

The Chemistry and Origin of Potash Deposits

Donald E. Garrett
Garrett Research and Development Company
1855 Carrion Road
La Verne, California

ABSTRACT

The potash salts occurring throughout the world are predominantly of oceanic origin, forming in the final period of desiccation of sea water basins. However, the physical chemistry of evaporating sea water does not allow sylvinite (KCl plus NaCl) to be directly crystallized under any circumstances, and also requires the formation of massive quantities of the relatively minor mineral, kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). A new theory is presented to explain these anomalies. It assumes the solar evaporating, closed sea water basins to have undergone extensive limnological stratification. The normally crystallizing potash salts (as required by the metastable solubility relationships) schoenite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), leonite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), and kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 2.75\text{H}_2\text{O}$) were converted to carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in passing through or residing in, the strong lower brines; the carnallite in turn was converted to sylvite (KCl) in the final flooding of the basin for that potash stage. Epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) was removed from the brine by being crystallized in the cooler evenings or winters in the shallower zones, and finally was redissolved and flushed from the deposit at the same time as magnesium chloride from the carnallite. Since halite (NaCl) crystallizes continuously, it would have occurred with the carnallite, forming sylvinite in the final mixture. Other potash minerals or mixtures could be formed as simple variations of this depositional sequence.

CHEMICAL DESCRIPTION OF POTASH DEPOSITS

Among the many geochemical mysteries of our times, perhaps one of the most thoroughly studied

and documented by physical chemistry and geological data, and yet one that is still very far from a satisfactory solution, is the chemistry and origin of potash deposits. The problem revolves around the fact that potash (here defined as all water soluble potassium compounds) is quite common, occurring with many halite (NaCl) deposits, and predominantly as sylvinite, a physical mixture of sylvite (KCl) and halite. Sylvinite represents perhaps 75 to 80 per cent of the K_2O content of known oceanic occurrences, whereas carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), found mixed with halite like the other potash minerals, may represent about 15 to 20 per cent of the K_2O content; the remaining 5 to 10 per cent is about equally divided between kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 2.75\text{H}_2\text{O}$) and polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Of course many other potash minerals are known, and some, such as langbeinite ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$), even occur in locally economic quantities. However, if a theory of origin were to explain sylvinite and carnallite it would quite adequately cover most of the world's potash occurrences.

Another unusual characteristic of potash deposits is the relatively small amount of MgSO_4 or its compounds in or near the deposits. Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) is common in a few deposits, but its total percentage in the world potash mineral inventory is very low. Double salts with MgSO_4 are more common, such as the kainite, langbeinite, and polyhalite previously mentioned, but these still would not represent an equivalent MgSO_4 content of more than a small percentage of the K_2O in most deposits. In the same manner, beds, adjacent deposits, or even remotely separated deposits involving sulfate compounds that might have been companion compounds to the potash are well

known, but their total quantity is also relatively small. These include minerals such as thenardite (Na_2SO_4), astrakanite or bloedite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), and many others.¹

These two basic characteristics of most potash deposits are in direct conflict with the physical chemistry of evaporating sea water, which as noted by Landes (1963), and Borchert and Muir (1964), is the unquestioned and well-substantiated origin of most of the world's potash deposits. First, sylvite cannot be deposited directly from sea water (i.e., it is neither a stable nor metastable phase) except after removal of most of the Mg and SO_4 in the sea water, or under extreme winter conditions. Also, secondary, or retrograde, crystallizations of the normal oceanic salts yield potash only under unusually demanding and special conditions. Thus, it is hard to explain on a widespread basis the mere presence of KCl, let alone its being the most common and dominant mineral.

Similarly, one of the hydrates of MgSO_4 should be present in an amount roughly equal to the potassium mineral, and various MgSO_4 double salts should also be present in about the same amount from any normal sea water depositional cycle. Usually the equivalent KCl content of potash salts deposited from sea water in solar ponds cannot rise above about 20 to 25 weight per cent during any portion of the evaporation cycle, and sulfate expressed as MgSO_4 varies between 25 and 50 per cent. In potash deposits, however, the sulfate content is normally low; at best there is occasionally a zone or seam all of one sulfate mineral. The sparsity of the magnesium sulfate compounds in the light of the stoichiometric amounts of Mg and SO_4 that should accompany potash depositing from sea water has never been adequately explained.

CURRENT THEORIES OF ORIGIN

In attempting to explain these anomalies and the origin of potash deposits, a great deal of excellent and generally quite useful physical chemical data have been developed. The comprehensive studies of Vant Hoff, D'Ans (1947) and their associates initially had the explanation of potash deposits as an objective, and rather completely defined the phase relations of the Ca-K-Mg-Na- SO_4 -Cl system and many of its sub-systems. This work, together with a large number of related studies, such as the trace mineral analyses of Braitsch (1966), has been very useful to potash processing plants as well as adding to general phase chemistry knowledge. It has also clearly indicated the mechanism of some alteration

and sub-sequence development in potash deposits, especially as they have occurred in Germany. However, it has done little to clarify the general mechanism of potash deposition.

Theories now prevalent on the origin of potash deposits start with the "no sulfate" part of the problem, and propose that either: (1) sufficient high-Ca, low- SO_4 ground water entered the sea water basin to precipitate most of the oceanic sulfate as gypsum (D'Ans, 1947) or, (2) the oceanic SO_4 was converted by sulfate reducing bacteria to H_2S (Borchert and Muir, 1964, p. 234).

Both theories are interesting, and both certainly could explain some local occurrences, but they have serious limitations as general explanations. Immense quantities of Ca-bearing water would be required for the precipitation theory. For instance, for the large Canadian potash deposit, a river the size of the Mississippi and with the mineralization of the Colorado would have to have flowed into the basin steadily for about 40 million years prior to the time of salt deposition, but after essentially complete isolation (or only inflow) of the brine from the sea. Thousands of feet of gypsum and limestone would have been deposited, and a connection with the sea could have been re-established only after the final potash formation. The salt deposited between the second and third potash layers would have had to originate from re-dissolved salt of the earlier deposited salt layers.

