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Geochemistry of rare elements in waters and sediments of alkaline lakes in the Sasykkul depression, East Pamirs

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Abstract

The saline lakes (Tuzkul, Chukurkul, Sasykkul Lakes) of the Sasykkul depression located in the semidesert part of the Pamirs provide a prominent example of the evaporative concentration of alkaline waters in a closed basin under arid climate conditions. Chemical evolution of the lake waters has resulted in the development of residual Na–Cl–CO₃–SO₄ and Na–Cl–CO₃ brines. The contents of a number of rare elements were determined in waters and sediments of the Sasykkul depression lakes. Speciation modelling suggests that the main aqueous species of Ag are chloride complexes, Cu, Pb, Zn, Mn are carbonate complexes, Be, Bi, Nb are hydroxocomplexes, Mo, W, As, V are oxyanions. It was established that the salt lake sediments are significantly enriched in B, Ba, Mo, W, U, Th. High contents of trace elements are considered to be due to chemical weathering of rocks within the catchment basin, significant contribution from thermal springs derived from the residual fluids associated with acid igneous and volcanic rocks, and following evapoconcentration in a closed basin. The processes of evaporative concentration, solution complexation, chemical precipitation, and water-sediment interaction lead to the partitioning of trace metals in the salt sediments. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Salt lakes; Geochemistry; Lake sediments; Trace elements; Rare earths; Evaporation

1. Introduction

In the Pamirs there are many lakes, that may be attributed to favourable geomorphologic, tectonic and climatic conditions. The majority of the Pamirs lakes belong to a Ca–HCO₃–SO₄ type and contain approximately 0.20 g/l of total dissolved solids. Certain lakes stand out as being much more saline than others—sometimes over 100 g/l of TDS. They are usually characterized by the absence of inflows and the prevalence of evaporation conditions. The lakes of the Sasykkul depression, which is a topographi-

cally enclosed fault-block basin in the semidesert region of the Pamirs, may be regarded as a prominent example of such salt lakes. Up to the present these lakes have been insufficiently studied, although geologists' attention has been attracted for a long time (Krainov, 1966; Krainov et al., 1971; Ozerov et al., 1988).

This study was made to bring together all available data on the chemical characteristics of the Sasykkul depression lakes, to present new analytical data on the trace element contents in their waters and sediments, and to discuss the possible effect of various factors on element partitioning in the whole system.

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2. General features of the lakes and their basin

The Sasykkul depression is a closed basin of 25 km² in an area located at altitudes of 3800 to 4000 m within the Alichursky Valley between the Alichursky Range from the south and the Bazardarinsky Range from the north (Fig. 1). The Alichursky Range is made of Upper Archean–Lower Proterozoic gneisses intruded by Mesozoic high-alumina granitoides of I- and S-types. The Bazardarinsky Range is composed of Mesozoic high-potassium granites of S-type and Late Eocene continental volcanic rocks of Cordilleran type. The volcanic rocks are represented by latites, trachyandesites, and toscanites. The climate of the region is semi-arid, dry and cold with sharp variations of daily and yearly temperatures. The air temperature ranges from –40°C in winter to +20°C in summer. The annual precipitation averages about 70 mm. In the depression floor there is a number of shallow salt lakes with depths of only up to 3–4 m, but with considerable water surface areas, for exam-

ple: Sasykkul Lake—7.02, Tuzkul Lake—1.63, Chukurkul Lake—25 km².

These lakes are of Na–Cl–CO₃–SO₄ type and are characterized by extremely high values of dissolved solids content (40 to 130 g/l) and high pH values (9 to 10), (Krainov, 1966; Krainov et al., 1971; Volkova et al., 1988). The lakes are bordered by many small peripheral springs, which also occur along or near faulted zones beside Chukurkul Lake. Some of the springs are thermal, their discharge rising apparently from considerable depth. The main part of the depression area, especially the southern and eastern coastal zones of Tuzkul and Sasykkul Lakes, is very salinized. Salt crusts lying on impermeable lacustrine sediments contain mostly halite, trona, burkeite, thenardite, borax, and mirabilite with an admixture of silicate minerals.

The waters of the lakes are derived from three main sources—precipitation on the lakes, small peripheral springs, and ephemeral runoff from mountainous areas.

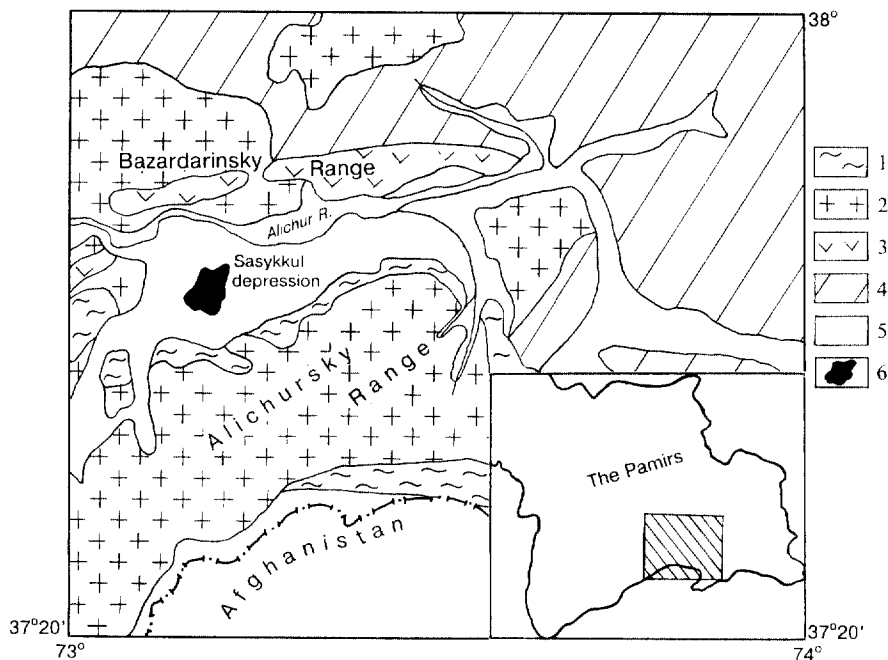


Fig. 1. Schematic geological map of the Southeast Pamirs showing localization of the Sasykkul depression. (1) Upper Archean–Lower Proterozoic gneisses; (2) Mesozoic granitoides; (3) Late Eocene volcanites; (4) sedimentary formations of different ages; (5) Quaternary; (6) Sasykkul depression.

