

Regularities of Trace Element Distribution in Water–Salt Systems as Indicators of the Genesis of Potassium Salt Rocks: An Example from the Upper Jurassic Halogen Formation of Central Asia

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Abstract—Main aspects of the theory and methods of measurement of trace element distribution coefficients in water–salt systems are discussed. Data on the interphase distribution of Br, Rb, Cs, and Tl in chloride systems were used to evaluate the abundances and distribution of these elements in the potassium salt rocks of the Gaurdak Formation of the Upper Jurassic halogen formation in southern Central Asia. It was concluded that these rocks were strongly metamorphosed after sedimentation, and some considerations were presented on the character, scales, and reasons of these processes. It is emphasized that the traditional factors used to decipher the genesis of salt minerals, rocks, and deposits should be supplemented by the determination of the contents of trace element that are incorporated into the crystal lattice of salts via isomorphic substitution.

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Potassium rocks spatially and genetically related to salt-bearing marine deposits are presently used all over the world as a raw material for the manufacturing of potash fertilizer. However, not all halogen formations contain potassium salts because the generation of a potassium deposit requires specific paleogeographic, tectonic, and climatic conditions. The combined influence of these factors causes cyclic changes in the concentration and composition of salt basin brines. Potassium salts precipitate during the final stages of salt accumulation owing to the oversaturation of oceanic water under favorable consedimentation movements of the brines. Time-consuming drilling operations, which often give no clear indications, are usually executed to discover such local occurrences among extended salt rock areas. In some cases, the mining of deposits began in not the most productive areas. This eventually resulted in the necessity to change projects and hindered the launching of potassium plants. Therefore, only 13 of 26 known salt-bearing series containing potassium salts are presently mined. The expediency of mining the other series has not been demonstrated [1].

It is evident that comprehensive genetic concepts are required to improve the methods of prospecting operations. Fersman noted that correct genetic interpretations are crucial for both prospecting and exploration operations, whereas incorrect genetic inferences often lead to gross errors and even fatal results during the organization of production [2].

Since the composition and texture of rocks reflect their genesis, the mineral, petrographic, and chemical

analysis of rocks has been the main method to solve genetic problems and determine the physicochemical and geochemical conditions of salt accumulation both during and after sedimentation [3–6].

The salt composition of rocks allows one to carry out facies analysis and determine the hydrochemical type of parent brines, which defines to a considerable extent the physicochemical evolution of the basin. The composition of salt-associated halopelite material is controlled by the same processes. The determination of assemblages of carbonate, clay, and salt minerals clarifies the trend and intensity of brine metamorphism and reveals the role of the facies environment in the compositional variations of carbonates and terrigenous clays. There are indicator clay minerals, the authigenic formation of which is strictly controlled by the composition of the halogen basin [7].

Trace elements are more sensitive to changes in the salt-forming environment than major elements forming mineral assemblages and bear, therefore, important genetic information. Some salt minerals form during particular stages of halogenesis, affecting the trace element composition of rocks. Consequently, they can be considered as chemical indicators of the thermodynamic conditions of sedimentation.

There are different types of interaction between the major and trace components of brines: (1) chemical interaction, (2) formation of solid solutions (isomorphous series), and (3) no interaction (occurrence as mechanical impurities in minerals). In the latter case, a trace element is entrapped with parent brine by growing

crystals or adsorbed on their faces. Among these mechanisms, the most thoroughly studied and informative is the second type of interaction leading to the formation of isomorphous series. It is known that the preferable isomorphic substitution of an atom in a particular mineral depends on many variables: chemical nature of the element, crystal structure, character of interatomic bonds in the mineral, physicochemical conditions of its formation, crystallization order, etc.

Isomorphic substitutions are presently studied by a number of instrumental methods, including X-ray structural and phase analysis, radiometry, isotope exchange, laser halography, and others.

The experimental determination of trace element distribution between solid and liquid phases in systems (solutions, melts) is used to quantify the formation of isomorphous series. Valuable information can also be obtained from a statistical determination of distribution functions and correlations of major and trace elements in rocks [8–13]. The thermodynamic analysis of the distribution of major and trace elements between equilibrium phases is similar, but in the case of trace elements, the calculation of distribution coefficients can be simplified. This is explained by the fact that variations in trace element content have practically no influence on the activity coefficient of all components of the system, including the trace component. Therefore, only the distribution of the trace element between solid and liquid phases should be considered instead of the complete phase diagram with the participation of this component [10].

Studies of V.G. Khlopin and his school showed that equilibrium distribution coefficients in crystal–solution systems can be determined by three methods. Two of them are based on prolonged recrystallization of sediment in solution (from above and from below), and the third method involves precipitation from oversaturated solutions (isothermal removal of oversaturation). The latter method had long been the subject of discussion, and no consensus was reached. However, the obtained experimental data showed that any of these three methods provides a homogeneous distribution of trace elements in major-component sediment, i.e., the attainment of true thermodynamic equilibrium in the system [14–17].

The function of trace-element distribution depends on the extent of equilibrium. When true thermodynamic equilibrium is attained, the Khlopin law can be applied: $D = x/y: (a - x)/(b - y)$, where D is the crystallization coefficient, x is the concentration of the trace component in the crystal, y is the concentration of the major component in the crystal, $(a - x)$ is the concentration of the trace component in the solution, and $(b - y)$ is the concentration of the major component in the solution. During co-crystallization of isomorphous components, a trace element is distributed between solid phase and solution with a constant D up to a certain concentration limit. This is caused by the fact that crystallization pro-

ceeds slowly enough and the chemical potential of the trace element becomes uniform over the whole system. If in each moment of crystallization, equilibrium is attained only between an elementary layer and solution rather than over the whole volume of growing crystals, the distribution can be described by the logarithmic law of H.A. Doerner and W.M. Hoskins:

$$\ln x/a = \lambda \ln y/b,$$

where λ is the distribution coefficient, a is the total concentration of the trace component in the solution and crystals, and b is the total concentration of the major component (in solution and crystals).

The coefficient D is a thermodynamic constant for the given trace component in the given system, whereas λ is not constant *sensu stricto*, because it depends not only on temperature and component concentration but also on mixing rate and other experimental conditions. During slow crystallization, the limiting λ value may be equal to D . The distribution coefficient is often calculated either as a ratio of trace element content (in wt %) in crystals to its content in the solid residue of liquid phase (J) or as a ratio of trace element content in crystal to its content in liquid phase (b). The distribution coefficients calculated in such a manner are somewhat different from D and λ and widely used in studies of salt systems and halogenesis. The distribution coefficient is a relative value; however, it depends on concentration units (wt %, at. %, mole fractions, and others), which are usually specified. This is important for a comparison of data obtained by different authors [18–20].

Experimental data can be checked by thermodynamic calculations. The following equation was proposed for the calculation of distribution coefficients:

$$\ln K_i = - \frac{\Delta H_{\text{melt}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{melt}}} \right) - \frac{\Delta H_{\text{mix}}}{RT}.$$

The first term relates the distribution coefficient with the heat (ΔH_{melt}) and temperature (T_{melt}) of melting of the trace component and the crystallization temperature of isomorphous series (T) in Kelvin. The mixing enthalpy (ΔH_{mix}) can be calculated as a function of composition for many isomorphous series in accordance with the energetic theory of isomorphism [21, 22]. The general formula for components with identical or similar chemical bonding is

$$\Delta H_{\text{mix}} = X_1 X_2 a (\Delta R/R)^2,$$

where a is the semi-empirical parameter depending on the type of chemical compounds, number and valences of atoms in the formula, and coordination number in the substitution site; $\Delta R = R_2 - R_1$ is the difference between the interatomic distances of components; and R is the average interatomic distance calculated from the Vegard rule. For alkali halides, ΔH_{mix} can be calculated from the following equation within a wide concentration range:

$\Delta H_{\text{mix}} = X_1 X_2 \times 390 \left(\frac{\Delta R}{R} \right)^2$ kcal/mol. The calculation of the limits of isomorphism is based on the proportionality between the heat of mixing and the parameter $\left(\frac{\Delta R}{R} \right)^2$.