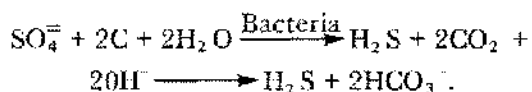
Although such a process may have operated to some degree, it would appear to be much too demanding for general application to most of the world's potash deposits. In some, however, such as in Ethiopia, where the amount of anhydrite associated with the sylvinite is much too large to be explained by the natural ratio in sea water, either an inflow of Ca-bearing water must be assumed during the potash crystallization period, or a Ca-rich intruding ground water must have entered at a later date. Likewise, seams of anhydrite, gypsum, or dolomite between layers of salts (such as in the Alsacian and Paradox Basins deposits) and as insolubles (when greater than about 2 per cent) in the salts, must have originated in this manner or alternatively during a prolonged interruption of the salt depositing cycle. However, the fact that the ratio of gypsum to halite or potash in the solid saline deposits is similar to the ratio in sea water further

1. It should be remembered that the only sulfate being considered is that present in the sea water after the basin was isolated from the sea. This consequently excludes much of the sulfate underlying most salt deposits.

reduces the plausibility of this explanation for the phenomenon of generally low sulfate in potash deposits.

The bacterial sulfate reduction theory would also appear to be too extreme for most chemists to accept. It is true that such bacteria are amazingly prolific, having been found in sea marshes, a few dry lakes, occasionally in some ocean basins or estuaries, and even in some ancient salt deposits. However, these occurrences still provide little evidence to support the bacteria's ability to convert most of the sulfate in a very great number of very large isolated ocean basins; even though some halite deposits contain traces of H_2S gas, and occasionally sulfide or sulfur zones are found nearby. In the most prolific sulfate reduction examples known today, the conversion has been extremely small, such as at the deepest Searles Lake high-sulfate zones (30,000 years old). The bacterial reduction has also been essentially nil in most sea water-type, salt-depositing or "closed," basins known today [Great Salt Lake, Caspian Sea, many coastal areas as shown by Kinsman (1966), and literally hundreds of basins containing related sulfate systems.]

A corresponding formation of Na_2SO_3 , $CaCO_3$, $MgCO_3$, sulfur, or similar material to match the SO_4 removal from the sea water would also be required, and should be quite noticeable with or near the potash deposits. The overall chemical reaction for the bacterial metabolism of organic matter and sulfate ion produces H_2S gas and CO_2 :



The CO_2 may be immediately reabsorbed, which is the basis for a popular Na_2CO_3 -origin theory; at least one soda ash (Na_2CO_3)-trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) deposit has been fairly certainly formed in this manner (Hash-Issa or the Wadi-Natroun in Egypt). However, since sodium carbonate compounds are essentially unknown in potash deposits (as is magnesium carbonate, except as dolomite), and the precipitation of calcium carbonate would have required the same aforementioned improbable amount of excess calcium to have entered in run-off waters, this lack of a companion product implies very strongly the absence of major bacterial reduction of sulfate in oceanic potash deposits.

A final consideration for the sulfate-reducing bacteria theory is the changes observed in the S^{34}/S^{32} ratio. The bacteria apparently have a fair selectivity for S^{32} and as a consequence, should

tend to deplete this isotope if H_2S escapes from the brine. This can be seen by a decrease in the $\delta S^{34}/S^{32}$ for sulfides formed by sulfate-reducing bacteria, not uncommonly reaching values of $\delta S^{34} = -20$, while the original sea water was about $\delta S^{34} = +20$. Thus, for a large amount of SO_4 to be removed by bacterial action, the SO_4 that survived and remained to be precipitated as potash double salts or kieserite ($MgSO_4 \cdot H_2O$) should be predominantly S^{34} , or have a high value of δS^{34} . Analyses of the sulfate content of the soluble salts present in several potash deposits have not shown this to be the case, and Holser and Kaplan (1966) noted an actual decrease in δS^{34} over the oceanic distribution. Since run-off waters have a low δS^{34} content, the sulfate isotope distribution would imply that at least a reasonable amount of fresh water had entered the salt and potash depositional basin.

In each of these theories the elimination of sulfate from the brine allows carnallite to become the stable potash mineral crystallized when the modified sea water is evaporated. The theories, as summarized by Borchert and Muir (1964), generally then go on to assume that ground water or water of hydration from any or all minerals nearby decomposes the carnallite into KCl. While this later conversion must accurately represent what in general did happen, it is very doubtful that the decomposition could occur so consistently and completely by such an uncertain and difficult means as ground water intrusion, and water of hydration could never accomplish more than part of the decomposition. Certainly a great deal of local alteration could, and must have, occurred from ground and hydration water, but not the general initial conversion of carnallite to sylvite.

Much attention has been given to secondary transformations that might occur long after the deposit was laid down. Useful data have been developed from this work, and some local occurrences in deposits with very simple and isolated systems have been quite positively identified. However, because of the great complexity of the basic sea water system under dynamic crystallizing conditions, much of this work is of little general value. The laboratory reactions do not usually coincide with the same reactions on a larger scale (such as a manufacturing plant), and are far from those found to occur in ponds or present-day deposits. Furthermore, these theories on retrogression, metamorphism, and diagenesis, have no possibility of explaining a removal of $MgSO_4$, or the crystallization of sylvite, since there is no more opportunity in a secondary reaction for either its removal or

formation than there was in the original sea water crystallization. This is the case irrespective of temperature, pressure, or time of reaction, (i.e., post-burial conditions), and can be simply verified by a host of recent data. As a consequence, the detailed work on metamorphism and diagenesis is most useful in explaining occasional unusual deposits (which are not the subject of this paper), but does little to explain the general origin of potash deposits.

