

Distribution of Rb and Cs in Potassium Salts—Experimental and Analytical Investigations

Hans H. Schock
Harold R. Puchelt

ABSTRACT

Using Rb-86 and Cs-134 as radioactive tracers distribution coefficients (D) of Rb and Cs between the saturated solutions and single crystals of carnallite have been determined. The Rb contents of the solutions were varied within the concentration range of about $2 \cdot 10^{-5} > (Rb/K)_{\text{liquid}} < 5 \cdot 10^{-3}$ and the Cs contents in the range of about $1 \cdot 10^{-7} < (Cs/K)_{\text{liquid}} < 1 \cdot 10^{-5}$. At 40°C the following distribution coefficients were obtained for atomic ratios $(Mg/K) \times 5.4$ in saturated solutions:

$$D = \frac{(Rb/K)_{\text{solid}}}{(Rb/K)_{\text{liquid}}} = 2.03 \pm 0.12 \text{ for Rb and}$$

$$D = \frac{(Cs/K)_{\text{solid}}}{(Cs/K)_{\text{liquid}}} = 0.87 \pm 0.05 \text{ for Cs.}$$

The investigation of the temperature dependence of the partition coefficients shows an increase in incorporation of Cs and Rb with decreasing temperature. At temperatures below 30°C the partition coefficient for Cs becomes greater than unity. With increasing (Mg/K) -ratio both coefficients decrease. Using neutron activation analysis the Rb and Cs contents of some hundred samples of carnallite from profiles of German Permian potash mines, of single carnallites from the upper Rhine Graben and of some sylvites (0.002–0.2 ppm Cs, 50–180 ppm Rb), kainites (10–50 ppm Rb), langbeinites (50–120 ppm Rb) and picromerite (200 ppm Rb) have been determined. In relatively undisturbed carnallite profiles the Rb content decreases continually from the base to the summit,

whereas the Cs content usually increases toward the end of the evaporitic sequence. These carnallites contain 0.2 to 1.5 ppm Cs and 80 to 40 ppm Rb. In heavily disturbed or secondarily altered carnallite bodies often considerably higher Cs contents were found. Furthermore the carnallites from the upper Rhine Graben contain Cs up to 15 ppm and Rb up to 1900 ppm, having also a higher average content than the Permian deposits.

The Rb and Cs content of oceanic salt deposits can be derived from the content of Rb and Cs in sea water. Bolter *et al.* (1964) performed many determinations of these elements in sea water using neutron activation analysis as the analytical technique. They obtained mean values of $125 \mu\text{g Rb/l}$ and $0.30 \mu\text{g Cs/l}$ for sea water with the standard chlorinity of 19‰ . The Rb value agrees within 1 percent with older determinations of other authors, but for Cs the values of Bolter *et al.* are much lower than data of Smales and Salmo (1955) ($0.5 \pm 0.07 \mu\text{g Cs/l}$) and Riley and Tongudai (1966) ($0.55 \pm 0.06 \mu\text{g Cs/l}$), the last value being obtained by combination of ion exchange and spectrographic techniques.

Within a saline cycle Rb and Cs can substitute for potassium in the crystal lattice of the respective salt. The K content of the present ocean is 390 mmol K/l. Using the Rb and Cs values of Bolter *et al.* one obtains the following atomic ratios for sea water:

$$(Rb/K)_{\text{sea water}} = 1.45 \cdot 10^{-4},$$

$$(Cs/K)_{\text{sea water}} = 2.3 \cdot 10^{-7}.$$

* Geochemisches Zentrallaboratorium, University of Tübingen, 7 Tübingen, 56 Wilhelmstraße, Federal Republic of Germany.

Starting with these values the Rb and Cs content of primary potash salts can be calculated if the partition coefficients between solution and the respective forming potash mineral are known.