According to the above equations, ideal systems entrap a trace component ($K > 1$) if its melting temperature (T°) is higher than the crystallization temperature of the isomorphous series (T), and $K < 1$ if T is lower than T° . The results of calculations by this model are consistent with experimental data within 30–40%, but in some cases, they cannot be performed because of the lack of thermodynamic data [21–25].

There is extensive literature on the application of data on trace element distribution in various systems. These publications have considered different aspects of this problem. Most often, they focused on the influence of an impurity on the properties of crystalline matters, isomorphic substitutions, methods of refinement, extraction of trace elements for accurate measurement, and others [26–28 etc.]. This raises the question of the development of databases of trace-element distribution coefficients in various systems [29, 30]. The use of trace-element distribution in salt systems and minerals of salt deposits for the solution of many problems in halogenesis, development of prospecting guides for potassium salts, and technology for the complex utilization of salt resources is one of the most important problems of halurgy [31].

The choice of trace elements for the analysis of the genesis of salt-bearing deposits depends on the lithological composition of rocks. This is especially important for chloride deposits because of the limited number of salt phases [32].

Among the numerous trace elements inherited by evaporites from seawater, bromine is of special significance. The content of this element in oceanic water is $6.5 \times 10^{-3}\%$; during evaporation Br is accumulated both in brine and in precipitating salts, where Br^- isomorphically substitutes for Cl^- in the crystal lattice, in spite of its somewhat larger radius ($R_{\text{Cl}^-} = 1.81 \text{ \AA}$ and $R_{\text{Br}^-} = 1.96 \text{ \AA}$).

The crystal–solution distribution of Br in water–salt systems and during seawater evaporation was studied by many authors. These studies were begun by Becke in 1908 and were continued by Yu.V. Morachevskii (1928–1950), V.I. Nikolaev (1932–1937), S.K. Chirkov (1933–1946), N.A. Shlezinger (1934–1939), and others. M.G. Valyashko together with T.V. Mandrykina and E.M. Petrova (1943–1949) refined the distribution coefficients of Br for chlorides crystallizing during seawater saturation up to eutonics: J_{Br^-} is 0.37 for halite, 0.28 for sylvite, 0.23 for carnallite, and 0.47 for bischofite. These data served as a basis for the construction

of the scale of typical Br contents and Br/Cl ratios for sylvite and carnallite in marine deposits [4, 32–35].

At the beginning of precipitation, halite contains 0.0068% Br and shows a $\left(\frac{\text{Br}}{\text{Cl}} \times 10^3 \right)$ of 0.1. These values increase up to 0.027% and 0.4, respectively, when sylvite begins to precipitate and up to 0.037% and 0.6 when carnallite begins to precipitate. These data allow one to address the important question whether the presence of potassium salts can be deduced from data on boreholes penetrating a potassium-free salt sequence [1].

The Br content of crystallizing sylvite increases from 0.13 in the first crystals to 0.26% during the latest stages. The Br/Cl ratio changes from 2.9 to 4.21. The Br content and Br/Cl ratio of carnallite increase from 0.24 to 0.60% and from 6.0 to 14.5, respectively.

These values were also determined for secondary minerals. Sylvite crystallizing from the brines that formed during dissolution of primary sedimentation deposits of this mineral, contains significantly less Br than primary sylvite. Sylvite formed during the incongruent dissolution of carnallite contains half as much Br as carnallite. Carnallite formed from the brines that previously dissolved carnallite deposits also has a lower Br content, because J_{Br} for this mineral is lower than one [33–36].

In order to estimate the deviation of Br/Cl ratios from normal values, Petrova [37] proposed to use relative Br/Cl coefficients. They are calculated as the observed Br/Cl ratios of the rocks expressed in percent to normal values taken as 100% [37].

These data serve for the estimation of cycling in salt accumulation, postsedimentation transformation of rocks, and for the solution of other problems of halogenesis. The Br content, Br/Cl ratio, and relative Br/Cl coefficient of rocks can be used as geochemical criteria during prospecting for potassium salts in salt deposits, in spite of some practical difficulties [1].

Other trace elements used to decipher the formation conditions of salt rocks and sedimentation are Rb, Cs, and Tl, which isomorphically substitute for K in its minerals.

The coefficient of equilibrium co-crystallization of trace Rb with potassium salts was repeatedly determined in experiments by different methods and in different systems; however, mainly in saturated KCl solutions with addition of RbCl [38–59 etc.]. It was established that J_{Rb} is more sensitive to temperature than to system composition (K/Mg ratio in the solution) [38–40, 43, 46–49]. The mass of solid phase also affects J_{Rb} . This is related to the fact that an increase in the mass of solid phase during mixing shifts the system closer to equilibrium owing to the higher probability of crystal collision, which accelerates the transition of the trace element into the solid phase and promotes its homogenization. It was noted that the influence of collisions on

trace element transition depends on the growth rate of the crystals, because the newly formed layers of solid phase have more point defects providing disordering during crystal collisions. The trace component that was entrapped by crystals above the equilibrium amount passes into solution [50–52].

According to experimental investigations of salt systems, the distribution coefficient of Rb varies for sylvite from 0.113 to 0.652 at 0°C, from 0.10 ± 0.01 to 0.21 at 25°C, from 0.09 to 0.984 ± 0.001 at 40°C and is 0.94, 0.103, and 0.119 at 30, 50, and 80°C, respectively.

Shaderman and Chelishchev [53] studied Rb distribution in the brines of evaporite formations rather than in experimental synthetic solutions. They obtained a Rb distribution coefficient of 0.11 for sylvite at its content in crystals of 0.005% [53].

Carnallite shows J_{Rb} from 2.17 to 2.9 at 25°C and 1.86 ± 0.03 at 50°C. The same variations were observed in distribution coefficients: a weak correlation with salt composition and a strong negative correlation with temperature.

The geochemistry of Rb in halogenesis can be elucidated using data on interphase distribution in salt systems obtained from experiments on Rb behavior during seawater evaporation [54–56]. The Rb content in seawater is $2 \times 10^{-5}\%$. During evaporations, Rb is accumulated in the solution up to the precipitation of potassium salt. The Rb content of the solution increases from 0.0008 at the beginning of sylvite crystallization to 0.0011% at the final stages, while the Rb content of sylvite varies from 0.0017 in the first crystals to

0.0053% in the last ones. The Rb/K ratio $\left(\frac{\text{Rb}}{\text{K}} \times 10^4\right)$

in the liquid phase varies from 0.32 to 1.02. When carnallite crystallization begins, the Rb content of the liquid phase decreases sharply (to 3.5 ppm) because of its almost complete incorporation into the solid phase. The Rb content reaches 0.0347% in the first carnallite crystals and decreases to trace amounts by the end of crystallization. The Rb/K ratio of the solution changes from 24.7 at the beginning of carnallite crystallization almost to zero at the end. Rb is not detected in the solution at the moment of bischofite crystallization. Such a behavior of Rb during carnallite crystallization is explained by the fact that this process is accompanied by intense changes in trace element proportions in the solution: a decrease in K/Mg and an increase in Ca and Mg. These variations under the deficiency of unbound water lead to dehydration of large cations (Rb^+ , Cs^+) with a lower charge density, which causes their almost complete transition into the solid phase. During simultaneous crystallization, the Rb content of carnallite crystals is 24.4 times greater than that of sylvite [45, 48, 49].

