

Potassic Salts in Phanerozoic Evaporite Basins and Specific Features of Salt Deposition at the Final Stage of Halogenesis

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Received July 25, 2005

Abstract—The study of the final stage of halogenesis is one of the most topical problems of evaporite sedimentation and formation of fossil salt deposits. The spatiotemporal distribution of various sulfate, sulfate–chloride, and chloride mineral assemblages of the final stage of Phanerozoic halogenic basins and the compositional trends of marine sulfate and chloride solutions indicate that crystallization of minerals followed a stable trend, while the metastable (“solar”) trend was typical only when the composition of ancient marine solutions fitted that of the condensed oceanic water. The formation of potassic and potassic–magnesian deposits of the sulfate and chloride types is related to the final stage of halogenesis, whereas magnesian and calcium chlorides are deposited at the eutonic stage. The difference between mineral assemblages of potassic and potassic–magnesian deposits in the Phanerozoic section was controlled by the evolution of marine solutions and the heterogeneity of hydrochemical environment in each halogenic basin.

DOI: 10.1134/S0024490206040080

INTRODUCTION

The study of evaporite basins has not still lost its urgency, first, because of their economic significance as sources of salt deposits (potassium sulfate and chloride ores, sodium and magnesium chlorides, borates, native sulfur, and soda). Genesis of potash ores was studied by Vant-Hoff (1909), Lotze (1938), Valyashko (1962), Ivanov and Voronova (1972), Fiveg (1977), Korenevskii and Voronova (1966), Zharkov (1978), Yanshin (1977), Sonnenfeld (1984), and others.

Potash deposits of different compositions were formed as a result of the evolution of marine solutions in partly or completely closed halogenic basins at the final stage of their development. The potash deposition postdated the formation of enormous bodies of rock salt in the course of progressive drying up and salinization or spatial differentiation of brine by its density within a basin. In addition, the formation of potash deposits was controlled by variation in volume of evaporating seawater. Therefore, the hypothesis of “dry lake” elaborated by Valyashko (1962) has expanded the system of halogenic basin by including older evaporite deposits.

According to (Kurnakov and Nikolaev, 1938), the trend of crystallization, i.e., variation of brine composition due to the precipitation of one or several salts or the transformation of one solid phase into another, eventually ends at the final crystallization (eutonic) point that is typical of each specific system. Therefore, the compositional limit of brines corresponds to the onset of bischofite crystallization in sulfate-type sedimentary basins and to the precipitation of tachyhydrite in chloride-type basins. Investigations of these researchers

devoted to salt crystallization from seawater at the Saki salt field led to the discovery of the solar trend of oceanic water crystallization and the creation of the solar diagram of evaporation.

Investigations carried out by many researchers have shown that the solar trend of crystallization is generally typical of natural processes and is rather simple in comparison with the stable trend of crystallization suggested by Vant-Hoff (1909). Unlike the latter diagram, the Kurnakov solar diagram lacks the astrakhanite, leonite, and kainite fields, but it includes the fields of magnesium sulfate (with 6H₂O and 7H₂O), potassium chloride, and some part of carnallite, the field of which is markedly enlarged. Fields of kieserite and magnesium sulfate hydrates (with 5H₂O and 4H₂O) are replaced by the hexahydrite field in the Kurnakov diagram. The solar eutonics is appreciably enriched in magnesium sulfate in comparison with the stable eutonics. Observations at many potash salt deposits have confirmed the reality of metastable solar equilibria. Valyashko believes that these equilibria control the deposition of enormous sequences of potash salts during various geological epochs. Sylvite and carnallite are the most abundant potassic minerals precipitated from oceanic water and products of its metamorphism. Magnesium sulfates + polyhalite, only polyhalite, and anhydrite assemblages occur with sylvite. Magnesium sulfates + anhydrite (in extremely rare cases, polyhalite) or only anhydrite assemblages occur with carnallite.

Nevertheless, the spatiotemporal distribution of sediments deposited at the final stage of halogenesis in the Phanerozoic potassic basins indicates that the crystalli-

zation in these basins not always followed the metastable (solar) trend. This problem has both theoretical and practical importance in the exploration of salt deposits. Resolution of this problem was provided by the supplementation of the classic mineralogical–petrographic investigations with the thermobarogeochemical analysis of potassic–magnesian chlorides and sulfates deposited at the final and eutonic stages of halogenesis.

POTASSIUM POTENTIAL OF EVAPORITE BASINS

At present, approximately 40 K-bearing evaporite basins with potassic and potassic–magnesian salt deposits are known in Europe, Asia, North America, South America, and Africa. The chart presented in this work (Fig. 1) is designated to specify the potassium potential of Phanerozoic evaporite basins and the spatiotemporal distribution of deposits formed at the final stage of halogenesis during the Phanerozoic geological history. This chart generalizes a great body of geological, geophysical, and geochemical information available in the Russian and foreign literature.