We define our distribution coefficient as follows:

$$D = \frac{(\text{trace element/carrier element})_{\text{solid}}}{(\text{trace element/carrier element})_{\text{liquid}}}$$

$$\text{for our purpose } D_{\text{Rb}} = \frac{(Rb/K)_S}{(Rb/K)_L} \text{ and } D_{\text{Cs}} = \frac{(Cs/K)_S}{(Cs/K)_L}$$

For values of D greater than unity, the crystals growing from a liquid are enriched in trace component with respect to the liquid. For values of D less than unity, the crystals are impoverished in trace component with respect to the liquid. It must be mentioned here that there are other definitions of distribution factors. In the literature dealing with salt problems, the data are often reported as ratios weight percent trace element in crystal/weight percent trace element in the solution. In this case exact data on the composition of the solution are of primary importance, as the distribution factor changes each time the denominator of the ratio is changed. However, if we use D as defined herein, the denominator does not change, for example, with the addition of Na or sulfate to the solution, as in our equation Rb and K or Cs and K are the only elements to occur.

In order to determine partition coefficients, the composition of both the solid and the liquid phase must be known. That requires in most cases an artificial growth of crystals. A frequent source of error in this procedure is the inclusion of mother liquor in the growing crystals. In order to avoid this possibility of contamination, we started out with rather large single crystals, which we hung in the saturated solution as seeds. The amount of crystal substance necessary for the determination of the distribution coefficient is several hundred milligrams, which was cleft from the artificially grown portion of the crystal.

The solution was kept at as little supersaturation as possible, i.e. close to the thermodynamic equilibrium. Average growth rates are about 4g per month. Normal experiments were conducted for three weeks. Rb and Cs labelled with radioactive tracers were used in the starting solutions. Thus the concentrations of these elements could be chosen

as low as under natural conditions, and nevertheless exact determinations could be made.

In the following part there is mainly dealt with the partition of Rb and Cs between carnallite and solution under various conditions. Distribution coefficients for sylvite and kainite, which were obtained from other experiments, will be used for the general discussion. One set of experiments for growing carnallite was performed at 40°C by isothermal evaporation close to the boundary to the sylvite field, i.e. with an atomic ratio Mg/K of about 5.5. Different Rb/K and Cs/K ratios were used in the individual runs. The results are given in Figure 1. At the ordinate the atomic ratio Rb/K in the carnallite crystal is given—that is the numerator

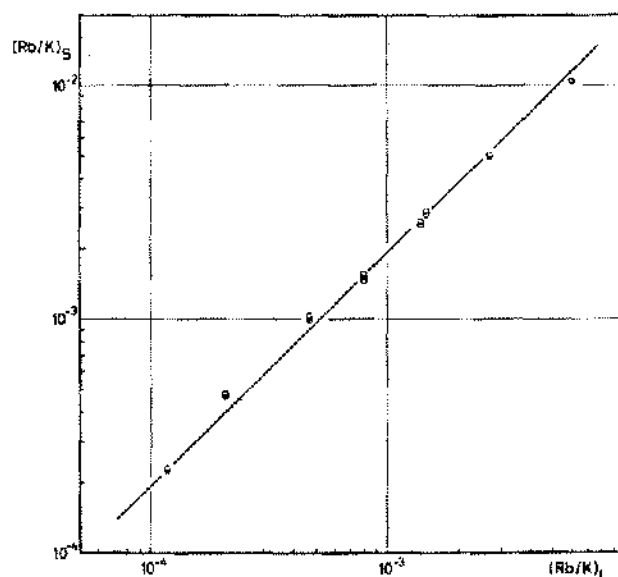


Figure 1. Distribution of Rb between solution and carnallite single crystals at 40°C.

of our defining equation—and at the abscissa the same ratio in the solution. We obtained a constant partition coefficient of $D = 2.03 \pm 0.12$ for Rb at 40°C. That means Rb is enriched in the crystal relative to the solution under the crystallization process.

Figure 2 shows the respective data for the Cs/K substitution with the same parameters, temperature and concentration of K and Mg. The distribution coefficient is constant within the Cs concentration range investigated, and has a value of $D = 0.87 \pm 0.05$. This coefficient is smaller than unity so that with proceeding crystallization of