3. Analytical methods

Separate aliquots of water were collected for metal determination (filtered through 0.4 μm acid-rinsed membrane filters and acidified to pH 3.0 using ultra-pure HNO_3). The samples were collected in pre-cleaned polypropylene bottles. The bottles were rinsed thoroughly with deionized-distilled water before use. The pH of the water was measured at the collection site.

Trace element abundances in the lake waters were determined by emission spectrochemical analysis with the preliminary concentration of the elements by co-precipitation on CdS in the presence of FeCl_3 from water samples and standard solutions in accordance with the VITR–LTI method (Sokolov, 1961) in the Institute of Chemistry (Dushanbe, Tajikistan). The co-precipitation of analysed elements was performed by adding 11 ml of 0.4 N solution of CdCl_2 , 10 ml of 0.4 N solution of Na_2S , and 2.0 ml of solution of FeCl_3 containing 2.5 mg/ml Fe^{3+} to 1 l of the water sample. For complete precipitation the mixtures are well shaken for 10–12 min. According to the VITR–LTI method, elements such as Cu, Zn, Pb, Bi, Mn, Nb, Mo, As, W, V, and Be go into concentrate by 80–100% of their contents in water samples, and Ag by 60–70%.

Obtained filtered concentrates are dried at $T = 100\text{--}110^\circ\text{C}$ and analysed using emission spectroscopy. For calibration, a series of standard samples is prepared by co-precipitation of trace elements from standard solutions by the same method. At least five standards for each element are prepared to cover the expected range of the analysed sample. Lower detection limits were the following: Ag—0.03; Bi—0.1; Mo—0.2; Pb, Be—0.3; Cu, Mn—2; Zn—3; As, Nb—5; V, W—10 ng/l. Analytical precisions for all the elements were within 20% at the 95% confidence level, and total chemical blanks were below the detection limits. For comparison, analyses of water samples from two fresh lakes—Bulunkul and Yashilkul—are included in Table 2.

The sediment samples were dried at 40°C , ground in an agate-lined disk mill and homogenized for neutron activation analysis. Concentrations of some major and trace elements in sediments of the depression were determined by standard INAA techniques at the Institute of Nuclear Physics (Tashkent, Uzbek-

istan). The analytical precision was better than $\pm 5\text{--}20\%$ depending on the element. Lower limits of detection were the following (in ppm): Ba—100; Sr—25; Cr, Ni—10; As, Rb, Zn—5; Ce—2; La, Mo, W, U—1; Cs, Se—0.5; Th, Co—0.3; Hf, Sm—0.2; Sc—0.1; Ag, Yb, Sb—0.05; Eu—0.03; Tl, Ta—0.01; Au—0.0005. The accuracy of the results was verified by replicate analyses of international standard samples used for calibration. Most of our trace element data on standards lie within 10% of the recommended values.

Ti, B, Zr, Zn, Pb, Cu contents in sediment samples were obtained using emission-spectroscopy analysis in the Institute of Chemistry (Dushanbe, Tajikistan) with the following sensitivity (ppm): Ti—100; B, Zr, Zn—10; Pb, Cu—5. The reproducibility based on repeated analyses is generally better than 10% for these elements.

4. Results

4.1. Geochemical features of the depression lake waters

The four most abundant dissolved constituents of the Sasykkul depression lakes are sodium, chloride, carbonate, and sulphate, which make up more than 96% of the dissolved solids (Table 1). The potassium concentration is unusually low. Calcium and magnesium are among the most abundant constituents of fresh lake waters, but they are nearly absent from these lakes and alkaline lakes in general. Compared to Yashilkul and Bulunkul fresh lakes (Volkova et al., 1988), which also lie within the Alichursky valley 20 km west from the depression, the measured epm (equivalents per million) percentages for sodium range from 34 to 49% of the cations at 197 to 230 ppm of dissolved solids in fresh waters to 96–99% in saline lakes of the Sasykkul depression. Among the anions, chloride is the most abundant in all the salt lakes under study, with the relative (percentage) amounts increasing as dissolved solids concentration increases (Fig. 2).

The water chemistry of the examined lakes shows an increase of Cl and Na in their contents somewhat greater than the total solutes, suggesting preferential inputs of these elements or significant losses of other

Table 1

The range of major (g/l) and minor (mg/l) element contents in the Sasykkul depression lakes and some selected analyses of the lake waters (meq/l)

Ion	The composition range			Selected analyses			
	Tuzkul	Chukurkul	Sasykkul	Tuzkul	Chukurkul	Sasykkul	Sasykkul
K ⁺	0.64–0.71	0.17	1.83–1.88	16.4	4.3	48.2	46.9
Na ⁺	13.60–13.61	12.33–38.43	28.48–49.62	592.0	1045.9	2190.0	1710.1
Ca ²⁺	–	–	–	–	–	–	–
Mg ²⁺	0.02	0.02–0.03	0.01–0.04	1.7	2.1	0.8	2.0
HCO ₃ ⁻	1.52–2.15	0.57–4.63	5.32–9.67	24.9	9.3	150.7	87.2
CO ₃ ²⁻	5.10–5.91	2.40–19.81	6.53–22.75	170.0	355.7	758.3	613.0
SO ₄ ²⁻	8.55–9.20	9.15–15.35	2.37–10.59	178.1	309.5	198.5	161.0
Cl ⁻	8.60–9.10	7.10–26.49	22.10–40.10	242.2	380.3	1129.6	895.8
TDS	38.74–40.00	32.62–96.67	72.30–133.03	38.74	63.89	133.03	103.71
pH	9.8	9.4–10.0	9.0–10.4				
Li	4.8–7.8	0.28–1.1	0.34–1.06				
Rb	–(1.6 ^a)	–	0.22–0.75				
B	–	30	20–26				
F	1.5	0.8–1.6	1.5–7.5				
I	2.0	2.0	2.0				
Br	16	35	52				
Ti	0.15–2.0	3.5	0.6–4.0				
REE	0.119	–	0.45				

Data from Krainov (1966), Krainov et al. (1971).