SOLAR POND EVAPORATION DATA

In considering what actually did cause potash deposits to form in their present state, it is immediately apparent that more information is needed. Geological guesses based upon equilibrium phase data and metastable or transient data, can show no logical path to convert sea water to KCl or even to account for most of the secondary transformations, so data must be examined which represent more accurately the actual evaporating basin conditions. Surprisingly, in the industrial practice of processing complex K-Mg-Na-SO₄-Cl-etc. ores or brines, and in the evaporation of sea water bitterns from solar salt plants, a great deal of pertinent data are available. Specific details of this industrial practice will first be examined in relation to various facets of the question of potash origin.

First, what salts actually do crystallize from sea water (bitterns) under dynamic crystallizing conditions? There is no single precise answer to this question, since the exact depositional sequence depends upon the climate of the area and the depth of the pond. However, for all cases that have been examined, including those from a wide variety of climates and basic dimensions, the pattern is reasonably similar to that shown in Figures 1 and 2.² It should be noted that at no point does the actual concentration path follow any published stable or metastable phase diagram, and yet the curve is very broadly reproducible in field (pond) conditions. Assuming that halite crystallizes at all times, epsomite (MgSO₄ · 7H₂O) is the next major mineral to crystallize, and it continues usually to the end of the achievable carnallite field, although perhaps changing to the 4-hydrate near the end. Mirabilite or glauber salt (Na₂SO₄ · 10H₂O) may precede epsomite in the winter or on cold evenings, and occasional small quantities of astrakanite or bloedite can form, but these are somewhat special occurrences. The epsomite crystallizes predominantly in the evenings, and although much of it

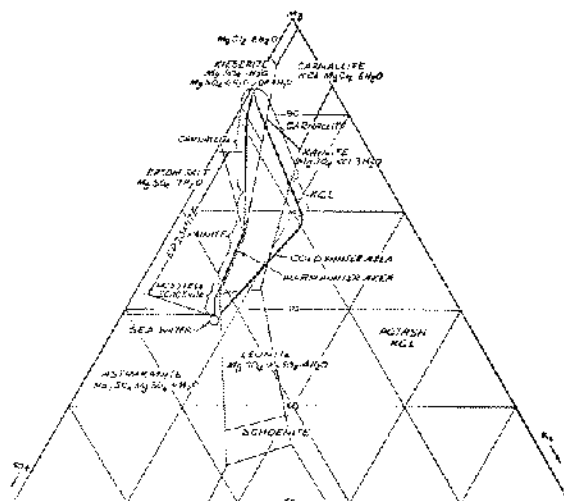


Figure 1. Approximate sea water depositional sequence for potash salts. Stable phase lines are for 25°C. Dynamic evaporation path for pond temperatures 10° to 30°C (winter temperatures to -10°C). NaCl crystallizes in all zones.

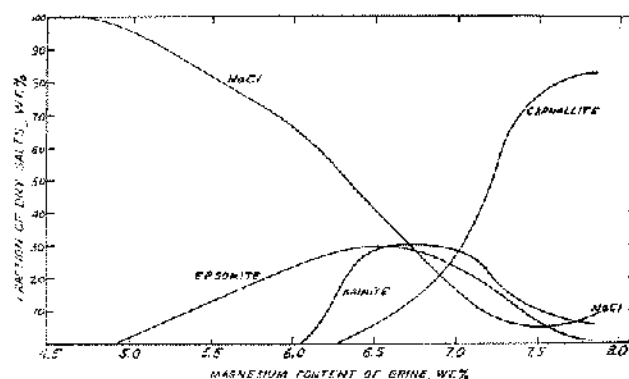


Figure 2. Typical potash salts composition during sea water evaporation.

may easily redissolve during the day, some remains crystallized.

Kainite is the next major crystallization, rising to a peak and then dropping off after carnallite has been well established. Some schoenite (K₂SO₄ · MgSO₄ · 6H₂O) may precede it, but the amount is normally not great unless the sulfate concentration is higher than normal. The final major product is

2. In all phase diagrams the physical chemists' conventions will be used. Thus NaCl and KCl will be shown as the equivalent divalent forms Na₂Cl₂ and K₂Cl₂.

carnallite, although bischoffite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) can follow if the ponds are shallow and the temperatures high. Normally, under good conditions, the total potash zone salts might be distributed as 60 per cent potash double salts, 25 per cent epsomite, and 15 per cent halite (± 15 per cent). The distribution of potash salts varies widely with the area, season, and evaporating conditions, but might typically be 70 per cent kainite and 30 per cent carnallite (± 20 per cent).

These data, along with processing experience, throw some light on the question of whether KCl can form directly from sea water. Actually it can in several different but very restricted ways. First, relatively short exposure of partially concentrated brine to modest winter temperatures (less than 10°C) can remove quite large quantities of sulfate (up to 60 per cent under the coldest conditions) as mirabilite (glauber salt), and similar amounts (up to 40 per cent) as mirabilite and epsomite from stronger brines—both with no loss of potash. At higher concentrations more epsomite can be removed but potash salts also begin to crystallize prolifically. If the sulfate removal is over about 20 per cent, the first potash salt to crystallize upon continued evaporation will be KCl. Not much of this sylvite will be formed, but whatever does will be fairly pure and relatively free of epsomite. Massive glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$), mirabilite, thenardite (Na_2SO_4), or kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) deposits that occur in the deep Nevada salt formation, Great Salt Lake brine (similar to sea water), and the upper Caspian basin (Borchert and Muir, 1964, p. 225) clearly indicate that such “cold weather” deposits can form, but their general importance to potash deposits is still probably minor. Such cold winter temperatures were probably not prevalent during the formation of most of the world’s deposits, and this mechanism cannot account for a large amount of potash, even if the cooling-removal of sulfate was very effective.

There are several other mechanisms used industrially by which KCl can be directly deposited from sea water, but the conditions are sufficiently demanding and the products so unstable that there is essentially no likelihood of their having occurred in nature. With unusually high temperatures early in the depositional cycle langbeinite could form, and at lower temperatures during the same period schoenite could form. Subsequent brines of medium-to-strong MgCl_2 concentration can convert these minerals to KCl in a quick metastable transformation. However, the companion product, epsomite, comparatively quickly (in one to several

days) will reunite with the KCl to form kainite and free water.