The left part of the chart reflects the stratigraphic (geochronological) scale modified after the *Supplements to the Stratigraphic Code of Russia* (2000). The chart scale corresponds to absolute time for certain periods and epochs (columns 1–5). The right part of the chart takes into consideration all known potassic basins of the world and the geochronological assignment of potassic, potassic–magnesian, and magnesian sulfates and chlorides in Phanerozoic sections. The location of the known potassic basins (column 6) in the Phanerozoic section has been specified up to the level of stages. Therefore, one can specify specific features of potassic and potassic–magnesian deposits.

The occurrence of potassic and potassic–magnesian chlorides is shown in Fig. 1 (columns 11–13). As compared to chlorides, potassic, magnesian, and potassic–magnesian sulfates are more diverse in mineral composition. Therefore, column 10 shows their occurrence in different-aged basins without specification of the mineral assemblages. Columns 10–13 are based on materials of Korenevskii and Voronova (1966), Zharkov (1978), Zharkov and Zharkova (1989), Ivanov and Voronova (1968, 1972), Kopnin (1995), Zaikov et al. (1967), Tikhvinskii (1976), Kislik et al. (1976), Derevyagin et al. (1981), Lupinovich and Kislik (1970), Minko (1972), Khrushchov and Petrichenko (1980), Makhnach et al. (1970), Chechel et al. (1981), Busson (1974), Hite (1961), Jones (1970), Kühn (1955), Smith (1981), Wardlaw and Nicholls (1972), Woods (1974), Anderson et al. (1979) and many others.

The chemical type of brines in different-aged basins (columns 1–3) is shown on the basis of the unique data on composition of fluid inclusions in salt minerals (Petrichenko, 1988; Kovalevich, 1990; Shaidetskaya, 1977; Moskovskii and Goncharenko, 2004; Goncharenko and

Moskovskii, 2004; Roedder, 1982, 1984; Herman and Borstel, 1991; Horita and Holland, 1996; Zimmermann, 2001; Bein et al., 1991; Garcia-Veigas et al., 1995; Hardie, 1996; Kovalevich et al., 1998; Petrichenko and Peryt, 2002; and Stain and Krumhansl, 1988).

The chart shows that potassic sedimentary rocks occur in all Phanerozoic geological systems except the Ordovician. One-half of the potassic basins is confined to Middle and Late Devonian, Permian, and Paleogene–Neogene periods. The Early Paleozoic includes two Early Cambrian (Iran–Pakistan and East Siberian) basins and one Early Silurian (Michigan) basin. The Carboniferous Period includes three (Maritime, Paradox, and Eagle) basins. In the Triassic and Jurassic, saliferous formations are widespread, but potash deposits were formed only in small areas (Late Triassic North African and Aquitanian basins and Late Jurassic Central Asian and Ciscaucasian basins). In the Cretaceous, potassic sediments were deposited in four (Gabon–Angola, Sergipe–Alagoas, Korat, and Sakon–Nakon) basins (Fig. 1).

Potash deposits in various halogenic basins of the world are mainly related to the chloride and sulfate types. Potassium chlorides are more abundant and largely represented by sylvite and carnallite. These minerals are present in all Phanerozoic (Cambrian–Quaternary) potassic basins. Sylvite is noted in the entire Phanerozoic section. Carnallite is absent in some basins (e.g., Middle Devonian Edaveil, Late Devonian Dnieper–Donets, Late Permian Amazon, Late Jurassic Ciscaucasian, and Miocene Ciscarpathian basins) (Wells, 1980; Vysotskii et al., 1988; Makhnach et al., 1970; Zharkov, 1978; Gerasimova and Sedletskii, 1969; Derevyagin and Sedletskii, 1977; Khrushchov and Petrichenko, 1980; Korenevskii et al., 1977). The wide abundance of sylvite in the potassic basins may be accounted for the decomposition of carnallite and its subsequent replacement by sylvite. The potassium chloride deposits are mainly composed of carnallite, sylvite + carnallite, and carnallite-bearing sylvinites. Deposits with carnallite prevailing over sylvite are also known in rocks recently studied in Africa (Upper Triassic rocks in the North African Basin, and Lower Cretaceous rocks in the Gabon–Angola Basin) and other regions (Lower Cretaceous rocks in the Sergipe–Alagoas Basin and Upper Cretaceous rocks in the Korat and Sakon–Nakon basins) (Amade, 1965; Busson, 1974; Salvan, 1974; Wardlaw and Nicholls, 1972; Zharkova, 1984; Zharkov and Zharkova, 1989). The carnallite-bearing rocks are most abundant in the Cambrian, Permian, Triassic, Cretaceous, and Miocene halogenic basins.

