

Major ions behaviour during evaporation of different saline type water of Western Mongolian lakes (geochemical modelling)

Marina N. Kolpakova and Olga L. Gaskova

ABSTRACT

The main Mongolian water resources are lakes whose volume has significantly reduced in recent years as a consequence of global warming. This article presents research on three different types of nearly disposed Western Mongolian lakes with a wide range of brines' composition: Shaazgai-Nuur (soda), Davsan-Nuur (chloride) and Tonhil-Nuur (sulfate). The aim of this study was to determine the differences in geochemical evolution associated with evaporation-crystallization processes of representative lakes of various chemical types. The modelling was performed by using PHREEQC and HCh software that allows application of Pitzer's approach for saline solutions. The modelling was performed for these natural objects for the first time. The model demonstrated that the evaporation-crystallization processes are different for soda and chloride/sulfate brines. Soda type lake maintained unchanged ion composition while chemical composition of chloride and sulfate lakes went through significant alterations according to a sequence of mineral precipitation. The calculated model did not confirm the possibility of long-term transformation from SO_4 -Mg brines to Cl-Mg due to evaporative concentration only; additional factors including mixing with inflow water also influence sodium and chloride increase. Close agreement between the model and the actual mineralogical data was observed, testifying to the proper software and reliability of our assumptions.

Key words | evaporation, geochemical modeling, HCh, Mongolia, PHREEQC, saline lakes

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INTRODUCTION

In recent years, there has been an increasing focus on the geochemical characteristics of various small lake systems (Krumgalz *et al.* 2000; Jones & Deocampo 2003; Leonova *et al.* 2007; Jones *et al.* 2009; Sklyarova *et al.* 2012; etc.). Some scientists have even suggested allocating salinology (Zheng 2001) as a separate science, in order to study the chemical, physical and biological processes observed in salt lakes and also their hydromineral resources with possible ways for their further application.

More than 84% of all water resources of Mongolia are enclosed in lakes (Williams 1991). Unfortunately, the water resources of lakes have been significantly reduced in recent years as a result of global warming. As shown in Jeppesen *et al.* (2015), these changes may have a significant effect on

the nutrient dynamics, nutrient concentrations, water quality and trophic state of lakes and reservoirs. Current study has led to a better understanding of the evaporation-crystallization process as one of the main mechanisms of geochemical evolution of various lakes (Yihdego *et al.* 2016). Monitoring of chemical composition and thermodynamic modelling of geochemical evolution of lakes help to indicate sources of dissolved major ions and identify the mechanisms controlling the water chemistry (Lytras 2007).

A significant number of publications (Gaskova *et al.* 2011; Mees *et al.* 2011; Sklyarova *et al.* 2012; Gaskova & Sklyarova 2013; Herrero *et al.* 2015; Yang *et al.* 2015; Surinaidu 2016) have been devoted to the question of chemical evolution of natural water and factors defining its

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geochemical specifics. However, after the fundamental works of Garrels & Mackenzie (1967), Hardie & Eugster (1970) and Eugster & Baumgartner (1987), limited information on evaporation dynamics and thermodynamic model variations in different salt lakes can be found. For example, Gamazo *et al.* (2011) suggested that mineral paragenesis might have a considerable influence on shallow brine lake evolution by fixing chemical composition for a significant proportion of time. Shvartsev *et al.* (2014) showed that the major factors controlling the formation of each lake type include evaporation and water–rock interaction processes, and the latter factor plays a critical role in freshwater and soda lakes and only a minor role in chloride lakes. At the same time, most work has been oriented on simulation of the association of climatic conditions with basin-level precipitation/stream flow (Wang *et al.* 2015). The modelling of hydrogeochemical processes with involvement of saline water and brines is a challenge due to insufficiency of a suitable thermodynamic database for an adequate simulation, namely, for a precise calculation of ions activity coefficient in real non-ideal systems (Blanc *et al.* 2012). Pitzer's approach (Garrels & Christ 1965) has been developed for PHREEQC (Bozau 2013) and also included into FREZCHEM (Marion *et al.* 2010) and HydroGeo (Bukaty 1997). The parameters of the Pitzer equations are linear combinations of parameters of a virial expansion of the excess Gibbs free energy, which characterize interactions among ions and solvent (Pitzer 1987). This geochemical software has been mentioned only as an example of a great number of other similar applications (Nordstrom & Campbell 2014).