^aDeterminations of Li and Rb in one of the small floor hollow from Boiko (1969).

constituents during the evaporative concentration. On the other hand, CO₃ and SO₄ did not increase as rapidly as the TDS concentration. The most obvious

explanation for the apparent loss of these constituents over the concentration range would be the precipitation of calcite and sulphates. The loss of Mg

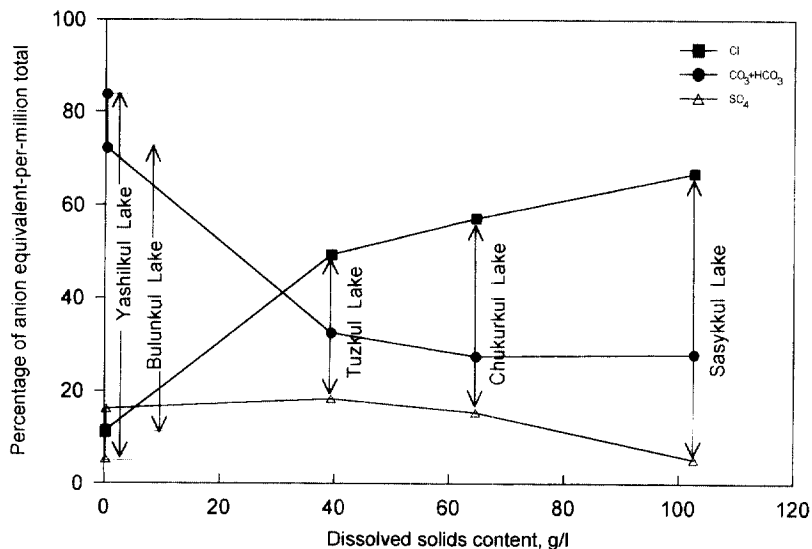


Fig. 2. Changes in the distribution of major anions with increase in dissolved-solids contents in the lake waters of Sasykkul depression and adjacent region.

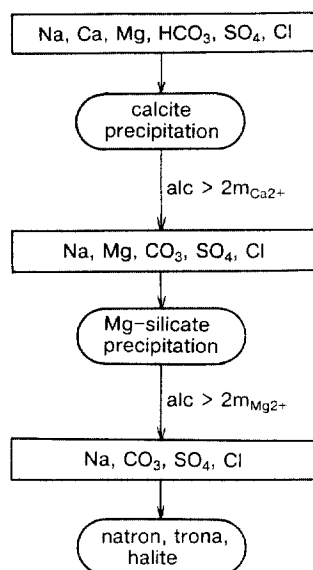


Fig. 3. Theoretical diagram for evaporative concentration of dilute waters, resulted in the formation of saline solutions of the Sasykkul depression lakes in accordance with the model of Hardie and Eugster (1970).

from the solution may be associated with smectite clay formation. The result is the trend toward Na–Cl–CO₃–SO₄-type (Tuzkul and Chukurkul Lakes) and Na–Cl–CO₃-type brines (Sasykkul Lake).

In accordance with the model proposed by Hardie and Eugster (1970), the chemical evolution of these

lake waters subjected to evaporation is interpreted through a succession of chemical precipitation events (Fig. 3). The first precipitated mineral is believed to be calcite, the next one is Mg-silicate or Mg-carbonate (Mg-rich smectite, sepiolite, dolomite, Mg-rich calcite). After that, the remainder of the solution is characterized by an excess of CO₃²⁻. The hydrologic budget for rainy periods suggested that the lake waters might have been evaporatively concentrated many times. The cited model shows that the evaporative evolution of the investigated lake waters and the precipitation of soluble salts and silicate phases could produce the alkaline brines with pH of 9 to 10. Based on the relationship between the main constituents of solutions, these lakes are comparable with Honey Lake, Mono Lake, Searles Lake, Soda Lake, CA (Eugster and Hardie, 1978; Drever, 1985), and with a few small Bolivian salars from the southern Altiplano (Lipez)—Laguna Kollpa and Laguna Cachi (Risacher, 1992; Orris et al., 1992), the waters of which have not been affected by the dissolving and oxidizing of natural sulphur.

The trace-element data for the lake waters are listed in Table 2. The data show that concentrations of trace elements are 1 to 3 orders of magnitude greater than oceanic and fresh lake waters. Moreover, in previous geochemical studies (Boiko, 1969; Krainov et al., 1971) it was established that the lake waters of the Sasykkul depression contain also high concentrations of Li—up to 7.8 mg/l, Rb—to 0.34,

Table 2
Trace-element data for the Sasykkul depression lake waters (ng/l)

Element	Tuzkul	Sasykkul	Bulunkul ^a	Yashilkul ^a
Ag	—	950	1.3	1.3
Cu	11.7	103	2.0	2.2
Pb	2.0	53	0.6	0.9
Zn	—	570	—	—
Mn	9.4	684	—	56.9
Be	—	5.7	—	—
Bi	0.7	2.8	1.1	—
Nb	5	57	—	—
Mo	0.3	570	0.3	0.3
W	150	1900	—	—
As	—	8000	—	—
V	—	57	—	—

^aThe analyses of trace element contents in waters of Bulunkul and Yashilkul fresh lakes are added for comparison.

Sr—to 0.75, Ba—to 0.32, B—to 30, F—to 7.5, Br—to 52, I—to 2, REE—to 0.45, Ti—to 4, Fe—to 360 mg/l (see Table 1).

Trace element species in natural waters depend essentially on the complexation and adsorption processes, and from physico-chemical environmental conditions (pH, dissolved solids content, anion concentrations). The main ligands of the lake waters are OH^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , Cl^- , F^- .

