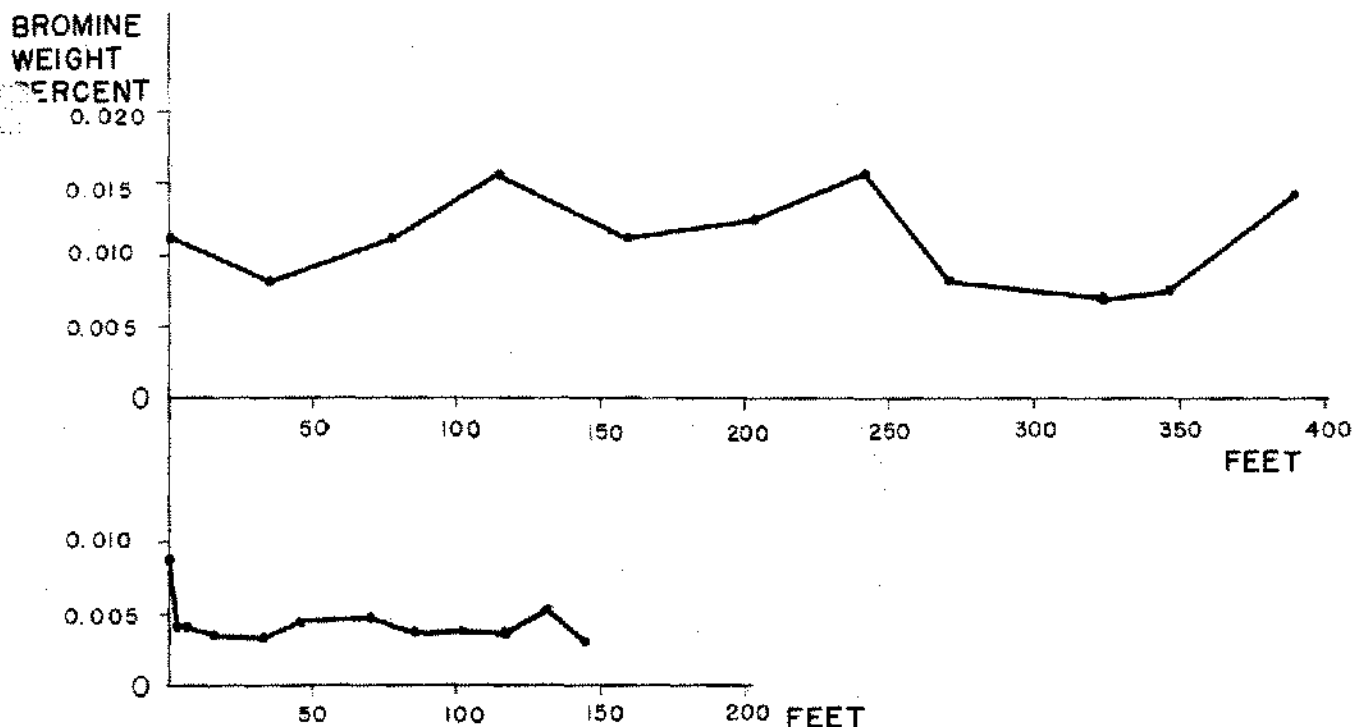


Figure 1. Bromine weight percentages for Winal Osler core above, and Tidewater Bryce Lake core below. Footage is measured from the first halite above anhydrite at the base of the Prairie Evaporite Formation.

Carnallite, sylvite, and minor kieserite was identified by optical methods. All magnesium and potassium in the halite is believed to occur in these three minerals. Because carnallite is the most abundant in the halite, potassium and magnesium are first accounted for as carnallite. Any excess potassium or magnesium is expressed as sylvite or kieserite. Kieserite, being a sulphate, contains no bromine and therefore its presence does not affect the bromine determination of halite.

Calculations for the amount of bromine in carnallite and sylvite are made under the assumption that precipitation of these minerals took place from marine brines. However, the secondary solutions from which the carnallite was in fact precipitated, as shown by the bromine content of the halite, which is that of the halite zone and very much lower than that of halite in the carnallite zone, probably had a different bromine content from that of marine brines. The resulting error is, however, negligible since the amounts of carnallite are very small. No account could be made for the liquid inclusions in the salt, which also will cause some error.