Western Mongolian saline lakes are unique natural objects containing a variety of chemical elements in water and bottom sediments, quite often of industrial values. Lakes, which radically differ not only in total dissolved salinity (TDS) but also in the chemical type, are located here in a relatively short distance from each other. Three main type of lakes were investigated (Shvartsev *et al.* 2014): chloride (49%), soda (35%) and sulfate (16%) lakes. TDS of lakes varies from 13 to 300 g/L. High salinity is typical for sulfate and chloride lakes, and high pH values (over 9.0) are common for soda lakes. It should be noted that a considerable amount of such trace elements as U, Si, As and Mo are accumulated in soda lakes; Sr and Li are usual for chloride

lakes. The lowest concentrations of valuable or toxic trace elements are typical for sulfate lakes.

The aim of the current work is to study the geochemical processes associated with evaporation of representative lakes of each chemical type (soda – Shaazgay-Nuur, chloride – Davsan-Nuur, sulfate – Tonhil-Nuur) in order to interpret more precisely the chemical differences in final composition of salt and brines of the continental lakes. All of them are shallow and endorheic and we suppose that evaporative concentration is the dominant mechanism affecting mineral formation and solute evolution in these basin systems.

STUDY AREA

The area of Western Mongolia is a part of the middle Central Asian fold belt. It is composed of uneven folded structures which include the ancient continental massifs and substructure blocks. Paleozoic sediments are represented by all systems except the Permian. However, Meso-Cenozoic continental deposits are most widespread and are covered by intermittent Quaternary sediments (Marinov 1967).

The specific climatic conditions of Western Mongolia are defined by the geographical location of the region in the northern part of Central Asia, the complicated orographic structure of the territory and the high average altitude which reaches 1,580 m.a.s.l. The most northern desert on Earth is located there and it is expanding to the north (Dagvadorj *et al.* 2010), thereby leading not only to salinization of the territory, but also to the disappearance of many water reservoirs (Figure 1). More than 46% of the whole territory of Mongolia has negative average annual air temperature that has a strong impact on the thermal regime of lakes. The isotherm 0 °C of average annual air temperature coincides with latitude 46 ° dividing the mountainous areas of Mongolia from the desert.

The annual rainfall in this area increases from 150 mm (at 560–1,000 m.a.s.l.) up to 400–450 mm (at more than 2,000 m.a.s.l.). The distributions of lakes by altitude and by the degree of salinity (TDS) are closely connected with the amount of rainfall. The small atmospheric precipitation is followed by a high level of evaporation. The potential annual evaporation (PE) varies from 400–600 mm in the mountain regions, 550–750 mm in the steppe zone and 1,300–1,500 mm in the

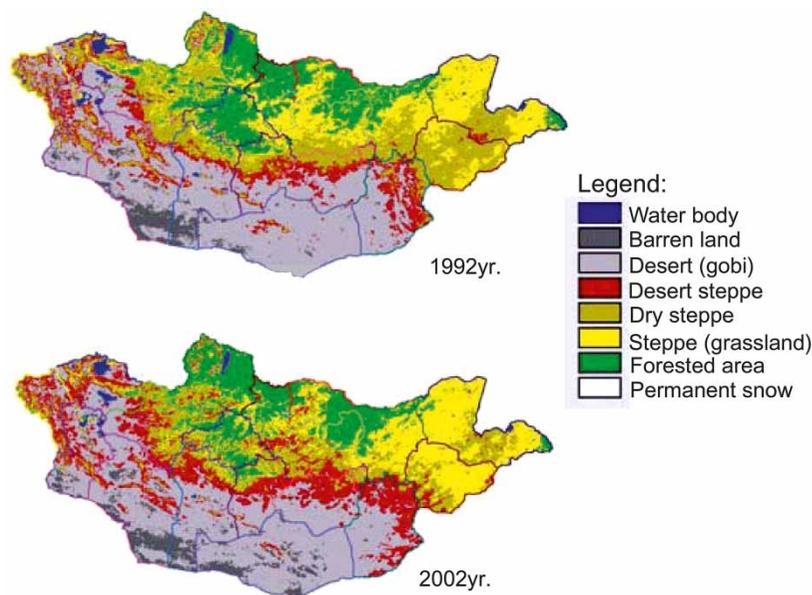


Figure 1 | Comparative land surface map of Mongolia in 1992 and 2002 (Dagvadorj *et al.* 2010).

desert-steppe and desert landscapes (Sevastyanov *et al.* 1994). Known atmospheric conditions from two weather stations (Omno-Gobi and Tonhil) nearest to the studied lakes are shown in Table 1. Despite the considerable evaporation rate, there is no possibility for the process of soil salinization due to the coincidence of rainy and warm seasons causing the leaching of calcium carbonates and soluble salts from the top layers (Dagvadorj *et al.* 2010).