For determination of the aqueous species of trace elements in the Sasykkul depression lakes we used physico-chemical calculations based on the known constants of stepwise hydrolysis and dissociation of complex compounds (Nazarenko et al., 1979; Turner et al., 1981; Byrne and Miller, 1985) and on the major solute chemistry of the lake waters. The method consists in the determination of the equilibrium speciation in lake waters by the simultaneous solving of the mass balance equation and equilibrium equations for hydrolysis and dissociation of complex compounds (Volkova et al., 1988; Ozerov et al., 1988). The aqueous species activities were calculated with the specific ionic interaction model proposed by Pitzer (1987).

Our calculations suggest that Ag chloride complexes (AgCl_2^- , AgCl_3^{2-}) are the predominant forms of dissolved silver in the saline, high pH waters of the Sasykkul depression lakes. Cu, Pb, Mn are complexed with carbonate ions with the formation of dicarbonate complexes $[\text{Me}(\text{CO}_3)_2^-]$, accounting for greater than 86% of each element, and carbonate complexes. Zinc carbonate complexes dominate the complexation behavior of Zn in these saline lakes (70–80%), and hydroxocomplexes of the element may also be of importance (20–29%). The main aqueous species for Be, Bi, and Nb in the alkaline waters of the Sasykkul depression lakes are their various hydroxocomplexes.

The characteristic features of examined lakes (high pH, alkaline water composition, the absence of calcium in brines) are favourable also for the accumulation of Mo, W, As, and V in the form of oxyanions (MoO_4^{2-} , WO_4^{2-} , HAsO_4^{2-} , NaHVO_4^- , HVO_4^{2-}), because molybdate-, tungstate-, arsenate-, and vanadate-ions form complex compounds with sodium, which are characterized by a high solubility. So their concentrations in alkaline lakes are usually proportional to the TDS content, and the alkaline medium

and complexation ability are favourable for their occurrence as aqueous species.

4.2. Geochemistry of the depression lake sediments

The present-day sediments of the Sasykkul depression belong to the formation of continental saline lakes (Boiko, 1973) and contain a high proportion of terrigenous-clay material, that is connected with the small size of the saline lakes. They are characterized by the presence of complex carbonates of sodium, simple and complex salts such as thenardite and mirabilite and others, and the absence of potassium salts as a consequence of a very low K content in the waters. The participation of underground waters and volcanic exhalations in the feeding of a salt-forming basin has resulted in the essential enrichment of both the waters and the lake sediments in a number of trace elements.

The sediments of the Sasykkul depression can be roughly subdivided into three main groups: (a) essentially clay, (b) essentially sand; (c) essentially saline. Trace-element contents in some samples of the sediments are given in Table 3. Clays and silts are enriched in Rb, Cs, Sr, Fe, Co, Sc, Pb, Zn, Ag, Th, La, Eu, Tb, and Yb in comparison with the sand and saline sediments. The maximum concentrations of Ti and Zr are observed in sands. The saline sediments accumulated Na, B, Ba, Mo, W, and U. For the first group of elements a trend increasing abundance with aluminosilicate content or with decreasing salt component in the sediment composition has been established; that is, these elements are the halophobe ones. The second group of elements (halophile) forms authigenic concentrations in saline sediments (Volkova et al., 1993).

In order to clarify the elements relationship we calculated the pair linear correlation coefficients and constructed a hierarchic dendrogram (Fig. 4) using the group unification method (Davis, 1977). It is worth noting that samples 4c and 14 were excluded from the data file because of anomalously high concentrations of a number of trace elements, that may give rise to the false strong correlations between the elements.

The correlation analysis data (Fig. 4) also exhibit on the one hand the presence of the 2 groups of elements, displaying halophobe and halophile proper-

Table 3

Chemical element contents in sediments of the Sasykkul depression (concentrations of Na, Fe, Ti are given in wt.%, Au—in ppb, the rest—in ppm)