Another factor of importance to the mechanism of potash origin is the porosity of the deposit. The potash salts vary widely in their crystal size and shape, a variance at least partly related to concentration of the brine from which they crystallize. However, the initial potash salt deposit usually contains 30 to 50 volume per cent voids, and over the normal day-night temperature cycle in basins less than 20 feet deep, much of the salt deposited in the evening redissolves during the day, and subsequently recrystallizes (this cycle would be longer for deeper basins). This tends to consolidate the deposit, and with the normal packing effect caused by the consolidation and filling-in of later deposited salts, the void volume progressively decreases. A typical example of such porosity values, estimated from many sea water-type deposits might be: 40 volume per cent initially, 30 per cent when under six inches of salt, 20 per cent under one foot of salt, 15 to 20 per cent under two feet of salt, 5 to 10 per cent under 20 to 40 feet of salt, and then gradually to nearly zero with deeper covering (some other salt systems might require several fold these packing depths). This implies that the mother liquor has only a limited time to reside with its salts, or to pass through them if the bottom structure is porous and allows brine leakage (as it nearly always does). Likewise, once the porosity is reduced, intruding ground water has very little opportunity to contact the salts. This is especially true if, as Landes (1963) reports, insolubles in the deposit further seal the interior as the exterior salts are dissolved; a classic example is the anhydrite mantle formed around salt domes.

PROPOSED THEORY OF ORIGIN

Characteristics of the depositional basin.

On the basis of these general background data, the specific formation of potash deposits can be considered. A typical sea water evaporation basin may be roughly characterized as shown in Figure 3. As Landes (1963) states, the evidence points toward subsiding basins as a necessary and characteristic feature of deep marine deposits, but this requirement has little importance for the potash portion of the cycle because of the comparative speed of deposition. The irregularly shaped, nearly closed basin, so common among both inland and oceanic basins today, is probably more characteristic and easier to visualize as the environment for potash deposits.

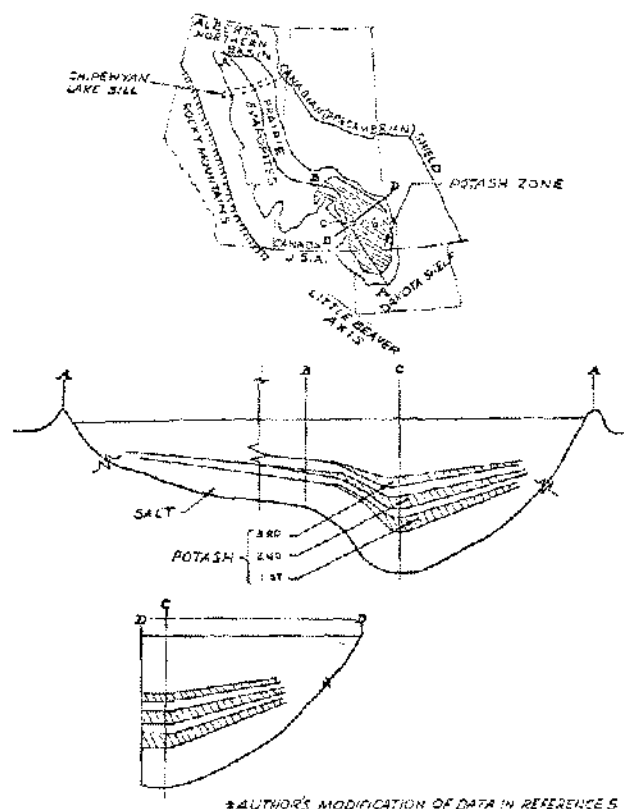


Figure 3. Schematic representation of the Canadian devonian potash deposit.

Various liquor depths can be expected in any natural basin, and there should always be some comparatively shallow areas. With such a shallow and deep configuration the classic limnological brine stratification gradients would exist. Evaporation proceeds more rapidly in the shallow zones, and the stronger brines that are formed migrate slowly as layers to the deeper parts of the basin. This in turn induces surface currents which cause a general flow from the deeper to the shallower zones, and tends to make the surface (top 10 to 20 feet) composition more uniform, with only a slight concentration gradient per unit of distance. Stronger brines as they are formed in the shallow zones continue to replace the layers formed earlier until a fairly well stratified sequence of brine densities exists. Such stratification is very common in all large bodies of water, and a present day example can be seen in the Red Sea, as well as (less exactly, but also typically) in the Black Sea, Caspian Sea, Dead Sea, and Great Salt Lake.

Brine layers of differing strengths in semiclosed evaporating oceanic basins adequately explains the

random, and sometimes low brine concentration from which salt crystallized just prior to the precipitation of potash salts, and the fossil content of salt deposits noted by Tasch (1963). Because of the comparatively constant distribution coefficient of bromides forming a solid solution in sodium chloride, kainite, carnallite, and sylvite, the analysis of bromide in evaporite deposits gives a good indication of the bromide concentration (and thus the extent of evaporation) in the brine from which the salt was deposited. However, while some salt deposits show a steady increase in bromide up to the potash point (Fig. 4), most do not. They show either a very erratic sequence, or low levels until

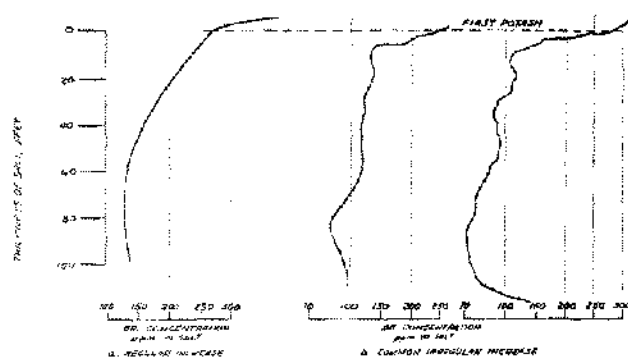


Figure 4. Typical bromide concentrations in halite deposits (from Raup, 1966).