Lakes are mostly endorheic and contain a considerable amount of dissolved salts. Water balance and level modes, hydrochemical and hydrobiological characteristics of lakes in Mongolia are substantially caused by regional climatic conditions. Seasonal fluctuations of the waterline in lakes are characterized by high amplitude, often exceeding 2 m, which depends on evaporation degree, on the amount of atmospheric precipitation falling on the lake surface and on the volume of water inflow (Sevastyanov *et al.* 1994).

SAMPLING AND THERMODYNAMIC MODELLING METHODS

Water samples were collected from the central part of the lakes using a polyethylene bailer in the summer period (July–August, 2009–2012) during the hydrochemical Russian–Mongolian expedition. The Shaazgay-Nuur and Davsan-Nuur lakes were studied each year and their composition varied depending on the climatic conditions of the year; Tonhil-Nuur lake was studied only in 2010 because of its difficult and remote location. Detailed chemical composition of the lakes had been published earlier (Isupov *et al.* 2013; Shvartsev *et al.* 2014). Unstable parameters were measured at each sampling location. Specific conductivity, pH, oxidation-reduction potential and temperature were measured by using platinum electrode. Field alkalinity titration using 0.1 N HCl was conducted in the field conditions.

Table 1 | Climatic data of Western Mongolia^a

Station ID	Coordinates	Period	Altitude, m.a.s.l.	Mean annual temperature, °C	Total precipitation, mm/yr	Mean vapor pressure, kPa
Omno-Gobi	N49.01 E91.43	2002–2015	1,590	−1.8... +1.5	88...238	2.6...5.2
Tonhil	N46.19 E93.53	2009–2015	2,222	−3.2... +0.8	58...177	3.3...5.1

^a<http://ftp-cdc.dwd.de>.

Major elements chemical analysis of water samples was carried out in the scientific research laboratory Hydrogeochemistry of the Scientific-Educational Center 'Water' IPR TPU (Tomsk) (POCC RU.0001.511901) by potentiometric, titrimetric, atomic absorption and photometric methods. Trace element composition was analyzed at the Institute of Solid State Chemistry and Mechanochemistry (ISSCM SB RAS, Novosibirsk) by mass spectral analysis using mass spectrometer with inductively coupled plasma Agilent 7500a. The deionized water from Direct-Q3UV Millipore equipment with resistivity 18.2 MΩcm at 25 °C was used for analyses. The reference solution and the solution to adjust the mass spectrometer was a 2% solution of HNO₃, containing 10 ppb Li, Co, Ce, Y, Tl (Tuning Solution; Agilent). The contents of Sr were determined by the spectrometer Saturn-2 M and Varian AA 280 FS mode emission and absorption, depending on the element being determined.

As the average water temperature of the lakes in the summer period varies from 20 to 30 °C, the modelling was performed at 25 °C and 1 atm total pressure using PHREEQC 3.1.4 (Parkhurst & Appelo 2013). The program algorithm is based on the equations of the mass action law and knowledge of the solubility and dissociation constants. The possibility of using the method of Pitzer (1987) designed for highly mineralized waters and brines (a virial expansion of the excess Gibbs free energy) is the reason for the software choice. PHREEQC includes the Pitzer database of the virial coefficients, but it contains only a small number of solution components. In this regard, the authors used the extended database developed by Bozau (2013).

The calculations were processed in the heterophase 13-component system: H₂O-Na-K-Ca-Mg-Cl-SO₄-CO₃-Si-Al-Ba-Sr. Modelling of the evaporation process of 1 kg of water was carried out in equilibrium mode where minerals are allowed to redissolve into the solution ('closed system') by stepwise removal of 1.0 M of water from the solution during 55 steps up to its complete exhaustion. Saturation tests were performed with respect to minerals shown in Table 2.