#### DESCRIPTION OF CORES

Three formations comprise the Middle Devonian Elk Point Group of Saskatchewan. They are, in ascending order, the Ashern, the Winnipegosis, and the Prairie Evaporite Formations. The so-called Second Red Bed overlies the Prairie Evaporite Formation.

In the Tidewater Bryce Lake core the upper part of the Winnipegosis consists of thinly laminated dolomite, with abundant thin black shale partings, overlain by 5 feet of anhydrite with some associated dolomite. The contact of anhydrite with overlying halite is abrupt (at 4,786 feet) as can be seen in the core, which includes the overlying 160 feet of halite. The halite is coarsely crystalline and appears to be pure, except for some units of anhydrite, particularly abundant in the upper part, which are less than 6 inches thick, and contain minor shaly partings.

The basal 15 feet of the Winsal Osler core is mainly anhydrite and dolomite and is assigned to the upper part of the Winnipegosis. The contact of overlying halite with anhydrite is abrupt (at 3,319 feet). Above this contact anhydrite is present only in minor amounts. The contact with the Second Red Bed is at 2,923 feet. The entire Prairie Evaporite core was examined with the exception of the uppermost 6 feet. The basal 150 feet of halite is coarsely crystalline and contains "hopper crystals," similar to those described by Dellwig, which generally are interpreted to be the result of growth on the surface water of the sea (7). Numerous, thin layers of anhydrite and layers of halite with conspicuous amounts of anhydrite impurity are spaced mainly 1/2 to 5 feet apart throughout the lower part of the core. They are generally less than 1/2 inch thick and contain minor amounts of clay. The upper 241 feet of halite contains large, irregularly scattered, reddish inclusions composed of carnallite, halite, and sylvite, which probably are all secondary minerals. In the upper 230 feet much of the halite is reddish brown, and clay is abundant.

The Tidewater Bryce Lake core is incomplete. It includes the basal 160 feet of halite of the Prairie Evaporite Formation which here has a total thickness of approximately 603 feet. The Winsal Osler core is almost complete for the entire Prairie Evaporite Formation, which here has a total thickness of approximately 396 feet.

Anhydrite underlying halite is more than 15 feet thick in the Winsal Osler core, whereas it is only 5 feet thick in the Tidewater Bryce Lake core, where the thickness of anhydrite is unusually small. The Tidewater Bryce Lake core is situated nearer to the center of the former evaporite basin, within the area in which potassium salts occur. The upper part of the core containing potassium salts was, however, not available for study. The Winsal Osler core is from a region nearer to the basin margin and is outside the region in which significant potassium salts were deposited.

#### BROMINE CONTENT OF LOWEST HALITES

In discussing the bromine content of the lowest halites above anhydrite, attention must be paid to certain inconsistencies in the publications of previous workers.

Differences exist in the German and Russian literature concerning the weight percent of bromine in the first halite to crystallize from present day sea water. These differences arise because of a lack of agreement on the bromine content of sea water at the point at which the first halite crystallizes and, more important, because of differences inherent in the German and Russian distribution coefficients. Kuehn stated that the bromine content of sea water, at the point when the first halite is precipitated, is 0.0802 percent (8). Valyashko found an average bromine content of 0.051 percent at the beginning of halite precipitation (9).

Table II shows the bromine weight percent in the first halite to precipitate from solutions having these two bromine contents, calculated first on the basis of the German distribution coefficient and then on the basis of the Russian distribution coefficient. From Table II it is clear that different values of bromine content of the first halites is mainly due to a difference in the distribution coefficients, rather than to the difference in the values of the bromine in solution at the point of first halite precipitation. Using the Russian coefficient, values are obtained which are approximately three times those arrived at when using the German coefficient. Accurate redeterminations of the distribution coefficients in chlorides are desirable.

Bromine contents of the lowest halites overlying anhydrite from the two Saskatchewan cores are, 0.011 and 0.0088 (expressed as weight bromine percent NaCl). Above the lowest halite there is a reduction in bromine content to values as low as .0070 and .0031 respectively in the two cores.