just before potash crystallizes, and then usually an abrupt increase. This can be explained by assuming for the uniform case (Fig. 4a) a rather well-mixed or isolated brine (at least in the initial NaCl crystallizing range), and in the other more general case (Fig. 4b) essentially only surface brines crystallizing salt from a well stratified basin. The periodic inflow of sea water to the basin would mix with a somewhat variable amount of the lower, stronger brine, and then evaporate to crystallize salt. Thus from a relatively thin layer of comparatively weak sea water on the surface, salt (NaCl) could be crystallized and deposited immediately before potash salts crystallized from the denser underlying brines. Such a mechanism would also explain much of the calcium sulfate with the salt in ratios similar to that in sea water, whereas most of the calcium sulfate should have deposited well before salt crystallized, and thus have been in beds or massive layers.

As salt crystallized in a basin of variable depth, it would, as a first approximation, deposit a uniform thickness of salt per unit surface area. This would, in general maintain the deep-and-shallow features of the basin, even though there would be some preferential filling in and smoothing of the bottom. A "sagging basin" would of course allow the underlying salt to have a variable thickness. Because of the constant shrinkage of the shore line and consolidation of the stronger brines into the remaining deeper areas it is quite common for thick salt zones to have thick potash deposits overlying them, especially over comparatively small or local deep structural features. The slow compaction (constant solution and recrystallization, some plastic flow, etc.) of the salts further aids this thickening phenomenon, since with the deeper salts the total amount of compaction is naturally greater.

Formation of carnallite.

In relating the foregoing factors to the formation of potash salts, it is first proposed that all of the potash was either deposited as, or soon converted to, carnallite. Laboratory and solar pond experiments can readily show the ease with which various potash salts are converted to carnallite by strong $MgCl_2$ brines. Concentrations easily obtained by the solar evaporation of sea water (greater than 65 moles $MgCl_2$ /1000 moles H_2O) can convert potash salts to carnallite, as indicated in Figures 5 and 6. Since in the shallower marginal zones of the basin evaporation is comparatively fast, there are ultimately produced strong $MgCl_2$ liquors which sink to the deeper area. The brine volume reduction required to deposit the potash is small compared to that required to initiate and maintain salt deposition, so this formation of high- $MgCl_2$ brine would normally precede the crystallization of potash salts in the deeper basin. The salts formed by evaporation on the surface would thus have to pass through the stronger $MgCl_2$ brine and come to rest in it. Depending upon the temperature and the $MgCl_2$ concentration, only contact for a few hours to a few days is required to completely convert schoenite or kainite to carnallite. The weaker (in $MgCl_2$ —the principal component representing density and extent of evaporation) brine produced from the reaction would ultimately be returned to the upper layers for further evaporation, and the carnallite would remain in the deposit (Figs. 7a 7b).

As a second and final means of completing this reaction, there is always some seepage down (or

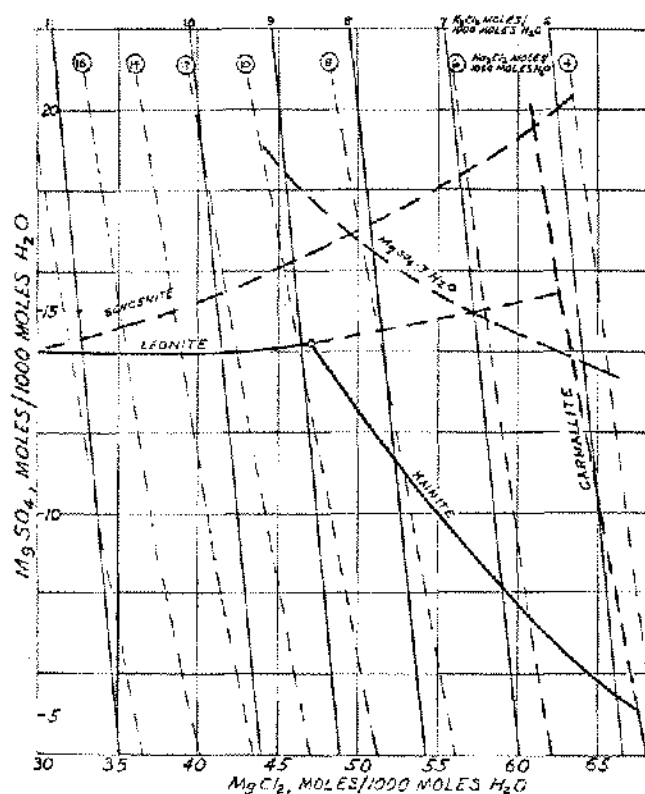


Figure 5. K-Mg-Na-Cl-SO₄ system at 25°C. Stable and metastable equilibrium data for epsomite and carnallite leaching.

along) and through the deposit, and the final brine undergoing this seepage loss would be the strongest $MgCl_2$ liquor. The floor of the basin is never completely impervious and often there is some escape route for denser brines through the floor of the deposit. Such is the case on a microscale for basins closed off by a sand bar such as the Sechura Desert estuary in Peru, where brines with densities above about 1.30 appear to have a sufficient driving force to escape through the bar. Whatever the driving force, this final contact with high $MgCl_2$ brines would be sufficient to convert all of the remaining potash salts to carnallite.

$MgSO_4$ removal.