Identification of chemical element species in solution and determination of saturation indexes (SI) were additionally calculated with 'HCh' computer code (Shvarov 2008) and database UNITHERM using a free energy minimization algorithm. In order to assess the extent of the water-rock

interaction from the state of thermodynamic equilibrium, saturation index was calculated:

$$\log SI = \lg \frac{[IAP]}{Ksp}, \quad (1)$$

where *IAP* is ion activity product; *Ksp* – solubility product constant.

If the determined lgSI is below -0.2, the solution is undersaturated with respect to the corresponding mineral. On the contrary, if *log SI* exceeds +0.2, the water is assumed to be supersaturated to this mineral and ±0.2 means equilibrium (Merkel & Planer-Friedrich 2005). These indexes are most applicable for quickly precipitated minerals such as NaCl or CaSO₄·2H₂O. Activity coefficients were calculated with the third approximation of the Debye-Hückel equation, which is valid for *I* < 0.5 mol/L. At more high ionic strength of a solution in equilibrium with NaCl or Na₂SO_{4(s)}, activity coefficients were calculated with the Helgeson equation (Helgeson *et al.* 1981):

$$\lg \gamma_i = -\frac{A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a_i \sqrt{I}} - \lg(1 + 0.018m^*) + [\omega_i b_{NaCl} + b_{Na^+Cl^-} - 0.19(|z_i| - 1)] \cdot I \quad (2)$$

where γ_i is the activity coefficients, m^* is the sum of molar concentrations $\sum m_i$, ω_i – absolute Born parameter and b_{NaCl} – solvation parameter. The first member of Equation (2) includes Debye-Hückel parameters *A*, *B*, *a* and the charge of species *z* and the ionic strength *I*.

Therefore, evaporation simulation was performed using two different programs based on the various principles of equilibrium assessment. Each of them has its own advantages. The special algorithm of PHREEQC allows the adequate discovery of not only progressive evaporation of solutions but also the water density, ion activity, salinity and resistivity. However, it is required first to establish mineral assemblages which are suggested to be the most expected to precipitate in specific conditions. In that case, it is important to predict the real equilibrium/disequilibrium situation (not only a saturation or undersaturation) with respect to the entire set of minerals, recorded in a database. This can be done previously using the algorithm of 'HCh' code.

The studied lakes have an insufficient interaction with the surrounding groundwater system in comparison with

Table 2 | Equilibrium phases formed during the simulation of evaporation processes

Name	Formula	Log K
Anhydrite	$\text{CaSO}_4 = \text{Ca}^{2+} + \text{SO}_4^{2-}$	-4.362
Aragonite	$\text{CaCO}_3 = \text{CO}_3^{2-} + \text{Ca}^{2+}$	-8.336
Barite	$\text{BaSO}_4 = \text{Ba}^{2+} + \text{SO}_4^{2-}$	-9.97
Bischofite	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} = \text{Mg}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O}$	4.455
Calcite	$\text{CaCO}_3 = \text{CO}_3^{2-} + \text{Ca}^{2+}$	-8.406
Carnallite	$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O} = \text{K}^+ + \text{Mg}^{2+} + 3\text{Cl}^- + 6\text{H}_2\text{O}$	4.330
Celestite	$\text{SrSO}_4 = \text{Sr}^{2+} + \text{SO}_4^{2-}$	-6.630
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = \text{Mg}^{2+} + \text{SO}_4^{2-} + 7\text{H}_2\text{O}$	-1.881
Glaserite	$\text{NaK}_5(\text{SO}_4)_2 = \text{Na}^+ + 3\text{K}^+ + 2\text{SO}_4^{2-}$	-3.803
Glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2 = \text{Ca}^{2+} + 2\text{Na}^+ + 2\text{SO}_4^{2-}$	-5.245
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.581
Halite	$\text{NaCl} = \text{Cl}^- + \text{Na}^+$	1.570
Hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O} = \text{Mg}^{2+} + \text{SO}_4^{2-} + 6\text{H}_2\text{O}$	-1.635
Illite	$\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{1.8}\text{Al}_{0.5}\text{Si}_{5.5}\text{O}_{10}(\text{OH})_2 + 8\text{H}^+ = 0.25\text{Mg}^{2+} + 0.6\text{K}^+ + 2.3\text{Al}^{3+} + 3.5\text{SiO}_2 + 5\text{H}_2\text{O}$	9.026
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O} = \text{Mg}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$	-0.123
Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = \text{SO}_4^{2-} + 2\text{Na}^+ + 10\text{H}_2\text{O}$	-1.214
Montmor-Mg	$\text{Mg}_{0.495}\text{Al}_{1.67}\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ = 0.495\text{Mg}^{2+} + 1.67\text{Al}^{3+} + 4\text{H}_2\text{O} + 4\text{SiO}_2$	2.39
Montmor-Ca	$\text{Ca}_{0.165}\text{Mg}_{0.33}\text{Al}_{1.67}\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ = 0.165\text{Ca}^{2+} + 0.33\text{Mg}^{2+} + 1.67\text{Al}^{3+} + 4\text{H}_2\text{O} + 4\text{SiO}_2$	2.49
Montmor-Na	$\text{Na}_{0.33}\text{Mg}_{0.33}\text{Al}_{1.67}\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ = 0.33\text{Mg}^{2+} + 0.33\text{Na}^+ + 1.67\text{Al}^{3+} + 4\text{H}_2\text{O} + 4\text{SiO}_2$	2.48
Nahcolite	$\text{NaHCO}_3 = \text{CO}_3^{2-} + \text{H}^+ + \text{Na}^+$	-10.742
Natron	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} = \text{CO}_3^{2-} + 2\text{Na}^+ + 10\text{H}_2\text{O}$	-0.825
Polyhalite	$\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O} = 2\text{K}^+ + \text{Mg}^{2+} + 2\text{Ca}^{2+} + 4\text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-13.744
Strontianite	$\text{SrCO}_3 + \text{H}^+ = \text{HCO}_3^- + \text{Sr}^{2+}$	-0.31
Sylvite	$\text{KCl} = \text{K}^+ + \text{Cl}^-$	0.900
Thenardite	$\text{Na}_2\text{SO}_4 = 2\text{Na}^+ + \text{SO}_4^{2-}$	-0.35
Trona	$\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O} = 3\text{Na}^+ + \text{H}^+ + 2\text{CO}_3^{2-} + 2\text{H}_2\text{O}$	-11.384