Rb does not form its own minerals during halogenesis. The majority of researchers believe that the simi-

larity of properties, ionic radii ($R_{\text{K}^+} = 1.33$ and $R_{\text{Rb}^+} = 1.49$ Å), and crystal chemical parameters of compounds favor the isomorphic substitution of Rb for K in the crystal lattice of potassium salts. However, there is an opinion that K and Rb carnallites form solid solutions. Slivko and Petrichenko [57] argued that both modes of occurrence are possible; however, solid solutions are predominant in carnallite, and isomorphous substitutions, in sylvite. The incorporation of Rb in the crystal lattice of sylvite is hindered by the close packing of ions in this mineral. Carnallite, sylvite (and kainite) are classified as Rb-concentrating minerals.

In terms of Rb content and Rb/K ratio, the potassium salts that were subjected to postsedimentation transformations significantly differ from pegnitogenous ones. For example, primary sedimentary sylvite contains from 0.0017 to 0.0053% Rb and its $\left(\frac{\text{Rb}}{\text{K}} \times 10^4\right)$

ratio is from 0.32 to 1.02, whereas secondary (redeposited) sylvite contains four times less Rb (from 0.0004 to 0.0019%). The Rb content of sylvite formed through the incongruent dissolution of carnallite is half that of the primary carnallite, which is 1.36 times higher than that of the primary sedimentary sylvite.

In accordance with the distribution coefficient, recrystallized carnallite (undissolved) contains up to 0.3550% Rb and has an Rb/K ratio of 252×10^{-4} , which is two orders of magnitude higher than the initial value. These data are used to determine the formation conditions of potassium sequences and are of special importance for the deciphering of postsedimentation processes [60, 61].

The Cs content of seawater is low ($3.7 \times 10^{-8}\%$); data on its behavior and distribution during water saturation and in salt systems are scarce and require refinement. This element shows a less distinct isomorphism with K as compared with Rb; nonetheless, the similarity of chemical properties and ionic radii ($\Delta R_{\text{Rb}^+ - \text{Cs}^+} = 9.7\%$) indicates that Cs behaves similarly to Rb during halogenesis, but occurs in smaller amounts in rocks [45, 54, 57, 58]. According to the available data [62, 63], the potassium salts of the Verkhnekamskoe deposit contain from 0.03×10^{-3} to $0.11 \times 10^{-3}\%$ Cs (averaging $5.6 \times 10^{-3}\%$), i.e., more than an order of magnitude lower than the Rb content. In carnallite, Cs isomorphically substitutes for K forming Cs-carnallite. However, owing to its high solubility, this mineral can form only during the last stages of carnallite crystallization, and its findings are extremely rare [57, 59].

The Tl content of seawater is also low ($1 \times 10^{-9}\%$), and Rb : Tl = 100 : 1. Thallium is an element of group III of the periodic table with valences of +1 and +3. However, because of the high redox potential of the $\text{Tl}^{3+}/\text{Tl}^{1+}$ pair (1.25 V), thallium occurs only in the univalent state and exhibits lithophile properties under hypergene conditions. The behavior of Tl as a chalco-

phile element is unclear; however, low-temperature hydrothermal deposits with marcasite and pyrite are especially favorable for Tl accumulation [64–68].

The geochemical evolution of dispersed Tl (similar to Rb and Ce) is closely related to K owing to similar ionic radii ($R_{\text{Tl}^+} = 1.49 \text{ \AA}$), electric affinities, and some chemical properties [63, 64]. The content of isomorphous Tl in K minerals, $\text{Tl}^{1+}/\text{K}^+$, and $\text{Rb}^+/\text{Tl}^{1+}$ are used to evaluate the genesis of igneous rocks [69]. The wide application of these parameters as genetic criteria for salt rocks is hampered, because the behavior of Tl during halogenesis and in salt systems is poorly known.

The available data indicate that Tl is accumulated in a liquid phase during halite crystallization ($J_{\text{Tl}} < 1$) and in a solid phase during sylvite and carnallite crystallization ($J_{\text{Tl}} > 1$). During sylvite crystallization in the $\text{KCl-MgCl}_2\text{-H}_2\text{O}$ system, J_{Tl} increases from 5.0 to 11.8 when temperature changes from 16 to 60°C; carnallite crystallization causes an increase in this value from 3.0 to 6.0 within the same temperature range [40, 58, 67].

Based on experimentally determined relations between solid and liquid phases during seawater evaporation, Tl content in brines during sylvite crystallization (0.03 ppm), and distribution coefficients, Boiko [59] calculated Tl content in chloride evaporites. He argued that the relatively high Tl content in sylvite was caused not only by the preceding precipitation stage but also by the formation of a poorly soluble compound, TlCl , the solubility of which (0.3 g/100 g H_2O) is 16.3 times lower than that of Tl_2SO_4 [59, 70].

The presence of 0.03×10^{-4} to $1.2 \times 10^{-4} \%$ Tl in salts and brines has been reported by several investigators. Since J_{Tl} for sylvite is higher than one, recrystallization should lead to Tl enrichment in secondary sylvinites. This is confirmed by the elevated Tl content and Tl/K ratio (7.4–58.8) in the redeposited sylvinites of Kalush and Stebnik (Carpathian region) [40, 58, 66, 71].

The above data were used for a detailed investigation of geological and structural features of the Gaurdak Formation of the Late Jurassic halogen formation in southern Central Asia [72–74].

These salt deposits occupy an area of about 30 000 km² within the southwestern spurs of the Gissar Range and have a thickness from 900 m in the south to 25 m in the northeast. They represent the uppermost unit of the Jurassic sedimentary sequence and mark a change from marine to continental sedimentation. The Gaurdak Formation overlies carbonate rocks and consists of four units: underlying gypsum–anhydrite (145–200 m), transitional anhydrite–halite (120–138 m), salt (K-bearing) (320–460 m), and cover gypsum–anhydrite (5–35 m) sequences.

Such a structure is preserved in all the deposits; however, the thickness and lithology of units vary and strongly depend on the area occupied by the deposit

within a halogen basin. The deposits located in the northeast (Tyubegatan, Akbash, Lyalimkan, and others) have thinner K-bearing beds of mainly sylvinite composition and show high contents of halopelitic material in salts. In the deposits of the southwestern part (Khodzha Ikan, Karabil, Karlyuk, and others), K-bearing beds are greater in thickness and number, being composed mainly of sylvinite–carnallite and carnallite rocks. The salt rocks contain no soluble sulfates; the main rock-forming minerals are halite, sylvite, carnallite, and anhydrite.

The sediments show no seasonal and annular bedding typical of halogen sequences. The salt rocks have an inequigranular texture with occasional large spotted crystals. Sylvite inclusions in halite and halite inclusions in sylvite of diverse size, shape, and arrangement were observed. Some layers contain fine sylvite crystals, the zoned color of which suggests their primary sedimentary origin. The zoned crystalline structure of halite occurs rarely and is usually poorly preserved. In the rock salt, sylvite often associates with carnallite. They show no distinct boundaries, giving the impression that sylvite develops after carnallite.