Sample	Na	Rb	Cs	Sr	Ba	B	U	Th	Zr	Hf	Ta	Mo	W	Pb	Zn	Cu	As
1a	2.38	74	5.5	364	581	56	17	36	80	10.1	0.60	15	3	30	204	30	15
2a	1.41	48	4.9	392	475	100	26	19	50	4.1	0.34	30	9	37	184	33	—
4f	2.28	41	3.6	250	813	34	24	19	30	6.2	0.55	10	5	15	164	20	—
10	2.20	20	3.4	1094	847	90	31	10	200	2.1	0.43	22	3	13	164	23	14
14	1.72	102	31.1	2131	1623	100	20	24	150	—	0.84	25	3	170	1212	50	35
20a	2.02	57	4.0	418	245	130	9	31	700	4.6	1.76	10	5	40	322	50	—
21b	4.40	59	6.4	1175	757	320	29	43	100	5.6	1.11	32	7	35	250	20	—
4c	0.57	—	4.6	1397	—	140	23	> 90	700	40.4	2.62	25	7	35	247	50	—
4d	1.83	88	2.8	140	386	20	3	21	100	4.9	0.15	7	3	13	121	15	12
4e	0.30	13	0.6	1080	523	10	14	6	30	1.0	0.03	—	—	10	49	15	5
15	3.23	—	5.8	350	—	120	3	10	200	—	0.70	10	4	15	140	20	—
15a	6.19	61	4.0	332	354	120	9	16	500	3.5	0.26	—	—	21	247	13	—
20b	2.03	83	5.6	427	238	40	2	24	100	6.3	0.40	5	2	10	232	20	—
3	13.80	—	0.1	81	3687	100	> 40	1	30	1.9	0.05	52	—	20	12	15	185
3a	3.70	21	1.3	106	14357	890	> 40	6	80	10.3	0.15	36	8	15	145	15	—
4g	0.50	16	0.5	786	379	10	24	6	10	0.5	0.04	50	—	10	99	13	—
5a	23.23	5	0.3	138	665	1400	21	2	80	0.9	0.02	50	10	10	27	20	—
20c	19.38	27	2.2	301	994	2000	38	8	100	2.4	0.16	30	14	10	123	50	—
Sample	Sb	Se	Fe	Cr	Ni	Co	Sc	Ti	La	Ce	Sm	Eu	Tb	Yb	Au	Ag	
1a	0.22	—	0.84	—	14	2.7	4.1	0.15	27.4	72.2	6.38	0.62	0.53	1.30	2.0	—	
2a	0.21	—	0.99	—	18	3.2	4.0	0.15	27.3	38.3	2.40	0.35	0.20	0.68	1.7	—	
4f	0.16	—	0.68	119	34	2.0	3.6	0.30	20.6	35.8	3.52	0.66	0.24	0.91	—	—	
10	0.19	2	1.41	218	26	4.3	4.1	0.10	7.9	24.3	0.47	0.17	—	0.43	2.2	—	
14	2.45	55	7.12	—	50	20.3	18.3	0.08	11.7	6.1	2.44	0.16	0.51	3.99	4.2	8.6	
20a	0.12	3	0.78	119	30	2.3	3.0	0.20	17.0	14.0	2.58	0.37	0.28	0.39	1.3	1.5	
21b	0.38	—	1.58	—	28	5.0	5.7	0.40	12.1	82.1	5.59	0.59	0.17	0.05	—	—	
4c	—	—	21.4	—	40	8.3	90.6	0.30	294.1	673.0	80.61	1.27	5.31	47.0	4.9	—	
4d	0.13	—	0.24	—	20	0.7	0.7	0.10	16.1	22.3	4.44	0.31	0.21	—	1.4	—	
4e	0.11	—	0.14	—	12	0.6	1.0	0.05	2.8	10.0	—	0.04	0.05	0.39	1.0	—	
15	—	9	0.43	88	18	4.1	3.2	0.40	21.6	10	5.44	0.45	0.16	0.09	1.5	0.4	
15a	0.08	—	0.66	—	24	2.0	1.7	0.30	13.7	27.1	2.44	0.26	0.20	0.41	2.6	—	
20b	0.15	—	0.98	—	26	3.7	3.1	0.60	16.3	38.2	2.79	0.36	0.33	0.69	1.0	—	
3	0.05	3	0.01	—	150	1.6	0.1	0.01	6.9	63.8	17.15	—	—	—	9.1	—	
3a	0.40	26	0.31	—	36	1.9	1.2	0.07	4.8	288.4	2.65	0.12	0.08	0.42	—	—	
4g	0.18	2	0.08	39	24	0.3	1.0	0.07	1.2	11.8	1.19	0.03	0.88	0.44	0.7	—	
5a	0.13	—	0.06	24	45	0.4	0.2	0.06	1.0	15.2	0.24	0.03	0.01	—	—	—	
20c	0.14	—	0.47	70	24	1.5	1.5	0.50	8.2	28.1	1.01	0.09	0.07	0.30	3.0	—	

1a, 2a, 4f—clays and floor silts from Sasykkul Lake; 10—clay, Chukurkul Lake, 14—sample from mud volcano, Chukurkul Lake shore; 20a, 21b—floor silts from Tuzkul Lake; 4c, 4d, 4e—sands from Sasykkul Lake shores; 15, 15a—sands from shore and floor of Chukurkul Lake; 20b—sand from Tuzkul Lake shore; 3, 3a, 4g, 5a—saline sediments of Sasykkul Lake; 20c—salt from Tuzkul Lake shore.

ties, and provide the means of distinguishing the close element associations within the groups, on the other hand. Thus, among the halophobe elements we can distinguish the following associations: Fe–Sc–Co–Ti, Rb–Cs–La–Eu–Th, Pb–Zn–Cu–Ag–Ta–Zr, Tb–Yb, and among the halophile ones: W–B–Na, Ni–As–Au–Sm–U–Mo, Ba–Ce–Se. Within these

associations, high positive correlations are established between all the elements, and on the contrary—halophobe and halophile elements are characterized by an inverse connection.

The main geochemical peculiarities of the lake sediments from the Sasykkul depression are more pronounced in the multi-element diagrams (Fig. 5).

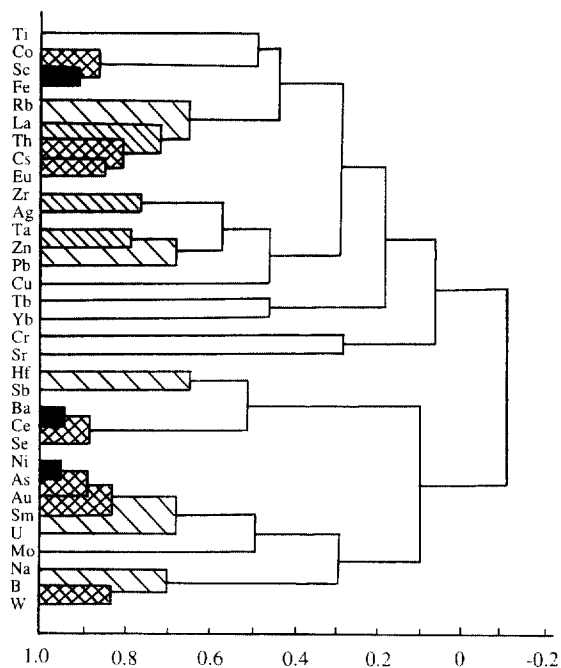


Fig. 4. Hierarchic dendrogram of correlation matrix of chemical element contents in sediments of brine lakes of the Sasykkul depression.

Normalizing values are those for the average upper continental crust (Taylor and McLennan, 1981). Notice that all these normalized patterns display the absence of any linear dependence. This can be explained by the effect of many different factors on the concentration and depletion of trace elements in lacustrine sediments (chemical specialization of the catchment basin rocks, hydrothermal influence, evaporative concentration, adsorption and chemical precipitation processes, etc.).