The stratigraphic position of bischofite deposits attracts special attention. In the Phanerozoic, halogenic basins first reached their eutonic stage in the Permian (Fig. 1). Bischofite deposits are found in the Dnieper–Donets, Pripyat, Caspian, and Central European basins

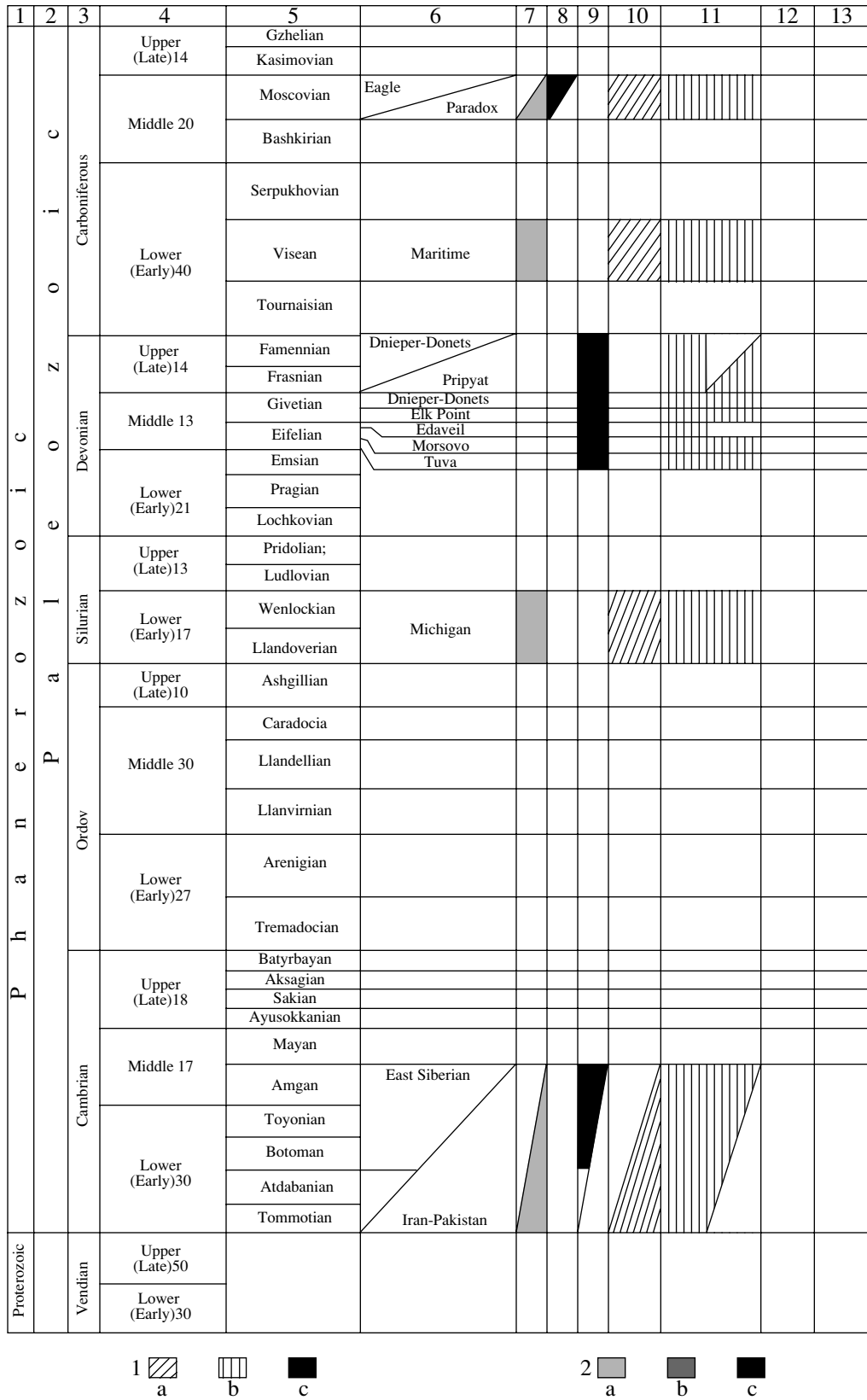


Fig. 1. (Contd.)