other continental lakes due to their insignificant depth (1–2 m). The low salinity of Shaazgay-Nuur lake reflects the substantial water import from the Hargayn-Gol River, but high salinity of the Davsan-Nuur and Tonhil-Nuur lakes is due to the intense evaporation provided by the large surface area/volume ratio and absence of surface inflow. The initial condition of the current model is the chemical composition of lakes at the fixed sampling time (summer period). The surface and sub-surface inflow was not included into the model due to the lack of a water balance knowledge for surface water in this region. Isotopic data of ^{18}O and D of lakes for this region have shown a similar trend with evaporation line. Due to this, we consider

evaporation and direct salt precipitation as the major factors of brine evolution of Mongolian lakes. We have found a lot of evidence for this point of view – from Jones (1966) to Yihdego *et al.* (2016). The boundary conditions are determined by water balance, i.e., water/rock ratio defined only by the pattern of the evaporation process simulation. The limiting condition was the existence of a quasi-equilibrium state between both saline aqueous solution and bottom sediment which was characterized by an infinitely slow transition from one state to the other. The initial composition of water is determined by chemical analysis; all possible intermediate thermodynamic states are discussed further. The evaporation process is bounded by ‘dry lake’ state.

RESULTS

Geochemical characteristics of lakes

The representative examples of three chemical types of lakes: Shaazgay-Nuur (soda), Davsan-Nuur (chloride), Tonhil-Nuur (sulfate) (Figure 2) were chosen to elucidate the influence of evaporation process on elements' concentration sequence and on the formation and transformation of minerals. Table 3 shows a variety of morphometric characteristics of the lakes. All of them are small in size (volume of water mass is less than 0.01 km^3) and thus

are more exposed to the evaporative concentration of salts.

The above-mentioned lakes significantly differ in the content of major ions except for high concentrations of Na^+ and Cl^- (Figure 3) (more than 50 eq.%). It should be noted, that, in comparison with the other two lakes, Shaazgay-Nuur Lake contains the smallest concentration of Ca^{2+} and Mg^{2+} (up to 1 eq.%) along with the highest content of CO_3^{2-} and HCO_3^- (about 30 eq.%).