Clays and silts of the region are enriched in U, Th, Pb, Sr, Zn, Cs (and also Mo, W—see Table 3) and depleted in Rb, Fe, Tb, Yb, Sc, Co as compared with the average upper continental crust and 'average' sedimentary rock. Sample 14 (black clay from a mud volcano, Chukurkul Lake shore), in which sulphides are visible to the naked eye, is especially interesting because of its extremely high contents of chalcophile elements—Se, Ag, Zn, Pb, As, Sb, Au and siderophile elements—Fe, Sc, Co (Fig. 5, Table 3), which suggests the strong effect of deep source. In this sample high concentrations of Cs, Sr, Ba, U,

Th, Mo, but low contents of some lithophile elements—Hf, Ta, LREE are observed.

Distribution of the analysed elements in sands of the Sasykkul depression is similar to pelites, but is distinguished by its somewhat lower contents of many elements. These sediments are also characterized by high concentrations of U, Th, Mo, W, Zn and are depleted in Rb, Fe, Cs, Eu, Yb, Tb, Sc, Ta (Fig. 5, Table 3). The unique exception is sample 4c (crimson-coloured sand from the northeastern shore of Sasykkul Lake), which contains anomalously high concentrations of Fe, Sc, Zn, Th, Mo, Zr, Hf, Ta, U, and REEs, that may be caused by high proportions of fragmentary accessory heavy minerals subjected to hydrolysis.

The trace-element distribution in salts and saline sediments of the depression contrasts with that of the terrigenous sediments. They are the concentrators of U, B, Ba, Mo, W, and sometimes—Se, Au, As, Ce, Sm (Fig. 5, Table 3). The contents of the remaining analysed trace elements are very low and increase only with the presence of terrigenous material in sediment composition.

In recent years, REEs increasingly are being used as chemical indicators of geologic processes, including assessment of crustal sources, the redox state of water, and of chemical sources to sediment, depositional environment. We know that high pH waters show enrichments in heavy REEs and the degree of HREE enrichment in alkaline terrestrial waters appears to increase with increasing alkalinity (Möller and Bau, 1993; Johannesson et al., 1994; Johannesson and Zhou, 1997). Moreover, we have also gained much information concerning the inorganic solution complexation behaviour of the REEs in terrestrial waters (Johannesson et al., 1994; Johannesson and Lyons, 1995). For the high pH, alkaline waters, the speciation modelling (Johannesson et al., 1994) indicates that REE dicarbonate complexes are the only important form of dissolved REE. The HREE are more strongly complexed with carbonate ions in alkaline solution, leading to enrichment of the heavy REEs over LREEs. This implies that certain sediments should be the site of preferential accumulation of LREE.

REEs are most stable in the trivalent oxidation state, although Ce may oxidize to Ce (IV) and Eu may reduce to Eu (II). These changes in the oxida-

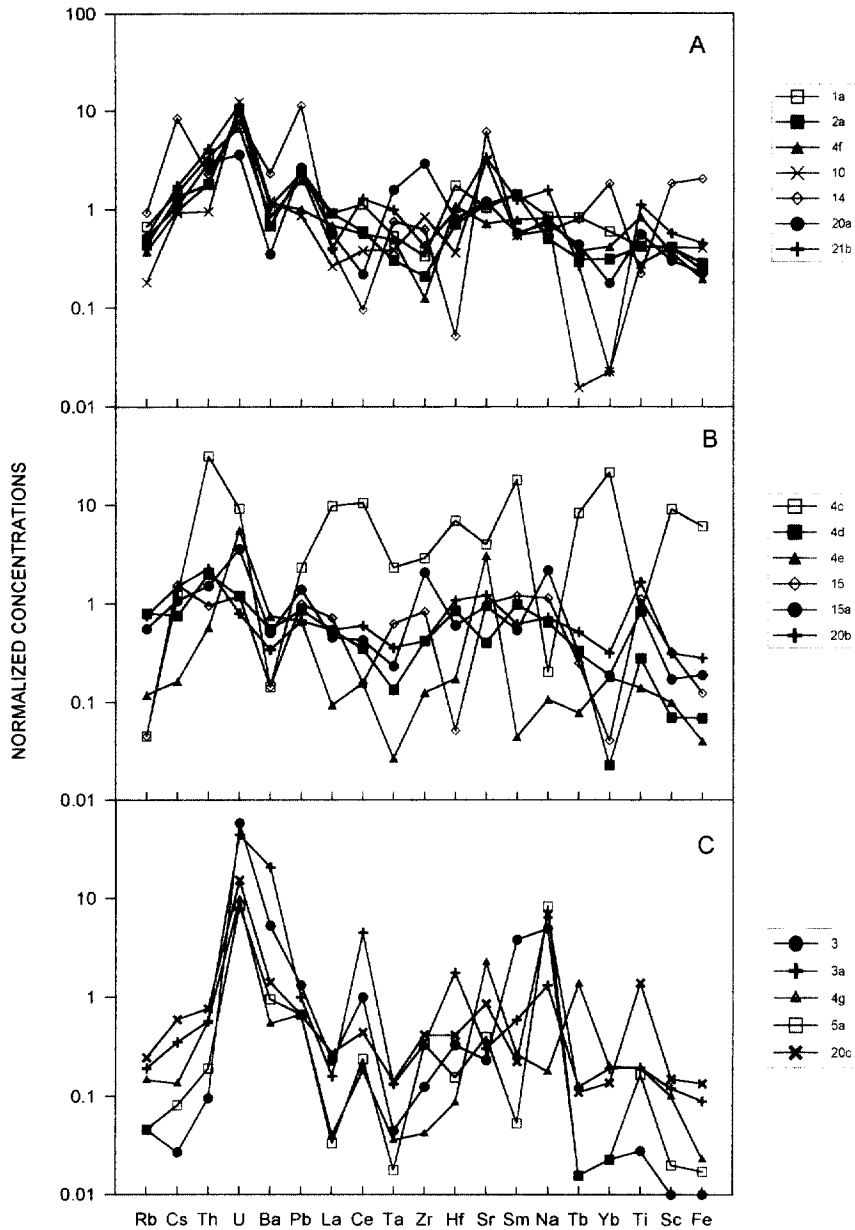


Fig. 5. Ratios of concentration of elements in samples of sediments from the Sasykkul depression to their values in upper continental crust. The sequence of elements is determined by their order of decreasing concentrations in the upper continental crust average of Taylor and McLennan (1981). (A) Clay sediments; (B) sands; (C) saline sediments. The numbers of samples correspond to Table 3.

tion state often result in anomalous behaviour of Ce and Eu with respect to their neighboring trivalent REEs.