These compositional, textural, and structural features have been repeatedly discussed but their interpretation remains controversial. It was supposed that the Gaurdak sequence was locally affected by extensive long-term recrystallization; however, the scales and reasons of this process have not yet been determined.

The compositions of rocks were studied using drill core samples from nine boreholes of the Tyubegatan deposit and sections of the Akbash, Lyalimkan, Khodzhiakan, Karabil, and Karlyuk deposits (>3000 samples). The major- and trace-element (Br, B, Li, Rb, Cs, Tl, Cu, Mn, and Fe) compositions of the salt rocks and associated halopelites were analyzed.

A characteristic geochemical feature of the formation is the low Br content in the salt rocks relative to normal contents found in salt minerals, marine rocks, and compositionally similar rocks from other regions. The calculated Br/Cl ratios and relative Br/Cl coefficients for different rock types from a number of boreholes revealed a significant depletion in Br. In particular, the Br content, Br/Cl ratio, and relative Br coefficient are as follows: 0.001–0.008%, 0.35–0.39, and 3.7–38.0% in the salt rock; 0.014–0.053%, 1.28–3.00, and 4.1–43.8% in the sylvinites; and 0.055–0.575%, 3.88–4.00, and 33.2–43.9% in the carnallites, respectively. The average deficit of Br relative to Br content in primary sedimentary rocks of the same composition is about 60% for halite, 60–80% for sylvinite, and 60–70% for carnallite.

The Br depletion in the rocks could be caused by the input into the salt basin of continental runoff, which bears a considerable portion of low-Br/Cl high-salinity waters. Eroding halite and potassium salt deposits, such waters could promote their redeposition and, correspondingly, a decrease in Br content. The process can

be reinforced by Br sorption on clay matter and carbonates [75]. This is supported by the fact that halopelite-rich rocks contain 3–4 times more Br than chemogenic rocks. The correlation coefficient between Br content and insoluble residue in various rocks indicates distinct stochastic dependence between the amount of carbonate–clay inclusions and Br content. This correlation was confirmed by the calculation of relative Br/Cl coefficients in various salt rocks from a series of boreholes in deposits located in different parts of the basin: K_{Br} increases from 19 to 45 from the boundaries to the center of the salt basin, where salt accumulated in a stable regime and there was no input of continental waters supplying terrigenous material.

However, one of the main reasons for the Br depletion is diagenetic recrystallization of salts with the participation of descendent solutions migrating into the consolidation sagged portions of the salt sequence. The differences in relative Br/Cl coefficients between sylvite and halite occurring in direct contact and, hence, crystallizing from the same brine can be explained by postsedimentation recrystallization only [76–78].

This suggestion can be supported by the Rb content and Rb/K ratio of the rocks. Low-grade sylvinites (KCl < 20%) have a Rb content of $2.5\text{--}4.8 \times 10^{-3}$ (averaging $3.2 \times 10^{-3}\%$) and a Rb/K ratio within 0.17–0.46 (averaging 0.35), which are within the ranges found in primary sylvite. In high-grade sylvinites (KCl > 20%), only the minimum Rb contents ($0.38 \times 10^{-3}\%$) fall within this range. Most sylvinite samples have a Rb content from 16.2×10^{-3} to $36.0 \times 10^{-3}\%$ (averaging $22.02 \times 10^{-3}\%$) and a Rb/K ratio $\left(\frac{Rb}{K} \times 10^4\right)$ from 5.0 to 15.3. Very rich sylvinites (KCl > 50%) show the highest Rb contents (from 55.30×10^{-3} to $102.01 \times 10^{-3}\%$), which are significantly higher than those of primary sylvite (from 1.7×10^{-3} to $5.3 \times 10^{-3}\%$) and sylvinites from other deposits [57–59, 79]. The carnallite-bearing sylvinites (5–10% carnallite) contain $6.6\text{--}42.0 \times 10^{-3}\%$ Rb, and carnallites, $9.2\text{--}67.1 \times 10^{-3}\%$ Rb. These values are in agreement with the data on secondary carnallites from the German Zechstein ($3.5\text{--}68.0 \times 10^{-3}\%$) [46].

The lognormal distribution of Rb in the potassium salts suggests its accumulation in one mineral [13]. To test this suggestion, pair correlation coefficients were calculated between the contents of Rb and rock-forming minerals. The obtained results showed a distinct, almost functional relation between Rb and sylvite ($r_{calcd} = 0.805$, $r_{0.05} = 0.22$; $r_{calcd} = 0.901$, $r_{0.05} = 0.53$; etc.). According to the calculated coefficient and regression equation, the Rb concentration increases by $0.12 \times 10^{-3}\%$ for each 10% increase of KCl in the rocks [80, 81].

The single-stage recrystallization of sylvite leads to an almost four-fold decrease in Rb content owing to the distribution coefficient of this stage, whereas the disso-

lution of carnallite produces sylvite containing 1.3 times more Rb than primary carnallite. This leaves no doubts that the sylvinites were generated by incongruent dissolution of secondary carnallite, which was enriched in Rb by a factor of ten compared with primary carnallite. However, the extent of this process was not uniform during all stages of salt accumulation and over the whole basin. This is seen, in particular, from the statistical heterogeneity of the dispersions of average Rb contents in the same rocks both within sections and over the area.

Carnallite decomposition in various portions of the basin was presumably stimulated by different factors. In the northeastern portion (Tyubegatan, Akbash, and other deposits), it could be related to high-salinity continental runoff. This is confirmed by the presence of abundant enclaves of carbonate–clay material in the K-bearing rocks. These influxes differently affected transformations of Rb-bearing minerals in the rocks. This resulted in considerable Rb variations and, correspondingly, high dispersion and variation coefficients. Indirect evidence for this interrelation is provided by Rb–Li correlation coefficients (e.g., $r_{calcd} = 0.49$ and $r_{0.05} = 0.31$); the presence of Li in terrigenous materials is beyond doubt [82].

Toward the central part of the basin (Karlyuk, Karabil, and other deposits), these influxes were local and less intense. Salt crystallization occurred there in a more stable regime. This is supported by the higher consistency of potassium beds and statistical parameters of Rb distribution (uniform average values, dispersion, and distribution functions corresponding to the normal distribution).

Our investigations showed that the generally accepted opinion that Rb concentration in potassium salts is correlated with carnallite content, which is true for many salt-bearing deposits, was not confirmed for the Gaurdak Formation. In this formation, there is no universal correlation between Rb and carnallite, and sylvite is an Rb-concentrating mineral. This is indicated by both the aforementioned Rb contents and the calculated correlation coefficients between Rb and sylvite in the sylvite-bearing rocks ($r_{calcd} = 0.97$; $r_{0.05} = 0.63$; $r_{calcd} = 0.99$, $r_{0.05} = 0.87$; etc.). In contrast, there is no stable Rb–carnallite correlation, which is typical of other occurrences (Carpathian region, Verkhnekamskoe, and others) [83, 84].

The stratigraphic position of sylvinite beds, their relations with carnallite beds, and a comparison of Rb contents and Rb/K ratios with those in primary sedimentary K minerals suggest that the high Rb contents in the sylvinites were inherited from carnallites, which were incongruently dissolved and produced sylvinite deposits.