The attractiveness of Shaazgay-Nuur Lake as an object of study resulted in high concentrations of U (up to 1.0 mg/L), As (up to 0.2 mg/L) and Li (up to 1.0 mg/L) in water and bottom

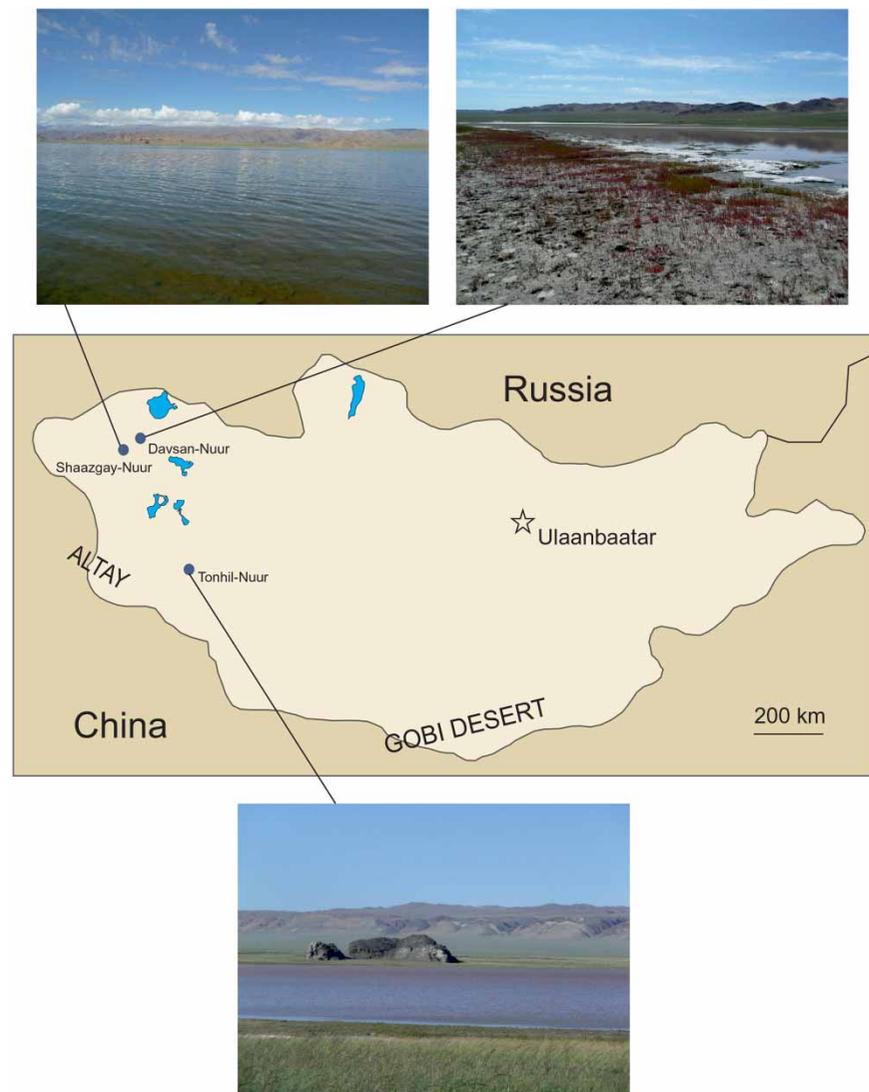
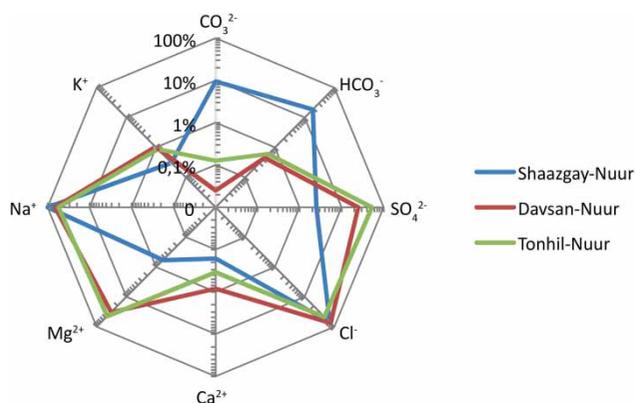


Figure 2 | Map and photos of investigated lakes.