The fate of the $MgSO_4$ can be explained by a somewhat similar mechanism. Figure 1 for the initial leaching, and Figure 5 for the final conversion, are informative phase relation guides, although the transient behavior of epsomite (or the six or four hydrates of $MgSO_4$) does not follow the diagrams very well. It is an easily demonstrable fact that the higher hydrates of $MgSO_4$, and especially

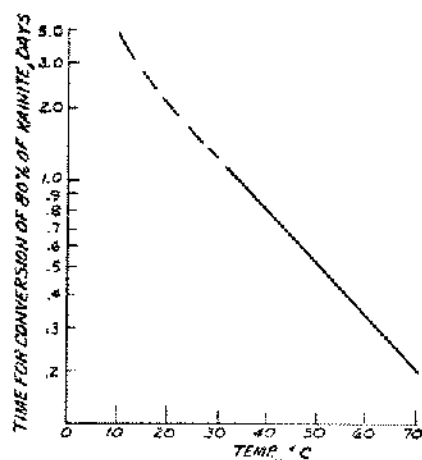


Figure 6A. Influence of temperature on conversion of kainite to carnallite. 80 moles MgCl_2 /1000 moles H_2O .

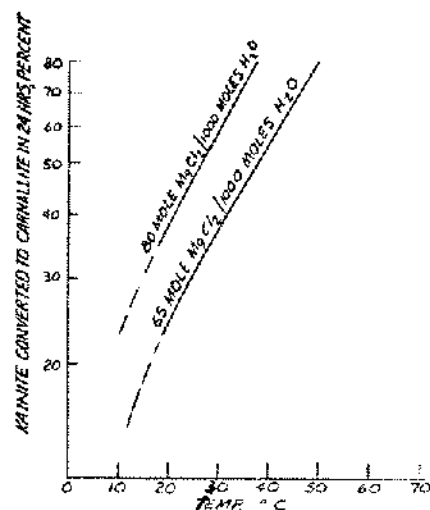


Figure 6B. Influence of brine composition on conversion of kainite to carnallite.

epsomite, will dissolve rapidly in most brines far beyond their metastable equilibrium values, and then slowly come back to equilibrium. In the oceanic potash deposits much of the epsomite that crystallized with the potash salts would be dissolved in falling through the stronger brines in the bottom of the basin, as would the epsomite formed by the conversion of kainite into carnallite. The lower level strong brines should be somewhat warmer than the surface brines, owing both to the transparency of the weak brine compared with the stronger ones (a phenomenon often noted in laminated layer solar ponds), and to the higher temperatures reached in the shallow marginal zones. This would increase the tendency of epsomite to dissolve and offset the cooling resulting from the exothermic heat of reaction of carnallite by the greater endothermic heat of solution of the epsomite. Considering the large mass of strong brine available for such leaching and the rapidity of the epsomite solution rate, very little epsomite should have reached the basin bottom with the carnallite. The MgSO_4 -rich brine, being lighter than the original strong MgCl_2 brine (both intrinsically and because of the seven moles of water liberated by the epsomite), would quickly rise to higher levels and mix with weaker brines where the MgSO_4 content would be stable. This phenomenon is illustrated in Figure 7.

Such a mechanism could adequately explain the scarcity or lack of sulfate in the potash deposit, but not its absence from the total salt basin. How-

ever, the winter cooling effect to remove both glauber salt and epsomite, and the evening cooling effect to remove epsomite, might provide a means for the sulfate's being carried along in a deposit (i.e., not being permanently removed from the solution) like the bulk of the MgCl_2 ; and finally either being flushed from the basin in the terminal flooding, or precipitated as gypsum (combining with excess calcium in run-off waters) during the last evaporation period when salt saturation was not realized. Prior to each potash deposition cycle the sulfate would have been crystallized by winter or evening cooling and consequently reestablished in the residual brine a near-normal sea water ratio of salts, largely in the enlarged salt margins on the basin, with the same mechanism of warm-brine leaching of surface-crystallized epsomite prevailing for its removal from the deeper zones. The sulfate salts in the margins would then be redissolved during each major reflooding cycle through surface contact or by percolation of the weaker brines through these higher, porous salt zones (Fig. 7c). This mechanism, along with a reasonable (and quite variable) amount of sulfate removal by excess calcium entering in surface and ground waters during the entire evaporation period, could well account for the total or partial absence of sulfate from each of the world's potash deposits.

Carnallite conversion to sylvite.

At the end of a potash deposition period one of two basic kinds of events could occur:

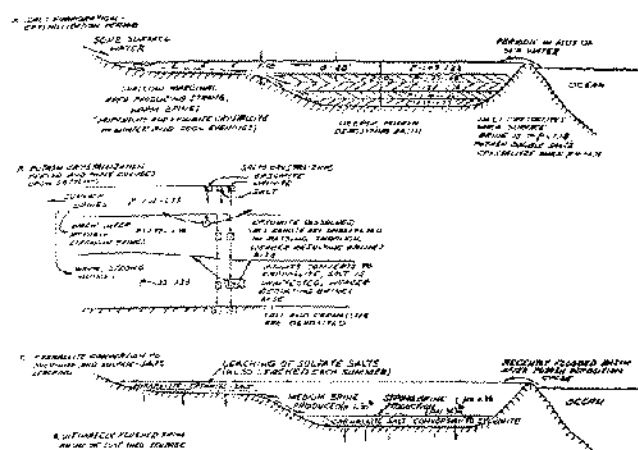


Figure 7. Hypothetical brine stratification pattern and salt deposition in a semi-closed oceanic basin.

(1) An earth movement, massive storms, long periods of nearly complete desiccation or other acts of nature could stop the potash cycle and lay down thick layers of clay or silt. Increased, but still modest, inflows of brine could also stop the potash cycle, but still allow deposition of salt. Either event could possibly seal off the deposit so that it remained as it was deposited—a carnallite-salt mixture.

(2) For the more general case, the depositional cycle would be stopped by an influx of fresh sea water entering the basin, now shallow enough, or with enough turbulence, so that considerable mixing took place between the previously stratified brine and the new sea water. This would interrupt the potash deposition process, as would turbulence or mixing in the stratified brine alone, and allow salt to crystallize again.