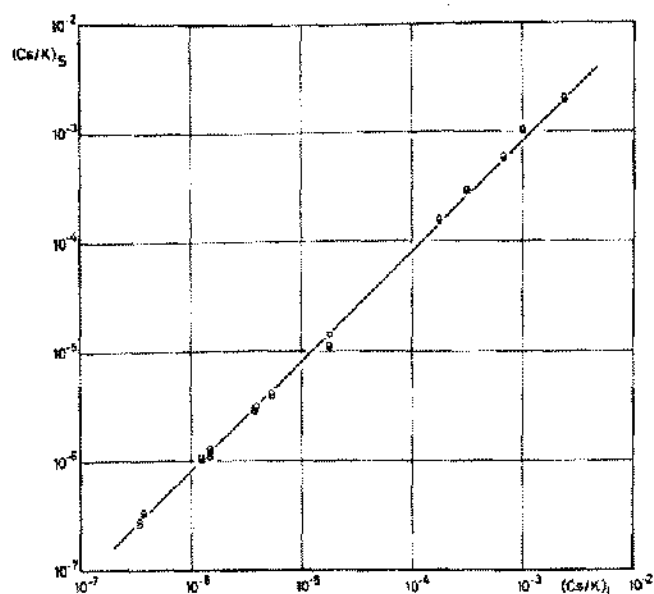


Figure 2. Distribution of Cs between solution and carnallite single crystals at 40°C.

carnallite a small enrichment of Cs in the solution is to be expected. The data concerning the concentration range between $3 \cdot 10^{-7}$ and $2 \cdot 10^{-5}$ were obtained from the same crystals that were used for Rb partition determinations. It was possible to do this as the RbCl used contained CsCl, and the commercial Rb-86 tracer was contaminated by Cs-134. With the datapoints between $1 \cdot 10^{-4}$ and $3 \cdot 10^{-3}$ Cs was the only added trace element. It can be learned from this diagram that the Cs distribution coefficient remains unaffected by the presence of Rb as an additional trace element.

A very important parameter for the formation of salts and the incorporation of trace elements in the different minerals is temperature. We found D values for both Rb and Cs distribution between carnallite and solution to increase with decreasing temperature. This series of experiments was also performed at Mg/K ratios close to the sylvite boundary. Table 1 demonstrates the experimental results. Again the D values represent means from measurements from wide concentration ranges as was mentioned for the 40°C experiments. In the upper line, the D values for Rb are given with the standard deviation, as calculated from the number of samples, n . From 80°C to 25°C the partition coefficient of Rb varies by approximately 25 percent. The partition coefficient of Cs, in the line below, changes by almost 50 percent in the same temperature range. Somewhat surprising is the observation, that at temperatures near to 25°C the Cs distribution coefficient becomes greater than unity. It is still to be investigated, whether the distribution coefficient of Cs increases further at even lower temperatures.

All the results which are reported up to here were obtained from solutions, the Mg/K ratio of which was always very low for the respective temperature. This had the advantage that the condition of compositional invariance in the solution could be closely fulfilled. With an increase of the Mg surplus, which normally is the case with any progressive crystallization of carnallite, the partition coefficients may change. The dependence of D for Rb and Cs at 40°C is given in Table 2. In the first column the range of variance for the Mg/K ratio is listed; column 2 shows the distribution coefficients as obtained for the Rb and Cs concentration ranges of column 3. At the extreme right the number of

TABLE 1. Temperature Dependence of Rb and Cs Distribution Between Solution and Carnallite Single Crystals.

Temperature	80°C	60°C	40°C	30°C	25°C
D_{Rb}	1.64 ± 0.07 $n = 12$	1.93 ± 0.08 $n = 18$	2.03 ± 0.12 $n = 23$	2.07 ± 0.11 $n = 23$	2.18 ± 0.11 $n = 20$
D_{Cs}	0.64 ± 0.08 $n = 12$	0.77 ± 0.03 $n = 15$	0.87 ± 0.05 $n = 36$	0.89 ± 0.08 $n = 31$	1.09 ± 0.18 $n = 29$

analysed samples is given. It is surprising and contrary to many other salt systems, that the partition coefficients of Rb and Cs are not independent of the composition of the mother liquor, but that they decrease rather strongly with increasing Mg/K ratio. In normal salt deposition these are the conditions of proceeding carnallite precipitation.

TABLE 2. Dependence of Rb and Cs Distribution Between Solution and Carnallite Single Crystals from Mg/K Ratio of the Solution.