Kuehn, takes 0.0032 as the theoretical bromine content of the first halite to crystallize from present day sea water and quotes figures ranging from 0.0029 to 0.007 as actually determined in the lowest halites from the Upper Permian deposits at various localities in Germany (10). He stated that these values agree so well with those calculated (using the German distribution coefficient) that it can be said with certainty that the Upper Permian sea had the same bromine content as the oceans of today. The bromine values in the Saskatchewan halites are such that this statement can be extended to them also. However, if the Russian coefficient is more accurate than the German, then the lowest bromine contents of the Saskatchewan as well as the German, halite

Br. in weight percent in solution	Br. in weight percent in solid halite
0.0820 0.051	Calculated using German coefficient
	0.0032
	0.00204
0.0802* 0.051	Calculated using Russian coefficient
	0.0108
	0.0068

\*Calculated on basis of Russian figure 27.49% for salt content of liquid phase when NaCl begins to crystallize.

Table II. Comparison of bromine contents in first halites to crystallize from solution, calculated using German and Russian distribution coefficients, and also the differing values for bromine content of solution at point where first halite crystallizes.

would have to be considered lower than is possible for primary precipitates from present day sea water.

If the Russian distribution coefficient is accurate, then either the Devonian seas of Saskatchewan and the Permian seas of Germany did not have the same bromine to chlorine ratio as present day sea water, or else the halites with a bromine content lower than 0.0068 are precipitates from brines which reached saturation partly by re-solution of salt.

It is known that within a single depositional basin the bromine content for the lowest halite above anhydrite is variable according to position within the basin.

Generally, towards a basin margin, anhydrite is relatively thick, thinning towards the basin centre, while a reverse relationship holds for halite, which is thickest near the basin centre. It has been shown by Baar that the bromine weight percent for the lowest halite above anhydrite, is greater near the basin margin than it is in the basin center (11).

The same relationships are suggested by the analyses of the Saskatchewan cores. A thicker anhydrite section underlies the halite of the Winsal Osler core than the Tidewater Bryce Lake core. The Tidewater Bryce Lake core is nearer to the basin axis, where the Prairie Evaporite Formation is 603 feet thick, compared to the 396 feet of the Winsal Osler core, nearer to the basin margin. The bromine weight percentages in halite, for the Winsal Osler core, are consistently higher than those in the Tidewater Bryce Lake core (Figure 1), but in the latter, only the lower part of the halite zone was available for examination.

Anhydrite and halite may be time equivalent in different parts of a basin (11, 12, 13). Conversely, the lowest halites in a basin need not be time equivalent, which may be the case with the Saskatchewan cores.

That the lowest halites above anhydrite in the Saskatchewan cores have differing bromine contents which are higher than would be expected, from either the German or Russian data, must be explained by movements of brines within the basin. The brines which precipitated the lowest halite examined had already precipitated halite at other localities. Detailed bromine analyses in a well-explored basin would provide the answer to many questions.

## FLUCTUATIONS IN BROMINE CONTENT

The bromine weight percentage curves for the Saskatchewan cores show fluctuations in bromine content, from the lowest halite upwards, without a progressive trend for an increase in bromine. These fluctuations probably reflect influxes of brines less concentrated than those precipitating halite in the basin, but more concentrated than normal sea water. Dilutions by fresh water could not produce these fluctuations, because such dilutions would not cause significant change in the bromine to chlorine ratio of the brine. Associated layers of clay and of anhydrite are probably also related to these influxes.

The bromine values determined correspond to those of the zone of normal halite, and are significantly lower than those of the zone of normal sylvinite and mixed potash salts. In the Winsal Osler core there are large crystals of carnallite which probably are secondary.

Bromine analyses for carnallite from Saskatchewan have not yet been made, but it is certain that the salt rocks in the upper part of the Winsal Osler core have been infiltrated by secondary brines, as the bromine content of the halite is much too low for a primary carnallite region (14). By partial replacement through the action of diluted brines the halite may now be a mixture of primary and secondary salt, which thus could have a lowered bromine content.

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