The Cs content of potassium salts of the Gaurdak Formation is usually almost two orders of magnitude lower than that of Rb; however, it is higher than the Cs contents of the variegated ($0.11 \times 10^{-4}\%$) and red ($0.14 \times$

$10^{-4}\%$) sylvinites and carnallites ($0.11 \times 10^{-4}\%$) of the Verkhnekamskoe deposit and secondary carnallites from the Kalush and Golyn deposits (5×10^{-4}) [57, 59, 62, 63].

Among the samples of potassium rocks, the highest Cs contents (from 10.41×10^{-3} to $11.14 \times 10^{-3}\%$) were found in the rich (almost monomineralic) sylvinites of the Karlyuk and Karabil deposits. Cs content tends to increase in the sylvite-rich rocks. In particular, the average Cs content varies from $1.5 \times 10^{-3}\%$ in the low-grade sylvinites (KCl < 20%) to $2.6 \times 10^{-3}\%$ in the high-grade sylvinites (KCl > 20%), reaching $5.56 \times 10^{-3}\%$ in the very rich sylvinites (KCl > 50%). This dependence can be quantitatively characterized by the Cs–KCl correlation coefficient, $r_{\text{calcd}} = 0.96$ and $r_{0.05} = 0.80$. In addition, some sylvinite samples containing 62.4–70.47% KCl have two–three times less Cs (from 2.6×10^{-3} to $1.35 \times 10^{-3}\%$). Poor and rich carnallite samples from other portions of the basin (Akbash, Tyubegtan, and other deposits) show approximately the same average Cs contents (from 0.88×10^{-3} to $2.10 \times 10^{-3}\%$). In general, Cs is uniformly distributed in all potassium rocks: the variation coefficient is always lower than 43.3%, the distribution is approximated by the normal law, and statistically significant differences of the average contents were obtained only in high-grade sylvinites from some sections, although the dispersions exhibit significant differences [80, 84, 85].

The obtained data indicate that, in addition to facies changes, the intensity of postsedimentation processes controlled the presence of Cs in the potassium salts of the Gaurdak Formation.

Additional data were obtained from a study of Tl content and distribution in the rocks [80, 84–86].

The content of Tl in sylvinites from the deposits varies from 0.17×10^{-4} to $0.87 \times 10^{-4}\%$, which is somewhat higher than the experimentally derived value for this rock type ($0.4 \times 10^{-4}\%$), and the Tl/K ratios $\left(\frac{\text{Tl}}{\text{K}} \times 10^4\right)$ in most samples are close to those calculated for the secondary sylvinites of the Stobnik and Kalush deposits [40, 58, 59].

The content of Tl in carnallites varies from 0.21×10^{-4} to $0.60 \times 10^{-4}\%$. The distribution of Tl is lognormal, indicating its accumulation in a single rock-forming mineral, sylvite. This is confirmed by the Tl–sylvite correlation coefficients: $r_{\text{calcd}} = 0.87$ and $r_{0.05} = 0.22$.

A comparison of Tl abundances in borehole sections from different deposits showed that the lower potassium horizons are enriched in Tl compared with the upper layers by a factor of almost six. For instance, Tl content in the Akbash deposit varies from 0 to $1.79 \times 10^{-4}\%$ (averaging $0.39 \times 10^{-4}\%$) in the upper potassium horizon and from 2.28×10^{-4} to $3.67 \times 10^{-4}\%$ (averaging $2.68 \times 10^{-4}\%$) in the lower horizon. The presence of

Tl (from 0.08×10^{-4} to $0.052 \times 10^{-4}\%$) was detected in some intervals of the underlying rock salt, which can be explained by the association of Tl with pyrite crystals occurring in this portion of the salt-bearing sequence. The presence of Tl in pyrite and marcasite was first noted by V.I. Vernadsky in 1909; there is evidence on the accumulation of colloidal Tl in iron (zinc) disulfides [66–69]. The formation of thallium sulfide in sediments of stagnate sea zones under H_2S contamination was also reported by other authors [64, 65]. The reducing H_2S regimes of the lower zones of the Gaurdak Formation caused no doubt. The smell of H_2S and bitumen was noted during crushing of drill core samples from almost all boreholes. Based on some parameters, the overlying rocks were formed in a more oxidizing environment. In addition, the migration of Tl into solution was facilitated by the formation of characteristic soluble complex compounds with chlorides [66, 70].

Since the distribution coefficient of Tl (J_{Tl}) is higher than one during sylvite crystallization, recrystallization should cause Tl enrichment in the secondary sylvinites [40, 45]. The Tl content in the sylvinites of the Gaurdak Formation is somewhat lower than could be expected from the experimentally determined J_{Tl} values for salt systems. This discrepancy is presumably related to Tl–Br interaction leading to the formation of poorly soluble Tl bromide.

Secondary alterations were distinctly recorded in the potassium salt rocks of the Gaurdak Formation in the above-described contents of Br, Rb, and Cs. In the case considered, they should also be considered as the main reason for the high Tl content and Tl/K ratio.

The obtained data indicate a considerable role of secondary processes, which caused significant changes in the pegnitogenous composition, texture, and structure of salt rocks of the Gaurdak Formation. During sedimentation, potassium salts precipitated repeatedly and not simultaneously in different portions of the Late Jurassic basin; they also differed in composition and genesis of minerals. A significant portion of primary sedimentary potassium salts presumably had a carnallite composition. This was provided by the extensive metamorphism of the brines and their transformation from the sulfate to chloride hydrochemical types. In accordance with physicochemical principles, carnallite can form at a very low MgCl_2 content under these conditions [4, 87].

The incongruent decomposition of carnallite plays a decisive role in sylvinite formation. This is primarily confirmed by the local development of sylvinite–carnallite rocks bearing evidence for carnallite decomposition, the abundance of carnallite with excess potassium chloride, as well as an inversion in the contents of Br–Rb, Cs, and Tl. The latter is quantitatively supported by the statistical parameters of distribution of these elements in the rocks and pair correlation coefficients.

We believe that one of the main reasons for the extensive transformation of potassium salts was the sig-

nificant undersaturation of parent brine during metamorphism. Calculations showed [88] that during early metamorphic stages (when sulfate ion content in the brine decreased to 65% of the initial value), the excess of water is 20.5% and increases up to 22.8%, when sulfate ions completely disappear. The second stage of metamorphism produces chloride brines and causes an increase in water excess up to 33.8% and then to 54.4%. At the same time the Mg deficits reach 74.5% relative to the value at the beginning of the second phase. Such changes make the brines aggressive relative to potassium salts and, primarily, carnallite, without any additional dilution.

The extensive metamorphism of the brines of the Late Jurassic halogen basin is suggested by the complete absence of soluble sulfate salts in the rocks, the frequent presence of CaCl_2 and rinneite, which are typical of the chloride system. This is also confirmed by the high carbonate content in the halopelites and their magnesite-rich composition [82–89].