(Mg/K)	D_{Rb}	Concentration range (Rb/K) _L	Number of samples
5.25 - 5.85	2.03 ± 0.12	$1.2 \cdot 10^{-4} - 6 \cdot 10^{-3}$	23
8.25 - 8.8	2.02 ± 0.16	$2.6 \cdot 10^{-5} - 1.9 \cdot 10^{-3}$	18
13.6 - 16.0	1.68 ± 0.11	$3.3 \cdot 10^{-5} - 7.3 \cdot 10^{-4}$	12
20.4 - 21.4	1.82 ± 0.06	$2.9 \cdot 10^{-5} - 3.7 \cdot 10^{-4}$	8
25.0 - 26.0	1.51 ± 0.07	$4 \cdot 10^{-5} - 1.7 \cdot 10^{-4}$	6
40.0 - 40.5	1.59 ± 0.09	$6.5 \cdot 10^{-5} - 2.7 \cdot 10^{-4}$	5

(Mg/K)	D_{Cs}	Concentration range (Cs/K) _L	Number of samples
5.0 - 5.45	0.87 ± 0.05	$3 \cdot 10^{-7} - 2.4 \cdot 10^{-3}$	36
8.25 - 8.8	0.80 ± 0.04	$7.4 \cdot 10^{-5} - 4.9 \cdot 10^{-3}$	20
13.6 - 16.0	0.73 ± 0.03	$3.5 \cdot 10^{-5} - 3.5 \cdot 10^{-3}$	18
20.4 - 21.4	0.68 ± 0.03	$7.6 \cdot 10^{-5} - 1.5 \cdot 10^{-3}$	13
25.0 - 26.0	0.66 ± 0.04	$8.2 \cdot 10^{-5} - 1.7 \cdot 10^{-4}$	9
40.0 - 41.0	0.63 ± 0.04	$7.4 \cdot 10^{-5} - 7.6 \cdot 10^{-4}$	7

The behavior of Rb and Cs within a salt formation process is to be demonstrated with a very simple model: the theoretical primary precipitation from normal sea water under static conditions at 35°C. From several analyses and experiments we know that up to the first precipitation of a potash salt practically no Rb or Cs is removed from the

solution. Thus kainite is the first mineral to incorporate Rb and Cs. Figure 3 illustrates the mode of Rb and Cs partition starting with kainite. The abscissa gives the decrease of the K content from 100 percent at the beginning of potash salt formation at the left to 0 at the right side. When about 20 percent of the original potassium content is left, under the chosen conditions carnallite begins to form together with kieserite. The ordinate of the diagram shows the relative contents of Rb and Cs at the left. Number 1 represents the initial concentration of Rb and Cs in sea water, e.g. for Rb the above mentioned ratio $(Rb/K)_{sw} = 1.45 \cdot 10^{-4}$.

We used the following distribution coefficients for our calculations: Rb in kainite 0.25, Cs in kainite 0.005. These are approximate preliminary values which we measured with only a limited

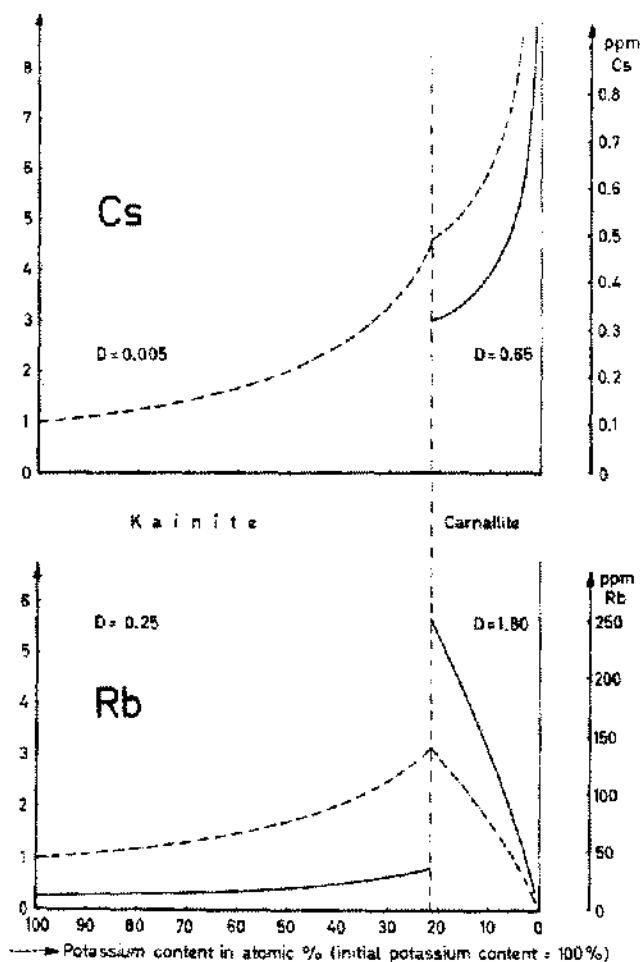


Figure 3. Theoretical development of Rb and Cs content in solution and the crystallizing potassium salts with proceeding evaporation.