(Korenevskii et al., 1968; Khrushchov and Petrichenko, 1980; Galitskii et al., 1972; Vysotskii et al., 1988; Zharkov, 1978; Ivanov and Voronova, 1972; Korenevskii and Voronova, 1966; Gorbov, 1973; Derovyagin et al., 1981; Diarov, 1974; Tikhvinskii, 1976; Fiveg, 1977; Kühn, 1955; Smith, 1981). In Permian basins, bischofite is associated with carnallite, magnesium sulfates (largely, kieserite), and halite. In the Cretaceous sequence of the Gabon–Angola Basin (Fig. 1), some thick bischofite deposits are associated with carnallite, tachyhydrite, and halite (Wardlaw and Nicholls, 1972; Zharkov and Zharkova, 1989). In the Neogene (Sicilian Basin), bischofite is associated with kieserite and carnallite (Ramberti, 1980). The Permian Period is distinguished by the highest abundance of bischofite in the history of the Earth's sedimentary shell.

Tachyhydrite is one of the rare and unique products of halogenesis. The tachyhydrite mineralization has been established in the Zechstein section (Central European Basin) and the marginal part of the Kungurian halogenic section (North Caspian Basin) (Smith, 1981; Dönnner, 1981; Goncharenko and Moskovskii, 2004). According to (Wardlaw and Nicholls, 1972; Zharkov and Zharkova, 1989), tachyhydrite sequences up to 100 m thick are present in the Aptian Gabon–Angola and Sergipe–Alagoas basins and in the Late Cretaceous Korat and Sakon–Nakon basins (Fig. 1). In the Permian basins, tachyhydrite is associated with bischofite. In the Cretaceous basins, the mineral is associated with bischofite plus carnallite or only carnallite (Korat and Sakon–Nakon basins).

In addition to potassic chlorides, some potassic basins contain variable amounts of potassic and magnesium sulfates. Such deposits are confined to the Lower Cambrian saliferous sequence (Iran–Pakistan Basin), with langbeinite and kainite as the predominant minerals and polyhalite and kieserite as the less abundant minerals (Jones, 1970; Vysotskii et al., 1988). Langbeinite, polyhalite, and kieserite are found in saliferous rocks of the Early Silurian Michigan Basin and in the Carboniferous Maritime, Eagle, and Paradox basins (Strakhov, 1962; Anderson et al., 1972; Hite, 1961, 1968). Potassium sulfates became especially abundant in the Permian time. Potassic and magnesium sulfates have been identified in all basins of this age (Dnieper–Donets, Pripyat, Caspian, and other basins) with the exception of the Amazon Basin. The assemblage of potassium sulfates in these basins includes a wide range of minerals (langbeinite, polyhalite, leonite, glaserite, gorgeyite, schoenite, kainite, kieserite, epsomite, and others). They make up both mono- and polymineral interlayers. They also occur as admixtures in rock salt; sylvinitic, carnallite, and bischofite rocks; and anhydrite–dolomite rocks (Galitskii et al., 1972; Diarov, 1974; Korenevskii and Voronova, 1966; Svidzinskii et al., 1982). Only insignificant occurrences of polyhalite and less frequent kieserite are found in Triassic halogenic sequences of the Aquitanian and North African basins (Amade, 1965; Busson, 1974; Smith, 1981).

Sulfate mineralization is developed poorly and represented by polyhalite in Jurassic potassic basins (Derovyagin et al., 1977). The role of potassium sulfates sharply increases in Cenozoic potassic basins. Sulfates are especially abundant in the Neogene Ciscarpathian and Sicilian basins (Korenevskii et al., 1977; Khrushchov and Petrichenko, 1980; Ramberti, 1980). In the potassic sulfate sediments of Neogene basins, langbeinite and kainite are the major rock-forming minerals. Polyhalite, kieserite, epsomite, glaserite, schoenite, astrakhanite, thenardite, mirabilite, loeweite, syngenite, and gypsum also occur.

The formation of mineral assemblages mentioned above in the Phanerozoic section was mainly controlled by the compositional evolution of marine solutions at the final stage of halogenesis. The available unique data on the composition of fluid inclusions in salts from the Paleozoic rocks in some potassic basins indicate that the Paleozoic marine solutions of the final stage of halogenesis fitted the sulfate or chloride type of brines (Table 1). The Cambrian and Devonian potash basins were distinguished by the chloride type of brines, whereas the Permian basins were characterized by the sulfate type of marine solutions metamorphosed to different grades (Table 1).

A more diverse compositional variation of marine solutions is observed in the evolution of the Mesozoic and Cenozoic potassic basins despite the preservation of the following general trend: Triassic sulfate basins–Late Jurassic magnesium chloride basins–Cretaceous calcium chloride basins (Table 1). Marine solutions of Neogene basins of the stage of potassic and potassic–magnesian sediments are similar to the condensed oceanic water (COW).