A comparison of theoretical salt columns with the observed sections of the salt-bearing Gaurdak Formation indicates that the Late Jurassic basin experienced metamorphism when the brines reached 15% salinity and halite began to precipitate after a prolonged stage of marine feeding. This is suggested by the presence of thick (400–500 m) underlying anhydrite sequences, confirming that the Thethys waters that fed the basin had a normal composition, i.e., belonged to the sulfate hydrochemical type. The evaporation of such solutions must lead to the precipitation of sulfate salts (epsomite and polyhalite), which were never found at the deposits studied. Single findings of loeweite and astrakhanite are presumably related to the contribution of salt clays to halogenesis, because these accessory minerals are always confined to clay interbeds [90]. Certain compositional, textural, and structural changes in the salts could be also caused by water liberated during gypsum dehydration (about 0.486 m³ per ton of rock). It is known that gypsum dehydration begins during diagenesis and continues in the stage of a buried basin without any change in the primary stratification of salt beds. As a result, salts within salt sequence can be dissolved and recrystallized during both the diagenetic and catagenetic stages of the formation of salt deposits. This model is based on the investigations of D.S. Korzhinskii, who showed that the dissolution of old minerals and crystallization of new ones occur almost simultaneously; the rock remains in a solid state, and the process occurs in the volume of pore solutions. According to Valyashko [91, 92], the primary porosity of salt rocks is 30 vol %.

It should be noted in conclusion that the traditional data set (mineral composition of salts and halopelites, texture of rocks, etc.) that is used for the determination of the genesis of salt deposits and provides a basis for the geochemical methods of prospecting for potassium salts should be extended by the determination of con-

tents and distribution of trace elements in salt rocks and minerals. These data must be evaluated accounting for experimentally or thermodynamically determined distribution coefficients in the corresponding salt systems. Such an approach can be used to refine genetic concepts.

REFERENCES

1. *Deposits of Potassium Salts in the USSR: Prospecting and Exploration*, Ed. by V. I. Raevskii and M. P. Fiveg (Nedra, Leningrad, 1973) [in Russian].
2. A. E. Fersman, *Geochemical and Mineralogical Methods of Prospecting for Mineral Deposits* (Akad. Nauk SSSR, Moscow, 1940) [in Russian].
3. D. N. Grigor'ev, "Corporeal Genetic Models of Minerals," *Zap. Vses. Mineral. O-va* **108** (2), 129–130 (1979).
4. M. G. Valyashko, *Geochemistry of the Formation of Potassium Salt Deposits* (Mosk. Gos. Univ., Moscow, 1962) [in Russian].
5. M. G. Valyashko, "A Method for Determining Salt Genesis from Chemical Analyses and Its Application in Studies of Fore-Carpathian Deposits," in *Problems in Mineralogy of Sedimentary Deposits* (L'vov, 1956), Vols. 3–4, pp. 252–265 [in Russian].
6. V. I. Borisenkov, "Development of M.G. Valyashko's Ideas on the Use of Geochemical Methods in Exploration of Potassium Salt Deposits," in *The Geochemistry of Halogenesis* (Mosk. Gos. Univ., Moscow, 1989), pp. 4–20 [in Russian].
7. T. N. Sokolova, *Authigenic Silicate Mineral Formation of Various Stages of Salinization* (Nauka, Moscow, 1982) [in Russian].
8. I. V. Melikhov and D. G. Berdonosova, "Equilibrium Impurity Partitioning between Solid and Liquid Phases," *Radiokhimiya* **10** (2), 137–145 (1968).
9. I. D. Ryabchikov, "Behavior of Isomorphous Impurities during Crystallization in a Multicomponent System," *Geokhimiya*, No. 12, 1046–1054 (1962).
10. I. D. Ryabchikov, *Thermodynamics of Trace Element Behavior in Crystallizing Silicate Melts* (Nauka, Moscow, 1965) [in Russian].
11. I. D. Ryabchikov, "The Effect of the Degree of Disequilibrium during Crystallization on Trace Element Behavior," *Geokhimiya*, No. 4, 345–354 (1960).
12. L. L. Perchuk and I. D. Ryabchikov, *Phase Correspondence in Mineral Systems* (Nauka, Moscow, 1976) [in Russian].
13. Yu. A. Tkachev and Ya. E. Yudovich, *Statistical Analysis of Geochemical Data* (Nauka, Leningrad, 1975) [in Russian].
14. G. I. Gorshtein, "On the Limits of Applicability of the Linear Distribution in Water-Salt Systems with Isomorphous and Isodimorphous Components," *Zh. Neorg. Khim.* **2** (1), 51–58 (1958).
15. V. G. Khlopin and A. E. Polesitskii, "Relationships between Solid Solutions and Mixed Crystals and the Conditions under Which True Equilibrium Can Be Reached in Experiments with Solutions," in *Selected Works of V. G. Khlopin* (Akad. Nauk SSSR, Moscow, 1957), Vol. 1, pp. 159–172 [in Russian].