Möller and Bau (1993) reported strong positive Ce_{SN} anomalies observed in REE_{SN} patterns of aero-

bic, alkaline, carbonate-rich waters from Lake Van, Turkey. These anomalies apparently result from the stabilization of carbonate complexes of Ce (IV) in solution, leading to enhanced abundances of Ce in comparison with its trivalent REE neighbors. The

authors believe that positive Ce anomalies may be general features of alkaline, carbonate-rich and aerobic lake waters.

The REE are insoluble and are present in low concentrations in terrestrial waters; thus the REEs present in terrigenous sediment are chiefly trans-

ported as particulate matter and reflect mainly the chemistry of their source. The source of the REEs to lake waters is undoubtedly the rocks within their catchment basin. Only chemical (saline) sediments are most likely to reflect the composition of the water from which they were precipitated.

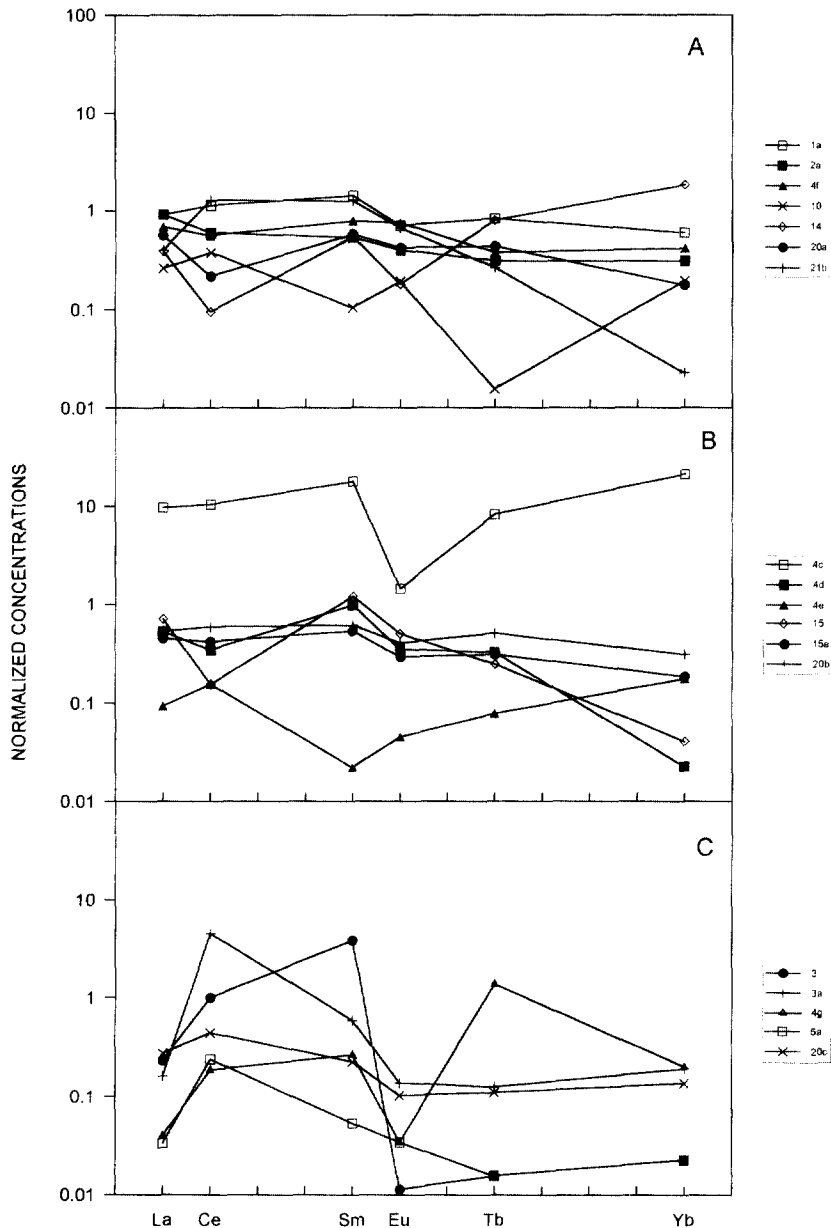


Fig. 6. The upper continental crust—normalized REE patterns for samples of lake sediments from the Sasykkul depression, the Southeast Pamirs. (A) Clay sediments; (B) sands; (C) saline sediments. The numbers of samples correspond to Table 3.

Average upper continental crust material—normalized REE patterns for the lake sediments of the Sasykkul depression are shown in Fig. 6. On the whole, the REE contents in the examined samples are somewhat lower than in common sedimentary rocks. Clay-bearing sediments of the Sasykkul depression lakes have a slightly enhanced concentration of total REEs than other sediments under study. The presence of salts has a diluting effect on REE concentration in them. The normalized REE patterns of clay sediments are usually characterized by enrichment of LREEs over HREEs. Only sample 14, collected from a mud volcano on the shore of Chukurkul lake, displays an essential enrichment of heavy REEs compared to light REEs, that apparently reflects the influence of a deep source. Some samples exhibit the presence of slight negative Eu anomalies in REE patterns.

The normalized REE patterns of sand sediments of the Sasykkul depression lakes are similar to the patterns of clay sediments. They are characterized by a relative enrichment of LREEs as compared to the HREEs and negative Eu anomalies. REE contents in the sand samples are usually somewhat lower than in analysed clay sediments. The only exception to this is sand sample 4c, in which the presence of heavy minerals has led to a significant increase of REE concentrations, being one order of magnitude higher than in the other sediments. In this sample we also determined unusually high contents of Th, Hf, and Sc. It is worth noting that the presence of heavy minerals may have a significant but erratic effect on the REE patterns of individual samples. The more coarse-grained sands contain lower quantities of total REEs (sample 4e in Fig. 6).