Thus, marine solutions of the halite and potash stage corresponded to the sulfate type in most of the Phanerozoic potassic basins, whereas the calcium chloride solutions have been established only in the Middle Cambrian, Middle–Late Devonian, Early Cretaceous (Aptian) and Late Cretaceous basins.

HYDROCHEMISTRY OF SEDIMENTATION AT THE FINAL STAGES OF HALOGENESIS

Evaporite sedimentation in halogenic basins was regulated by the intensity of evaporation, the chemical type of primary marine solutions, and dynamic parameters (mainly, temperature and depth of sedimentation). Keeping in mind that the chemical type of initial marine solutions and their further evolution in the development of halogenic basins controlled a variety of mineral assemblages of potassic–magnesian sediments, it is necessary to dwell on the main compositional trends of marine solutions during their condensation in more detail.

As has been shown above, the potassic and potassic–magnesian salts crystallized from sulfate- and chloride-type brines. The compositional evolution of

Table 1. Average chemical composition of solutions in halite-hosted fluid inclusions from Phanerozoic halogenic deposits

Period	Basin	Content, g/l					Ion content (%) in (2K ⁺ – Mg ²⁺ – SO ₄ ²⁻) diagram (Fig. 2)			
		NaCl	KCl	MgCl ₂	CaCl ₂	MgSO ₄	2K ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻
Є	1	75	57	175	181	n.d.	10	45	45	–
D	2	350	8.7	20.8	6.6	tr.	17	65	18	–
		350	8.7	20.8	tr.	2.2	20	77	3	–
	3	325.5	14.6	20.4	27.7	n.d.	17	39	44	–
	4	60	5.7	58.8	277	n.d.	1	23	76	–
	5	70	7.6	105.8	216.1	n.d.	2	35	63	–
	6	150	1.9	86.2	166.2	n.d.	1	38	61	–
	7	30	11.6	135.2	245.2	n.d.	2	39	59	–
	8	10	26.6	196.0	277.0	n.d.	4	44	52	–
P	9	220	32.3	99.9	n.d.	27.5	11	76	–	13
	10	140	52.4	158.8	n.d.	30	14	77	–	9
	11	210	20.9	136.2	n.d.	6.2	8	88	–	4
	12	200	9.5	176.2	n.d.	6.2	6	89	–	5
	13	20.0	95.0	345.9	n.d.	8.7	14	84	–	2
	14	75	32.3	208.8	n.d.	69.8	7	78	–	15
J	15	150	30.9	204.2	1.3	n.d.	9	91	–	–
	16	50	14.1	309.2	1.4	3.1	3	96	–	1
P	17	15	76	313.3	1.4	0.7	13	87	–	–
	18	310	7.9	16.5	54.1	n.d.	7	27	66	–
	19	290	23.6	48.6	27.7	n.d.	8	77	15	–
N	20	110	53.2	141.1	n.d.	85	11	67	–	22
	21	260	15.9	75.8	n.d.	24.9	8	76	–	16
	22	80	32.3	198.8	n.d.	64.3	7	78	–	15

Note: (1) East Siberian; (2) Morsovo; (3) West Canadian; (4–6, 9, 10) Dnieper-Donets; (4) Middle Devonian, (5) Frasnian, (6) Famennian, (7, 8) Frasnian and Famennian Pripyat, respectively; (9) Asselian, (10) Sakmarian; (11) Caspian; (12) Cisuralian; (13) Central European; (14) West Texas (Midcontinent); (15) Ciscaucasian; (16) Central Asian; (17) Upper Rhine; (18) Rhône; (19) Erevan; (20, 21) Ciscarpathian; (22) Sicilian. Average chemical compositions of solutions in halite-hosted fluid inclusions from the Phanerozoic halogenic deposits were recalculated on the basis of data in (Petrichenko, 1988; Kovalevich, 1990; Shaidetskaya, 1977; Moskovskii and Goncharenko, 2004; Goncharenko and Moskovskii, 2004; Roedder, 1982, 1984; Herrman and Borstel, 1991; Horita and Holland, 1996; Zimmermann, 2001; Bein et al., 1991; Garcia-Veigas et al., 1995; Hardie, 1996; Kovalevich et al., 1998; Petrichenko and Peryt, 2002; Stein and Krumhansi, 1988). (n.d.) Not detected.

ancient marine solutions at the final stage was deduced from the study of fluid inclusions in halite from ancient potassic basins (Table 1), taking into account the results of homogenization of multiphase inclusions captured by minerals from productive units. The stable SO₄²⁻ – Mg²⁺–2K⁺ diagram at 40°C was used for this purpose (Stewart, 1956).