The dilute brines would be effective in decomposing the carnallite into KCl (Fig. 5), and the resultant higher $MgCl_2$ brine produced would form a new stratification layer to protect the KCl from being leached or reconverted to double salts until additional halite, carnallite, or insolubles had been deposited (Fig. 7c). Because of seepage and lateral flow through the salts, the weaker (lower in $MgCl_2$) brine would pass through the deposit and eventually decompose all of the carnallite except for those pockets and zones from which it became blocked by clay, lack of porosity, etc. This brine would also have a fairly good dissolving capacity for $MgSO_4$, and could remove small quantities of epsomite or other sulfate compounds that were

still present. This would be especially true if the percolation rate were moderately rapid and equilibrium could be maintained at the metastable carnallite-KCl-epsomite composition (Fig. 5) where the $MgSO_4$ concentration is quite high. Because of the generally higher potash content over a broad range of the mixed, partially evaporated brines, the carnallite decomposition can result in more KCl crystallizing than was originally present in the carnallite. Of course, some potash loss would have resulted if the carnallite were in contact with very weak brines, but as evaporation continued, the chance for this loss would become progressively less.

Consequently, there should have been considerable opportunity for potash to form from the decomposition of carnallite, continuing until such time that a sufficient depth of additional salts crystallized to "compact" or seal the underlying salts and minimize further brine penetration through the potash zone. The six molecules of water in the carnallite molecule should have further aided in the decomposition process, since as much as 40 per cent of the water needed for the decomposition could come from this source alone. The slow-to-moderate percolation rates and the counter-current nature of the contact would allow large KCl crystals to grow. The high NaCl content of the brine would also result NaCl deposition. Later, the variation in temperature within the bed, either with or without a major liquid phase present, would result in crystal growth and consolidation to enlarge both the NaCl and KCl crystals.

This interruption of the potash crystallization cycle followed by decomposition of the carnallite and additional salt crystallization appears to have occurred with some frequency, at least for brief periods, judging by the layering effect noticed in many potash deposits. This thinner bed decomposition of the carnallite would have aided in the complete formation of KCl.

Kainite deposits.

The basic theory as outlined above satisfactorily explains the sylvinite deposits, but needs some modification to explain more complex deposits. There are a few areas, such as Sicily, where a fairly pure kainite-salt mixture is found. Since the solution concentrations for $MgSO_4$ removal are nearly the same as those required for carnallite formation, it is likely that the deposit was originally a carnallite-salt mixture, with perhaps some extra undissolved epsomite, and that it was formed in the normal manner. A small amount of epsomite in the

deposited salts is not strictly necessary for the later formation of kainite, but it is quite likely that under some circumstances it could occur. If the basin were shallow, and/or the leaching zone thin or cold, or very little sulfate were removed by precipitation with calcium in surface waters, some epsomite might get through intact. The principal mechanism for the formation of kainite, however, must occur in the leach cycle. If the amount of new sea water entering at the end of the potash depositional cycle was limited, or if only a small amount of mixing took place, the carnallite decomposition could be effected by brines of a composition that remained in the kainite field (Fig. 5). With a sufficient flow of these brines, or with sufficient epsomite originally present, all or part of the carnallite might have been converted to kainite. Such a conversion can be produced in the laboratory and is even practiced commercially. Its occurrence in oceanic basins can be visualized by merely adding one more requirement to the sequence producing sylvinite.

Sylvinite-kieserite-kainite deposits.

As a variation on this type of deposit, if some epsomite were carried through with the carnallite, or if some kainite were formed as discussed above, later when high $MgCl_2$ brines began to percolate through the salt mass, some epsomite would be reformed from the kainite transformation into carnallite. Such brine could also reconvert KCl to carnallite, but since this brine would normally develop at a much later period when the porosity was reduced, both carnallite from this source and epsomite should be less abundant and more restricted in extent than sylvite. The strong brines would slowly convert epsomite into the stable form, kieserite. In this manner complex mixtures of sylvite, kieserite, carnallite, and kainite can occur and even be quite variable within a restricted zone or the total salt deposit depending upon the basin depth, the salt porosity, and its content of insolubles. As with the pure kainite deposits, however, such occurrences require a more complex set of environmental conditions than the formation of sylvinite and consequently are somewhat less common.

Langbeinite deposits.

Langbeinite in a deposit represents a rather special case and yet its formation must have followed the same general rules. It has been assumed that the stronger, deeper brines were somewhat hotter than the surface waters, this accounting for the

dissolving of epsomite formed at the surface. Sometimes, however, very shallow basins or pools must have occurred adjacent to deeper ones which fed them brine, and bottom temperatures could have become very high (over $55^\circ C$). Under these conditions langbeinite is stable, and can form rapidly and in large quantities. Since it generally precipitates as very small crystals, the permeability of the salt mass would be low, and modest amounts of wind-blown or river sediments would tend to make it sufficiently impervious to be stable against later leaching. However, its presence in a salt deposit should never be more than an unusual seam, zone, or pocket, which appears to be the case.

Tracer analysis

An interesting comment on this proposed theory can be seen in the bromide tracer analyses mentioned previously. Work on the Canadian potash deposits by Schwerdtner (1964) and on the Zechstein 2 unit in Germany has revealed bromide content in KCl that was much too low for the KCl to have been crystallized from sea water directly, and yet too high to have come from a fresh water (or hydrate) decomposition of carnallite. Consequently, an intermediate-strength oceanic brine decomposition of carnallite would appear to be the most logical explanation, as is further borne out by the low bromide value in the accompanying salt which would have resulted from the deposition of new salt from the brine onto the existing salt deposit. In the same study it appeared that some of the carnallite found in the deposit had bromide values similar to those in deposits precipitated from strong $MgCl_2$ bitterns, while other portions of the deposit had much lower values indicating a secondary formation. Each of these facts ties in well with the proposed theory. Since the bromide content of the chloride salts is less than that in the brine from which they crystallized, and the rubidium content of the potash salts is much higher, more detailed examination of potash deposits with both tracers should greatly aid in testing this theory.

MISCELLANEOUS FACTORS

Brine depth in depositional basin.