16. V. I. Grebenshchikova, "Co-precipitation of Micro-Impurities with Crystalline Sediments," *Zh. Neorg. Khim.* **3** (2), 20–24 (1958).
17. V. I. Grebenshchikova and R. V. Bryzgalova, "Determination of the Khlopin Partition Constant by the Method of Partial Recrystallization of a Solid Phase," *Zh. Neorg. Khim.* **3** (1), 36–45 (1958).
18. S. K. Chirkov, *Crystallization of Isomorphous Substances from Water Solutions*, Issue 5 of *Proceedings of the Ural Branch of Academy of Sciences of the USSR* (Sverdlovsk, 1936) [in Russian].
19. M. G. Valyashko, "The Geochemistry of Potassium Salt Deposits," in *Problems in the Geology of Agricultural Ores* (Akad. Nauk SSSR, Moscow, 1956), pp. 182–197 [in Russian].
20. I. V. Melikhov and M. S. Merkulova, *Co-crystallization* (Khimiya, Moscow, 1975) [in Russian].
21. V. S. Urusov and I. F. Kravchuk, "Thermodynamic Analysis and Calculated Partition Coefficients of Isovalent Isomorphous Impurities during Melt Crystallization," *Geokhimiya*, No. 8, 1204–1223 (1976).
22. V. S. Urusov, *Theory of Isomorphic Solid Solutions* (Nauka, Moscow, 1977) [in Russian].
23. V. S. Urusov, "Thermodynamic Characteristics of Essentially Ionic Solid Solutions of the Substitution Type (Isomorphous Solid Solutions)," in *Problems in the Study of Isomorphous Substitution in Crystals* (Nauka, Moscow, 1971), pp. 62–164 [in Russian].
24. V. S. Urusov and V. B. Dudnikova, "A Mechanism of an Increase in the Partition Coefficient of Trace Components during Crystallization (Trapping Phenomenon): Isovalent Systems" *Geokhimiya*, No. 4, 499–514 (1993).
25. L. A. Nisel'son and A. G. Yaroshevskii, "Estimation of the Reliability of Experimental Data from Partition Coefficients in Crystal–Melt Equilibria," *Zh. Fiz. Khim.* **56**, 2928–2933 (1984).
26. B. D. Stepin, I. G. Gorshtein, G. E. Blyum, *et al.*, *Methods of the Synthesis Ultrapure Inorganic Compounds* (Khimiya, Leningrad, 1969) [in Russian].
27. A. N. Kirgintsev and V. A. Isaenko, *Fractionation of an Impurity during Directed Crystallization* (Nauka, Novosibirsk, 1997) [in Russian].
28. V. K. Vigdorovich, *Refining of Metals and Semiconductors by Crystallization* (Metallurgiya, Moscow, 1969) [in Russian].
29. Ch. V. Kapetskii, I. P. Boglaev, V. I. Korotitskii, *et al.*, "Database on Crystal–Liquid Partition (Equilibrium) Coefficients," *Dokl. Akad. Nauk SSSR* **293**, 413–415 (1987).
30. G. G. Devyatykh, "Compilation of a Database on Ultrapure Chemical Compounds," *Vestn. Akad. Nauk SSSR*, No. 7, 25–31 (1982).
31. *New Data on the Geology, Geochemistry, Ground Waters, and Minerals of Evaporite Basins*, Ed. by V. V. Blagovidov, M. G. Valyashko, M. A. Zharkov, *et al.* (Nauka, Novosibirsk, 1982) [in Russian].
32. M. G. Valyashko, "Bromine Geochemistry during Halogenesis and Bromine Content as a Genetic and Prospecting Criterion," *Geokhimiya*, No. 6, 33–48 (1956).
33. M. G. Valyashko, I. K. Zherebtsova, A. N. Lavrova, and Wu Bi Chao, "Bromine Partitioning between Salt Crystals and Solutions of Various Compositions and Concentrations," in *Bromine Concentration of Evaporates and Brines as a Geochemical Indicator for Their Genesis and Evolution and as a Prospecting Guide* (Mosk. Gos. Univ., Moscow, 1976), pp. 381–404 [in Russian].
34. I. K. Zherebtsova, "Bromine Behavior during the Eutonic Stage of Brine Formation," in *Geology and Potassium-Bearing Potential of the Siberian Platform and Other Evaporate Regions of the USSR* (Nauka, Moscow, 1970), pp. 272–279 [in Russian].
35. A. S. Kolosov and A. I. Pustyl'nikov, "Bromine Partitioning between Chlorides of Potassium-Bearing Rocks," in *Geology and Potassium-Bearing Potential of the Precambrian in the Southwestern Siberian Platform* (Nauka, Novosibirsk, 1974), pp. 317–322 [in Russian].
36. M. G. Valyashko and N. S. Petrova, "Bromine and Rubidium as Geochemical Indicators of Potassium Rock Origin," in *Bromine Concentration of Evaporates and Brines as a Geochemical Indicator of Their Genesis and Evolution and as a Prospecting Guide* (Mosk. Gos. Univ., Moscow, 1976), pp. 418–427 [in Russian].
37. E. M. Petrova, "The Relative Bromine–Chlorine Ratio and Its Use in Studies of the Origin of Potassium Salts," in *Bromine Concentration of Evaporates and Brines as a Geochemical Indicator of Their Genesis and Evolution and as a Prospecting Guide* (Mosk. Gos. Univ., Moscow, 1976), pp. 9–26 [in Russian].
38. J. D'Ans and F. Busch, "Über die Fraktionierung incongruent löslicher isomorpher Doppelsalze: Die quaternären Systeme KCl–RbCl(CsCl)–MgCl₂–H₂O bei 25°C," *Z. Anorg. Allgem. Chem.* **252**, 337–368 (1987).
39. A. D. Ratner and L. A. Makarov, "Thermodynamic Analysis of Co-crystallization in the KCl–RbCl–H₂O System," *Zh. Neorg. Khim.* **3** (1), 46–51 (1958).
40. I. N. Ladynina and G. N. Anoshin, "Rubidium, Thallium, and Bromine Partitioning during Formation of Potassium Salt Deposits," *Geol. Geofiz.*, No. 3, 64–67 (1962).
41. J. Reicher, "Verteilung anorganischer fremdionen beider Kristallisierungen Alkalchloriden," *Contrib. Mineral. Petrol.* **13**, 134–160 (1966).
42. W. McIntire, "Effect of Temperature on the Partition of Rubidium between Sylvite Crystals and Aqueous Solutions," *Geol. Soc. Am., Spec. Pap.*, No. 88, 505–524 (1968).
43. A. M. Kropachev and M. S. Kropacheva, "Rubidium Isomorphism in Sylvite and Carnallite of the Verkhnekamskoe Deposit," *Vestn. Leningrad. Gos. Univ.*, No. 6, 94–96 (1967).
44. H. H. Shock and H. Puchelt, "Rubidium Distribution in Salt Minerals: Experimental Investigations," *Geochim. Cosmochim. Acta* **35**, 307–311 (1971).
45. Yu. Z. Vlasov and L. A. Makarov, "On the Theory of Solid Solutions of Alkali Halides," *Zh. Fiz. Khim.*, No. 4, 806–812 (1967).
46. R. Kuhn, "Zur Kenntnis der Rubidiumgenalte von Kalisalzen ozeanischer Salzlagerstätten nebst einigen Lagerstätten kundlichen: Ausdeutungen," *Geol. J.* **90**, 131–144 (1972).
47. D. G. Berdonosova and I. V. Melikhov, "On the Problem of Verification of the Theory of Solid Solution by the