number of experiments at 60°C. Under the chosen conditions the carnallite precipitation starts with the rather high Mg/K ratio of almost 20. Therefore D values of 1.80 and 0.65 were used in the calculations for Rb and Cs respectively.

One recognizes the relative enrichment of both elements in the solution during the kainite phase (dashed line). The enrichment is by a factor of 3 for Rb and of 5 for Cs. With the beginning of the carnallite precipitation, the Rb content of the solution decreases rapidly, due to the fact that D_{Rb} is greater than unity. The Cs is still relatively enriched. In the diagram we also plotted the Rb and Cs concentrations of the forming potash salt with solid lines. Their course is similar to the development in the solution. It is rather simple to convert the data given into the absolute concentrations. This is done for carnallite and the values are given on the scale at the right side of the diagram. (This scale even holds approximately for kainite, as both minerals have almost identical molecular weights and both molecules contain only one potassium atom.) In this example the first carnallite should contain 250 ppm Rb and 0.3 ppm Cs. The Rb content will decrease continuously to values of 50 ppm and even lower. The Cs content in carnallite will increase continuously. The tendency of this development can be shown more obviously by the ratio Cs/Rb. At the beginning it has a value of $0.7 \cdot 10^{-3}$. The increase is such that after 90 percent of the possible carnallite is precipitated the ratio is larger by a full order of magnitude.

This simple example shows the order of magnitude which is to be expected for Rb and Cs contents in potash minerals in various stages of an evaporitic sequence. The absolute values for Rb and Cs in carnallite depend mainly on the percentage of potassium from the initial solution which is still in the solution at the beginning of the carnallite precipitation. The more potassium removed from the solution by precipitation of salts with a very low distribution coefficient for Rb and Cs, the higher the enrichment of these elements at the beginning of the carnallite precipitation, i.e., the higher the absolute concentrations of Rb and Cs in carnallite.

Parallel to the experimental investigations regarding the trace element distribution, there have been analysed several hundred potash salt samples for Rb and Cs using neutron activation analysis. Figure 4 shows one example of a rather undisturbed carnallite profile from the Staßfurt horizon (Z2) of German Zechstein of the Salzdetfurth mine. It is the same profile which was analysed by