The volumetric relations in a sea water cycle provide an interesting set of limits on the depth of the brine in the basin. The equivalent KCl content of evaporating sea water brines cannot rise much above 4 weight per cent KCl even under super-saturated conditions, and the total salts content at

this point is about 30 weight per cent, with the Mg concentration about 4.5 per cent. Potash salts begin to crystallize slowly from that point until the Mg content is about 6.0 per cent, at which time they begin to crystallize prolifically. About 90 per cent of the potash has been crystallized at an average end point of 7.5 per cent Mg, when the total solids content is about 35 per cent. Thus, a 10-foot bed of 31 per cent K_2O sylvinite (about 50 per cent KCl) would have required roughly 220 feet of original (4 per cent KCl) brine, 110 feet of end liquor (assuming 50 per cent entrainment), and 80 feet of water evaporated. Seepage losses and greater initial entrainment could partially account for lowering the depth of the end liquor (possibly even reducing it to nearly zero in some cases). Shallow adjacent basins could also account for a concentration action, and thus reduce the initial depth. However, examination of such possible prepotash crystallizing areas indicates that in salt deposits the ratio of salt to potash areas would rarely be greater than ten to one, and usually not over three to one (Richter-Bernburg, 1964; Wardlaw and Schwerdtner, 1966). To reduce the initial brine depth by these ratios would require a leach and secondary recovery and redeposition of the small amount of potash that formed in the shallow zones. However, this probably did happen to some extent, and thus basins with an average depth of from 50 to 200 feet at the start of potash deposition, and from 10 to 50 feet at the end of the potash cycle, might have been minima, and perhaps somewhat close to typical. Of course, in industrial solar ponds, such deposits could have formed with no more than 6 inches to 10 feet of depth, but it is most unlikely that such exactly sequenced brine movements would have been approached on a common, naturally occurring basis. Fairly deep basins must thus be inferred even with a reasonably well sequenced progression of brine.

Time required for deposition.

Evaporation in such deep basins would not be unusual at a net rate of about one to two feet per year, assuming that little fresh or sea water entered the basin, and that a warm, dry climate prevailed. Thus, only about 80 years could have been required to deposit a 10-foot bed of potash, and it would be very hard to explain much more than a moderate multiple of this figure. Wardlaw and Schwerdtner (1966) report that seasonal deposition cycles for salt in Devonian deposits have typical values of 2 to 10 cm per cycle, the former figure also implying about 75 years to deposit the

10 feet of potash in the above example, assuming that two seasonal layers occurred per year. Studies of other deposits have indicated deposition of a lesser thickness of salt per year, some as low as several tenths of a centimeter. This could most likely result from heavy rainfall or inflow of river water during that period, but nevertheless would have lengthened the potash period only several fold.

Insoluble matter.

Insoluble matter in the sylvinite can perhaps best be explained as either wind-born sediment or clay and silt from surface runoff waters entering the basin. Commercial solar ponds might typically contain 0.1 to 0.2 per cent wind-blown insolubles in a year's cycle, thus implying that the 0.5 to 10 per cent commonly found in sylvinite deposits may have required a 5 to 50 times slower evaporation rate (2 to 3 feet evaporation per year might be typical in commercial ponds), or 2 to 20 times the previously estimated 80-year formation time. However, the very fine clay minerals that Droste (1963) has found to predominate in many deposits, rather than the wide variety of particles (and of a generally larger size) that might be expected from wind, transport perhaps throws more evidence toward runoff water entering the basin as a major agent of transport of the insolubles. This would help explain clay seams in the deposits, as well as some sulfate removal, and would account for the fairly high percentage of anhydrite and dolomite often found in the insolubles.

Residual brines.

As one final factor in examining the origin of potash deposits, attention might be turned to the brines that seep through the deposits, or the mother liquor that is squeezed from them. The rather common occurrence of polyhalite can probably be explained by the slow penetration of such brines through underlying gypsum or anhydrite beds, slowly surrendering their potassium content. Likewise, it has been long established that such brines on encountering limestone will convert it to dolomite. Both reactions can be demonstrated in the laboratory or by recent geological transformations (Kinsman, 1966). Even though these high $MgCl_2$ "end liquors" from the ancient potash deposits must have almost entirely escaped back to the sea, it is very interesting to note that perhaps some of these brines have remained trapped underground. Near the potash deposits in Utah, Pakistan, and elsewhere, brines characterized as strong

Ca-Mg-K-Na-Cl solutions, such as would result from the dolomite formation reaction, have been reported. They could very well represent a portion of the potash deposit's mother liquor, and by inference, be more common than hitherto expected near potash deposits.

SUMMARY

To summarize, a theory has been presented for the origin of potash deposits that assumes a limnological stratification of brines of various strengths in relatively deep basins with some shallow marginal areas, and with a surface evaporation and salt crystallization sequence and transformation that is similar to present-day solar evaporation ponds. All crystallized potash salts while dropping through the lower, high $MgCl_2$ brines, or soon thereafter, are transformed into carnallite. The more concentrated brine zones are warmer because of their greater absorption of solar radiation and their origin in shallower and thus warmer areas. They dissolve all of the epsomite passing through. The sulfate content of the brine is partially removed through crystallization during winter and evening cooling on the shallower margins of a basin prior to a potash deposition cycle, and later re-dissolved and, like the $MgCl_2$ brine, removed from the system into the final flushing and draining sea. Some sulfate is also removed from the brine in the trapped evaporating basin by precipitation with excess calcium entering in surface or ground waters throughout the evaporating cycle. Carnallite is later decomposed by the contact and seepage of the weaker, sea water-diluted brines at the end of the potash cycle, unless covered with impervious clay or salt and preserved. Kainite deposits occur by the leaching of carnallite with stronger (less diluted) brines; and kieserite either from originally crystallized, unleached epsomite, or from kainite reconverted to carnallite. Carnallite can also be formed by stronger brines re-converting the KCl.

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