- Example of the KCl-RbCl-H₂O System,” *Vestn. Mosk. Gos. Univ.*, No. 1, 116–117 (1973).
48. M. G. Valyashko and N. S. Petrova, “Experimental Study of Rubidium Partitioning between Sylvite Crystals and Solution in the NaCl-KCl-MgCl₂-H₂O System at 25°C,” *Geokhimiya*, No. 4, 589–594 (1973).
 49. N. S. Petrova, “Experimental Study of Rubidium Partitioning between Carnallite Crystals and Solution in the NaCl-KCl-MgCl₂-H₂O System at 25°C,” *Geokhimiya*, No. 6, 919–924 (1973).
 50. N. P. Mokachev and L. G. Pakhomov, “Partition Coefficient of a Trace Component between Liquid and Solid Phases with Distortions,” *Zh. Fiz. Khim.*, No. 12, 3099–3102 (1981).
 51. I. V. Melikhov, D. G. Berdonosova, and L. P. Pakhomov, “The Effect of Crystal Collisions in Mixed Suspension on Rubidium Migration from Solution to KCl Crystals,” *Radiokhimiya* **16** (3), 297–300 (1974).
 52. G. I. Gorshtein and B. I. Zhelnin, “Fractionation of Isomorphous Impurities during Solid Phase Crystallization through a Parent Solution,” in *Mass Crystallization* (IREA, Leningrad, 1936), pp. 88–97 [in Russian].
 53. F. I. Shederman and N. F. Chelishchev, “Geochemical Differentiation of Elements during Concentration of Chloride Brines,” *Sov. Geol.*, No. 7, 80–86 (1988).
 54. M. G. Valyashko, A. I. Polivanova, I. K. Zherebtsova, *et al.*, *Geochemistry and Origin of Brines in the Irkutsk Basin* (Nauka, Moscow, 1965) [in Russian].
 55. I. K. Zherebtsova and N. N. Volkova, “Experimental Study of Trace Element Behavior during Natural Evaporation of Black Sea Water and Sasyk-Sivash Brine,” *Geokhimiya*, No. 6, 832–845 (1966).
 56. N. A. Solodov, L. S. Balashov, and A. A. Kremenetskii, *Geochemistry of Lithium, Rubidium, and Cesium* (Nauka, Moscow, 1980) [in Russian].
 57. E. P. Slivko and O. I. Petrichenko, *Lithium, Rubidium, and Cesium Admixtures in Ukrainian Evaporates* (Naukova Dumka, Kiev, 1967) [in Russian].
 58. I. N. Malikova, *Distribution of Rubidium, Thallium, and Bromine in Potassium Salt Deposits* (Nauka, Novosibirsk, 1967) [in Russian].
 59. T. F. Boiko, *Rare Elements in Halogenic Sequences* (Nauka, Moscow, 1973) [in Russian].
 60. M. S. Petrova, Extended Abstract of Candidate’s Dissertation in Geology and Mineralogy (MGU, Moscow, 1978).
 61. V. I. Borisenkov and Kh. Shnaider, “Rubidium as a Geochemical Indicator of the Conditions of Postsedimentary Alteration of Potassium Sulfate Salts,” *Geokhimiya*, No. 12, 1730–1739 (1988).
 62. S. I. Mormil’, “On the Geochemistry of Cesium in the Halogenic Sequence of the West Ural Foredeep,” *Litol. Polezn. Iskop.*, No. 5, 78–94 (1974).
 63. S. I. Mormil’ and P. V. Pokrovskii, “Modes of Cesium Occurrence and Its Distribution between Natural Salt Components,” in *Yearbook 1973 of the Institute of Geology and Geochemistry, Ural Scientific Center, Academy of Sciences of the USSR* (Sverdlovsk, 1974), pp. 43–47 [in Russian].
 64. D. Shaw, “The Geochemistry of Thallium,” *Geochim. Cosmochim. Acta* **2**, 118–154 (1952).
 65. V. V. Ivanov, V. Yu. Volgin, A. A. Krasnov, and N. A. Lizunov, *Thallium: Geochemistry, Mineralogy, Genetic Types of Deposits, and Geochemical Provinces* (Akad. Nauk SSSR, Moscow, 1960) [in Russian].
 66. Yu. E. Baranov and V. V. Ivanov, “Thallium,” in *Metals in Sedimentary Sequences* (Nauka, Moscow, 1966), pp. 206–228 [in Russian].
 67. V. I. Lebedev, “Geochemistry of Thallium: Isomorphism,” *Geokhimiya*, No. 1, 76–81 (1970).
 68. N. P. Voskresenskaya, “Geochemistry of Thallium in the Sedimentary Process,” in *Reports of Soviet Geologists at the International Geological Congress: 10. Geochemistry* (Nauka, Moscow, 1972), pp. 60–73.
 69. L. H. Ahrens, “Geochemical Correlation between Thallium and Rubidium in Magmatic Minerals,” in *Trace Elements in Magmatic Rocks and Minerals* (Inostrannaya Literatura, Moscow, 1952), pp. 51–57 [in Russian].
 70. V. A. Isaenko and A. N. Kirgintsev, “Equilibrium Coefficients of Thallium Chloride Partitioning during Directed Crystallization of Alkali Chlorides,” *Zh. Neorg. Khim.* **21**, 2443–2449 (1976).
 71. S. M. Korenevskii, *Mineral Deposits of Halogenic Rocks* (Nedra, Moscow, 1973) [in Russian].
 72. N. P. Petrov and P. A. Chistyakov, *Lithology of Evaporates and Red-Colored Deposits in the Southwestern Branches of the Gissar Range* (Nauka, Tashkent, 1964) [in Russian].
 73. V. I. Troitskii, *Upper Triassic and Jurassic Sedimentary Deposits in Southern Uzbekistan* (Nedra, Leningrad, 1967) [in Russian].
 74. V. S. Popov, *Potassium and Sulfur Contents of Late Jurassic Halogenic Rocks in Central Asia* (Fan, Tashkent, 1988) [in Russian].
 75. A. I. Mun and A. B. Bekturov, *Distribution of Trace Elements in Water Basins of Kazakhstan* (Nauka, Alma-Ata, 1971) [in Russian].
 76. E. M. Petrova, “Geochemical Study of the Starobinsk Potassium Deposit,” in *Potassium-Bearing Potential of Siberian Evaporates* (Nauka, Novosibirsk, 1965), pp. 85–94 [in Russian].
 77. V. S. Popov and R. G. Osichkina, “Bromine Behavior during Halogenesis in the Late Jurassic Evaporate Basin of Central Asia,” *Geokhimiya*, No. 3, 404–415 (1973).
 78. R. G. Osichkina, “Geochemistry of Bromine in the Late Jurassic Halogenic Rocks of Southern Central Asia,” *Geokhimiya*, No. 10, 1530–1535 (1978).
 79. V. I. Sedletskii and V. S. Derevyagin, “Rubidium Distribution in the Potassium-Bearing Evaporate Basin of Central Asia,” *Geokhimiya*, No. 9, 1125–1129 (1979).
 80. M. N. Nabiev, R. G. Osichkina, U. S. Kasymkhodzhaeva, and L. Kh. Dzhuraeva, *Potassium Salts and Trace Elements of the Akbash Deposit* (Fan, Tashkent, 1972) [in Russian].
 81. R. G. Osichkina and D. O. Dzhumaklychev, *Rubidium and Cesium Contents in the Evaporates of the Late Jurassic Halogenic Sequence of Central Asia*, Available from VINITI, No. 2654-77 (Moscow, 1977).
 82. V. S. Popov and R. G. Osichkina, “Clay Mineral Indicators of the Conditions of Evaporate Formation,” in *Chemistry and Technology of Mineral Fertilizers* (Fan, Tashkent, 1971), pp. 155–177 [in Russian].

83. R. G. Osichkina, "Rubidium and Cesium in the Evaporates of the Late Jurassic Halogenic Sequence as Indicators of Their Formation Conditions," *Geokhimiya*, No. 6, 921–925 (1978).
84. R. G. Osichkina, Kh. N. Tillyakhodzhaev, M. Nazarova, and M. Mumindzhanova, "Use of Trace Elements for the Determination of the Conditions of Evaporate Formation and Prospecting for Potassium Salts," in *Main Problems in Salt Accumulation* (Nauka, Novosibirsk, 1981), pp. 71–78 [in Russian].
85. U. S. Kasymkhodzhaeva and R. G. Osichkina, "Rubidium, Cesium, and Thallium Impurities in the Evaporates of Uzbekistan," *Chemistry and Technology of Mineral Fertilizers* (Fan, Tashkent, 1971), pp. 177–183 [in Russian].
86. U. S. Kasymkhodzhaeva and R. G. Osichkina, *Distribution of Lithium, Rubidium, and Thallium Admixtures in the Evaporates of Uzbekistan*, Available from VINITI, No. 3552-71 (Moscow, 1971).
87. M. G. Valyashko, "Geochemical Conditions of Tachyhydrite Formation," in *Problems in the Lithology and Geochemistry of Sedimentary Rocks and Ores* (Nauka, Moscow, 1975), pp. 297–311 [in Russian].
88. V. I. Borisenkov, "A Method of Superposed Projections for the Analysis of the Composition of Multicomponent Water–Salt Systems and Its Use in the Geochemistry of Halogenesis," *Geokhimiya*, No. 9, 1382–1391 (1973).
89. L. E. Filatova and F. M. Gabril'yants, "Rinneite from the Late Jurassic Evaporate Sequence of the Western Branches of the Gissar Range," *Dokl. Akad. Nauk Uzb. SSR*, No. 7, 47–49 (1966).
90. L. S. Efimenko and E. I. Azarova, "On the Mineralogy of the Okuz-Bulak Salt Deposit," *Izv. Akad. Nauk Turkm. SSR, Ser. Fiz. Tekh.*, No. 3, 38–42 (1960).
91. M. G. Valyashko, "Volume Proportions of Liquid and Solid Phases during Oceanic Water Evaporation as a Factor of Formation of Potassium Salt Deposits," *Dokl. Akad. Nauk SSSR* **77**, 1055–1058 (1951).
92. D. S. Korzhinskii, *Theoretical Basis for the Analysis of the Paragenesis of Minerals* (Nauka, Moscow, 1973) [in Russian].