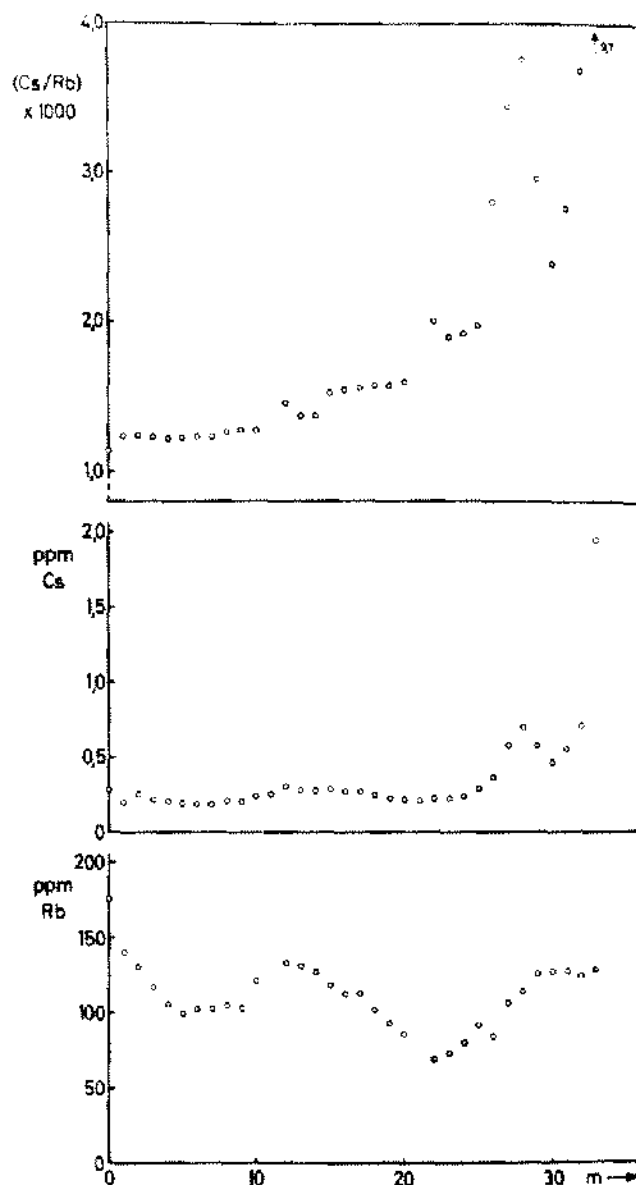


Figure 4. Rb and Cs profile from the Staßfurt seam (Z2) in carnallite facies; potash mine Salzdetfurth.

flame-photometer by Kühn (1963) for Rb. The abscissa gives distances from the base at the left through the whole thickness of the carnallite sequence up to the summit in meters. The ordinates give Rb and Cs concentrations in ppm. In the uppermost diagram the atomic ratio $(Cs/Rb) \cdot 1000$ is plotted. The Rb curve exhibits the expected steep initial decrease of Rb concentration. This tendency is not continued throughout as we expected from our simple one-cycle model.

TABLE 3. Rb and Cs Concentrations in Various Natural Salt Minerals.

	ppm Rb	Number of samples	ppm Cs	Number of samples
Carnallite				
Permian				
Werra-Series (Z1)	220 - 520	70	1.0 - 1.5	70
Stassfurt-Series (Z2)	80 - 150	40	0.3 - 0.7	40
Leine-Series (Z3)	80 - 300	70	0.3 - 3.4	70
Tertiary				
Upper Rhine Graben	800 - 1900	35	8.6 - 15	35
Sylvite				
Permian			0.005 - 0.04	7
Tertiary	60 - 180	25	0.06 - 0.5	10
Kainite	10 - 60	7	-	
Halite	< 0.5	5	< 0.002	5
Langbeinite	50 - 120	3	< 0.07	3
Picromerite (secondary large single crystal)	200	1	0.4	1

It is easy to recognize that during the carnallite precipitation several additions of brine occurred, which contributed additional Rb. Distinctly expressed is the pronounced increase of Cs content in carnallite towards the end of the sequence. The continuity of the carnallite precipitation is interrupted by a layer of kieserite and rock salt between 28 and 30 m above the base. Most obviously shown is the opposite tendency of Rb and Cs distribution in the plot of their ratios. No error-bars are put into the diagrams. The relative errors are almost the same for both elements and amount to less than ± 5 percent.

Several further profiles from the Staßfurt seam gave Rb and Cs concentrations which covered the same range as the one just mentioned. In carnallite profiles from the older Hessen and Thuringen seams from the Werra series (Z1 of German Zechstein), Rb and Cs content is higher by a factor of 3. A compilation of our analytical data is presented in Table 3. It can be recognized that the

Tertiary carnallite exhibits higher Rb and Cs concentrations than all Permian carnallites, i.e. with the beginning of the carnallite precipitation the main part of the potassium was already removed as sylvite, with the much lower partition coefficient of 0.1 for Rb (Reichert, 1966) and 0.0001 for Cs (Schock, 1966). This process must be considered as the reason for the high enrichment of the solution prior to carnallite formation.

The purpose of our investigations was to learn something about the behaviour of Rb and Cs in an evaporitic sequence. Some fundamental rules about partition of these elements were established and reasonable predictions can be made regarding Rb and Cs concentrations in simple undisturbed salt series. As a number of secondary processes influence the chemistry of salt deposits, not all features which we observed in analysing carnallite profiles, can be interpreted adequately at the moment. There are indications, however, that the investigation of Rb and Cs distribution in potash

sequences may provide--possibly by combination with other trace element work--a valuable tool in studying processes of formation and metamorphic changes in these deposits.

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