In contrast to the COW composition, the disposition of data points of fluid inclusions in minerals formed at the final stage of evolution of many ancient basins indicates that the marine solutions became progressively depleted in the sulfate component (e.g., in Permian

basins). However, an enrichment of brines in SO₄²⁻ at the potash stage of basin evolution is also possible (e.g., in Neogene basins). In this case, K and Mg contents in brines correspond to the COW composition (Tables 1, 2). The enrichment in potassic and magnesian chlorides was caused by condensation of brines and controlled by natural processes of mineral formation (Fig. 2).

Proportions between potassium, magnesium, and sulfate ion varied along the line of metamorphism of solutions of the oceanic origin (OC–OC') as a result of the interaction of brine with calcium carbonate supplied by surface water. In the case of metamorphism caused by cation exchange, proportions of the major

Table 2. Contents (g/l) of major components in oceanic water at various degrees of condensation

Stage of enrichment in salt	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻
COW	0.43	1.3	11.3	0.4	20.1	2.9
Gypsum	1.75	6.3	43.8	1.4	80.2	12.3
Halite	0.42	15.5	104.1	3.4	191.2	21.0
Epsomite	1.09	73.6	26.3	15.3	203.2	90.8
Sylvite	n.d.	75.7	17.6	33.8	223.0	79.1
Carnallite	1.55	90.7	13.9	22.1	256.8	68.6
Eutonics	2.38	117.4	7.6	1.4	324.6	43.5
	n.d.	121.3	3.8	1.0	334.0	36.4

Note: The chemical compositions were taken from (Valyashko, 1962; Petrichenko, 1988; Kovalevich, 1990; Moskovskii and Goncharenko, 2004; Goncharenko and Moskovskii, 2004). (n.d.) Not detected.

components will change in the OC–OC' direction. Increase in the Mg content in brine of potassic basins with increase in the sulfate ion concentration from 10 to 0.5 g/l (Table 2) produced eutonic solutions, e.g., Central and East European basins in the Permian and Ciscarpathian and Sicilian basins in the Neogene (Fig. 2, trend 1).

Condensation of the sulfate-type brine up to the stage of magnesium sulfate (kieserite), sylvite, carnallite, and bischofite was controlled by depletion in sulfate ion along with the successive enrichment in potassium and magnesium, e.g., in the Permian Central and East European basins and the Late Carboniferous Monkton and Paradox basins (Fig. 2, trend 1).

Enrichment of marine solutions in the sulfate ion up to 60 g/l after crystallization of halite, magnesium sulfates, and sylvite can be caused by natural concentra-

tion of this component as a result of the progressive condensation of brine. Furthermore, a periodic supply of the continental surface water into the basin, especially at the stage of potash precipitation, led not only to desulfatization of solutions, but also to their reverse metamorphism. As a result, the potassic–magnesian deposits of sulfate type were formed, e.g., in the marginal part of the Permian Caspian Basin and in the Neogene Ciscarpathian and Sicilian basins (Fig. 2, trend 2).

Two trends may be outlined in the compositional variation of the chloride-type brine in the course of halogenesis. According to the first trend, the content of calcium chloride gradually decreased along with enrichment in potassium chloride, and to a lesser extent, in magnesium chloride, as, for example, in the Devonian Pripyat Trough and later in the Dnieper–Donets halogenic basin (Fig. 3, trend 1). The second trend was characterized by the enrichment of solutions in magnesium and calcium chlorides together with an insignificant variation in the content of potassium chloride. The Cretaceous West African, East Brazilian, and Thailand basins and the southwestern marginal part of the Permian Caspian basins serve as examples (Fig. 3, trend 2).

Thus, the sulfate type of solutions largely displays variations of components similar to the present-day oceanic water. In brines of the chloride type (magnesium chloride and calcium chloride), Na, Cl, K, and Mg contents similar to those in the sulfate-type solutions should be retained until the halite precipitation. The main difference between solutions of these types consists in contents of calcium and sulfate ions. The sulfate-type brines are characterized by high SO₄²⁻ concentrations (21 g/l) at the onset of the halite stage; the chloride-type solutions, by low contents of both SO₄²⁻ and Ca²⁺ at the beginning (within the range of CaSO₄ solubility); and calcium chloride solutions, by high Ca²⁺ contents (~10 g/l) at this stage. At the potash stage of the basin evolution, the magnesium and potassium–