The normalized REE patterns of saline sediments from the region under study markedly differ in their appearance from that of the other sediments. They are usually characterized by sharp distinctions in LREE and HREE contents and significantly lower concentrations of total REEs. The REE patterns of saline sediments show strong positive Ce_N and more rarely Sm_N anomalies. It seems likely that enhanced abundances of Ce in comparison with its REE neighbors in alkaline, carbonate-rich lake waters (Möller and Bau, 1993) are responsible for the presence of pronounced Ce anomalies observed in the REE patterns of saline sediments of the Sasykkul depression

lakes. The other feature of alkaline lake waters, namely, the enrichment of shale-normalized contents of HREEs over LREEs (Möller and Bau, 1993; Johannesson and Lyons, 1995; Johannesson and Zhou, 1997), is not usually reflected in the distribution of REEs in saline sediments under study. Only sample 4g displays signatures of such enrichment in its REE pattern (Fig. 6).

5. Discussion and conclusions

Various factors may be responsible for the high concentrations of a number of minor elements in waters and sediments of the Sasykkul depression lakes. It seems likely that the 'excess' of trace elements (Li, U, Mo, W, As B and others) in the lakes examined originates from thermal springs associated with granite intrusions and felsic volcanites, or may be leached from the same rocks. The widespread occurrences of granitoides and acid volcanic rocks, the presence of tungsten and polymetallic deposits in the region, the present-day manifestations of hydrothermal activity within the depression floor, and the block-faulting tectonics are evidence in favour of this assumption. The relatively high ratios of conservative elements to chloride (Br/Cl, Li/Cl, B/Cl) and the increased value of Li/Na-ratio also confirm the participation of deep ground water in the feeding of the saline lakes.

The chemical evolution of the Sasykkul depression lake waters has resulted in the development of residual Na–Cl–CO₃–SO₄ and Na–Cl–CO₃ brines. The trace element contents have been increasing in the lakes with the rise of their TDS content in waters and their alkalinity, and with the precipitation of the major dissolved components during repeated annual cycles of evaporative concentration under arid climate conditions. Specific features of the lake waters (high pH values and the practical absence of calcium in brines) result in stabilization of various complex compounds of trace elements in the solution, leading to their enhanced abundances in comparison with natural fresh and marine waters.

The Sasykkul depression lakes are comparable to some other alkaline saline lakes—Searles Lake, Mono Lake, Soda Lake, USA (White et al., 1963; Drever, 1985), Zabuye Lake, China (Zheng, 1992;

Zheng and Qiwen, 1996) and some Bolivian salars from southern Altiplano (Rettig et al., 1980; Risacher and Fritz, 1991; Risacher, 1992) in the pathways for the evaporative evolution of water in closed basins and water chemical composition. All these lakes share a number of common traits in relation to geological and geomorphic localization, climate and hydrological conditions. Based on the similarity in geochemical associations, the saline lakes of the Sasykkul depression are most akin to Laguna Cachi, Bolivia (Risacher, 1992; Orris et al., 1992), which is characterized by enrichment of brines in sodium carbonate, boron, lithium, molybdenum, fluorine, arsenic, and tungsten.

Evolution of the sedimentation process in the salt-forming basin of the Sasykkul depression has resulted in the pronounced separation of chemical components as a consequence of their fractionating both in an aqueous solution and between water and sediment. Based on the contents of trace elements in sediments of the Sasykkul depression lakes (Table 3, Figs. 5 and 6) and the correlation analysis data (Fig. 4), we can subdivide all the analysed elements as follows.

(a) Ti, Fe, Sc, Cr, Co, Ni—siderophile elements depleted within the lacustrine sediments under study compared to 'average' sedimentary rock.

(b) REEs, Zr, Hf, Ta, Th, Fe, Sc—a set of elements, increased concentrations of which in terrigenous sediments are controlled mainly by the presence of heavy minerals (see sample 4c in Figs. 5 and 6).

(c) Rb, Cs, Sr, Ba, U, Th, Mo, W—trace elements, which may be adsorbed or co-precipitated with clay particles. Notice that although uranium should be extremely mobile in the alkaline aqueous system, it may be adsorbed to clays in surficial sediments.

(d) Cs, Sr, Ba, Pb, Zn, Sb, Ag, Se, Fe, Sc, Co—trace elements, which may be considered as tracers of the hydrothermal influence in such a closed-basin system (see sample 14 in Figs. 5 and 6);

(e) B, Ba, U, Mo, W, As, Ce, Se—trace elements, which may be considered as tracers of the evapo-concentration process of natural solutions produced by weathering of alkaline volcanic rocks. High positive correlations between U, Mo, As, and Se concentrations in saline sediments are noteworthy, because

the geochemical association As–Se–Mo(+V) is a suite of elements in groundwaters, which is usually used as an exploration tool for uranium deposits.

Undoubtedly, the chemical weathering of rocks within the catchment basin and thermal springs represent the source of trace elements to the Sasykkul depression lakes. Thus, the general enrichment of the lake sediments in Mo, W can be attributed to polymetallic veins or tungsten–molybdenum deposits in the region. Sediment samples that contain elevated levels of barium are numerous and extensive in the study area. The source may be vein barite, which occurs as an accessory mineral in polymetallic veins. The silver anomalies also can be attributed to polymetallic veins or molybdenum deposits. High concentrations of U and Th are considered to indicate the presence of mineralization enriched in these elements in the drainage basin of the Sasykkul depression lakes. But the processes of evaporative concentration of alkaline lake waters in such a continental closed basin, surface and solution complexation, chemical precipitation, and water interaction with sediments play an important role in the fractionating of trace elements in the water-sediment system as well as in their redistribution between terrigenous and saline sediments.

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