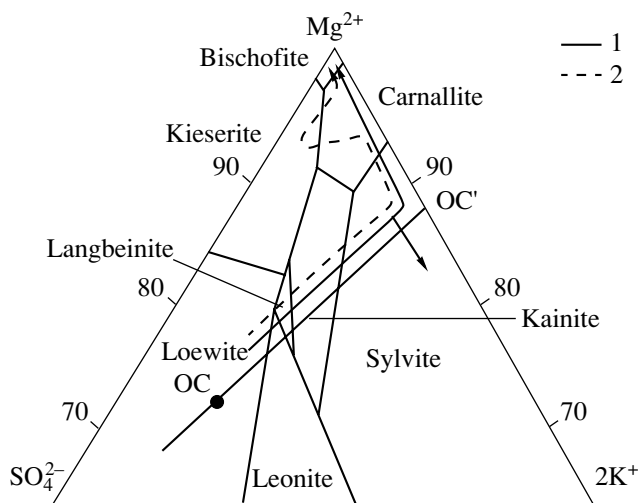


Fig. 2. Compositional trends of sulfate-type brines deduced from the compositions of fluid inclusions in minerals from productive units (plotted on the stable diagram for 40°C). (1) First trend; (2) second trend; (OC–OC') trend of seawater metamorphism.

magnesium sulfates and potassium and potassium–magnesium chlorides largely precipitate from sulfate-type brines; potassium and potassium–magnesium chlorides precipitate from magnesium chloride brines; potassium, magnesium, and calcium chlorides precipitate from calcium chloride brines. Magnesium chlorides are the major components at the eutonic evolution stage of sulfate and magnesium chloride solutions, whereas magnesium and calcium chlorides dominate in calcium chloride solutions.

Thus, the spatiotemporal abundance of various sulfate, sulfate–chloride, and chloride deposits formed at the final stage of halogenesis in the Phanerozoic potassic basins, as well as compositional trends of the evolution of sulfate-type marine solutions at this stage indicate that minerals crystallized in halogenic basins along the metastable trend only when the composition of ancient marine solutions fitted the COW composition. These observations confirm the statement set forth by Valyashko (1962) that transition from the metastable solar equilibria to their stable counterparts is most readily realized in the solutions, the composition of which is close to the onset of carnallite crystallization in the solar diagram. In other words, the concentration of sulfate ion in brine drastically drops after crystallization of the main mass of magnesium sulfates and sylvite. Therefore, the stable trend of mineral crystallization from marine solutions controls the sedimentary or early diagenetic origin of stable assemblages of kainite, langbeinite, halite, sylvite, and carnallite.

Since potash salts started to precipitate in many ancient basins from solutions characterized by a high degree of metamorphism or the virtually absence of sulfate ion, magnesium sulfates are not formed in halogenic deposits prior to the crystallization of sylvite. However, periodic enrichment of solutions in sulfate ion as a result of the progressive evaporation of brine fostered the crystallization of magnesium sulfate in association with potassic–magnesian chlorides, e.g., in the Early Carboniferous, Permian, and Neogene basins. The rock association formed from marine solutions with the sulfate ion content of no less than 65 g/l is distinguished by a complex composition owing to the appearance a wide range of sulfate minerals: epsomite, epsomite–kieserite, kainite, kainite–langbeinite, langbeinite–kainite, sporadic schoenite, leonite, glaserite, and gorgeyite. Halogenic deposits formed at the final stage of halogenesis are represented by mineral assemblages of sylvite, sylvite–kieserite, sylvite–carnallite–kieserite, carnallite–kieserite, and carnallite. The eutonic stage of halogenesis includes the carnallite–kieserite–bischofite, bischofite, and bischofite–kieserite assemblages, in which kieserite replaces the primary magnesium sulfates (epsomite and hexahydrite). Solutions characterized by the highest grade of metamorphism (the sulfate ion content does not exceed 2–3 g/l) and a temperature of more than 40°C produce the halite–sylvinite and sylvinite–carnallite assem-

blages at the final stage of halogenesis and the bischofite assemblage at the eutonic stage.

Magnesium and potassium sulfates are absent in basins with the chloride-type brine. The mineral assemblages consist of sylvite, sylvite–carnallite, sylvite–carnallite–bischofite, carnallite–bischofite, bischofite, carnallite–bischofite–tachyhydrite, bischofite–tachyhydrite, and tachyhydrite. Tachyhydrite is likely to crystallize if the Ca content in marine solution is no less than 70 g/l Ca (e.g., Cretaceous basins). If the Ca content is <30 g/l, tachyhydrite is found only in carnallite–bischofite deposits (e.g., Permian basins).

Examination of the data mentioned above and scrutinization of trends of salt deposition at the final stage of halogenesis in the Permian Caspian Basin (Moskovskii and Goncharenko, 2004) indicate that the formation of potassium and potassium–magnesium chlorides at this stage is followed by the deposition of potassium and potassium–magnesium sulfates when the sulfate ion content in brines reaches 20 g/l or more. Eutonic solutions are formed as a result of the further concentration of Mg owing to specific conditions (the additional delivery of Mg to brines of the basin due to its leaching from previously formed potassic–magnesian deposits). Thus, the final stage of halogenesis (after the precipitation of enormous mass of rock salt) may be divided into two substages: (1) precipitation of potassium and potassium–magnesium chlorides and sulfates and (2) precipitation of magnesium and calcium chlorides. At the first substage, epsomite, kainite, langbeinite, glaserite, gorgeyite, sylvite, and carnallite precipitate from the solutions saturated with sulfate ion, i.e., enriched in potassium and magnesium sulfates and/or in potassium and magnesium chlorides. Only sylvite and carnallite precipitate from chloride-type solutions saturated with potassium and magnesium chlorides.

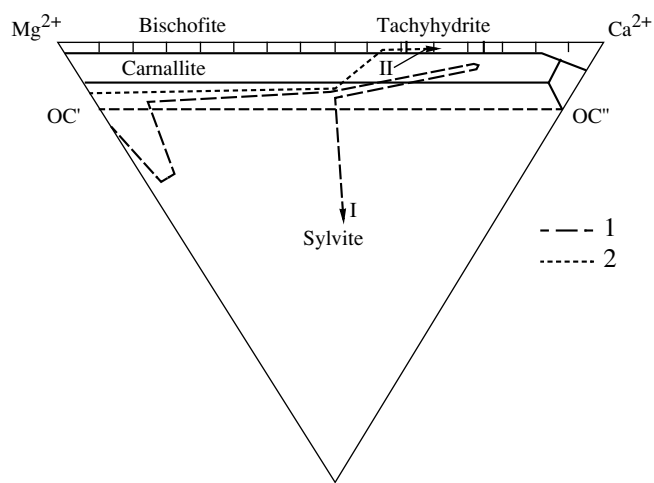


Fig. 3. Compositional trends of chloride-type brines deduced from the compositions of fluid inclusions in minerals from productive units. (1) First trend; (2) second trend; (OC'–OC'') trend of seawater metamorphism.

The eutonic solutions (stages) are defined as the final products of the evaporation of seawater enriched in magnesium (sulfate type of brines) or in magnesium and calcium (chloride type of brines). Bischofite precipitates at the second substage from sulfate-type solutions, whereas bischofite and tachyhydrite precipitate from chloride-type solutions.

At the same time, thermobarogeochemical and geological data together with a great body of the published information on potassic basins have shown that the mineral composition of deposits formed at the final and eutonic stages is much more complex. Halite and kieserite are also formed at the final sulfate stage, and halite precipitates at the final chloride stage. Deposits of the eutonic sulfate stage are enriched in halite, kainite, and kieserite. Deposits of the chloride eutonic stage are enriched in halite, sylvite, and carnallite.

CONCLUSIONS

The difference in mineral assemblages of the Phanerozoic potassic and potassic–magnesian deposits was controlled by the evolution of marine solutions and nonuniform hydrochemical settings within each potassic basin. The formation of potassic and potassic–magnesian deposits of sulfate and chloride types was related to the final stage of halogenesis, whereas magnesium and calcium chlorides precipitated at the eutonic stage.

Potassic sequences are known in all geological systems except the Ordovician. The majority of potassic basins developed in the Middle–Late Devonian, Permian, Paleogene, and Neogene. Potassic deposits in various halogenic basins are mainly related to the chloride and sulfate types. Potash salts of chloride type are more abundant than the sulfate-type salts and are known in all of the Phanerozoic potassic basins. Significant occurrences of potassium and magnesium sulfates fall on the Permian and Neogene. Halogenic basins reached the eutonic stage only in the Permian, Cretaceous, and Neogene. The eutonic stage of bischofite deposition reached its maximum in the Permian, and the tachyhydrite deposition was most abundant in the Cretaceous basins.

In the Phanerozoic, basins with the sulfate type of marine solutions at the halite and potash precipitation stages are more abundant than basins with the chloride type of marine solutions. Crystallization of minerals in halogenic basins mainly followed the stable trend. If the ancient marine solutions fitted the COW composition, the crystallization followed the metastable trend.

ACKNOWLEDGMENTS

I thank M.A. Zharkov from the Geological Institute, Moscow and G.A. Moskovskii from the Saratov State University for their consultations during preparation of the manuscript.

This work was supported by the Program *Universities of Russia*, project no. 09.01.383.

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