Table 3 | The morphometric characteristics of the lakes (Tserensodnom 2000)

Lake ID		Shaazgay-Nuur	Davsan-Nuur	Tonhil-Nuur
Location	N	49° 14'	49° 13'	46° 11'
	E	91° 17'	92° 03'	93° 53'
Altitude	(m.a.s.l)	1,698	1,522	2,064
Lake surface area	(km ²)	8.3	0.7	6.2
Length	(km)	4.9	1.8	4.6
Width	Av. (km)	1.6	0.4	1.4
	Max. (km)	2.4	0.8	2.6
Depth	Av. (m)	1.2	0.3	1.0
	Max. (m)	6.0	1.1	1.6
Volume of water	(km ³)	0.01	0.0002	0.006
Length of the coastline	(km)	13.8	4.2	12.3
Catchment area	(km ²)	437	n.d.	230

**Figure 3** | Major elements' composition of lakes (%).

sediments (Isupov *et al.* 2013; Gaskova *et al.* 2015). The lake is located at an altitude of 1,700 m.a.s.l. and has a significant surface area (approximately 8 km²) and volume of water (about 0.01 km³) (Table 3) (Tserensodnom 2000). TDS of water ranges from 14 to 22 g/L (Shvartsev *et al.* 2014). The average pH is 9.4, reaching 10.4 in the year 2010 (Table 4). The lake was attributed to the soda type based on its high alkalinity ($\text{HCO}_3^- + 2\text{CO}_3^{2-} > 35 \text{ eq.}\%$) and pH values (>9.0) in spite of the fact it has a high Cl^- concentration ($\text{Cl}^- > \text{HCO}_3^-$ -Na type based on equivalence percentage of major ions). The Hargayn-Gol River is the main source of water for the lake. TDS of the river water is about 0.2 g/L and it is $\text{HCO}_3^- > \text{Cl}^-$ -Na type.

The Davsan-Nuur Lake is $\text{Cl}^- > \text{SO}_4^{2-}$ -Na > Mg type and is used as a salt source by the local community. It is located at an

Table 4 | The initial chemical composition of lake water used for calculations of the evaporation process and molal ratios of indicative parameters

Parameter	Units	Type and name of lake		
		Soda Shaazgai-Nuur	Chloride Davsan-Nuur	Sulfate Tonhil-Nuur
pH in./pH end		9.40/8.99	7.30/7.08	7.60/6.05
Eh	mV	357	340	340
TDS	g/L	13.5	195	278
CO_3^{2-}	mg/L	612	25	174
HCO_3^-	mg/L	2471	927	1,696
SO_4^{2-}	mg/L	260	40,249	116,616
Cl^-	mg/L	5,325	88,478	75,550
Ca^{2+}	mg/L	7	560	318
Mg^{2+}	mg/L	15	12,956	24,140
Na^+	mg/L	4,760	50,684	57,977
K^+	mg/L	25	1370	1,562
Si^{4+}	mg/L	6.30	0.64	6.51
Al^{3+}	mg/L	0.012	0.015	0.21
Ba^{2+}	mg/L	0.017	n/a	n/a
Sr^{2+}	mg/L	0.29	7.71	6.18
SO_4/HCO_3 in./end ^a	-	0.09/1.47	29.7/72.2	44.58/17.73
SO_4/Cl in./end	-	0.02/5.69	0.11/0.10	0.37/0.08
Na/Ca in./end	-	1220/515852	158/65.5	318/546

n/a, not available.

^aInitial and end values; TDS calculated as a sum of major ions.

altitude of 1,500 m.a.s.l., the area of the lake surface is 0.7 km² and the volume is about 0.0001 km³ (Table 3). The peculiarity of the lake is a significant fluctuation of water TDS along its perimeter, which is about 195–279 g/L in the north-western part of the lake but sharply increases up to 418 g/L in the southeast part (Table 4). The mean value of TDS can reach 360 g/L in the eastern part of the lake, which is considerably higher than the average TDS for the whole lake (310 g/L Table 4). The lake contains a larger amount of K^+ and Ca^{2+} (up to 4 g/L) in comparison with data of other chloride type lakes in this region (Shvartsev *et al.* 2014). The concentration of some trace elements in the lake water reaches an economic value: Li (average is 82 mg/L), Sr 6 mg/L, As 0.5 mg/L, B 100 mg/L. The irregular rising and falling in TDS distribution in the lake can be explained by two main factors: the structure or relief of the lake bottom and the arrangement of the inflow

groundwater. The analysis of the satellite images and the morphological analysis of the territory showed that the northern part of the lake is much deeper than the rest. As well, during the sampling of nearby wells, it was noticed that the level of groundwater in the northern part of the lake was also higher (0.8–1 m from the surface) than in the southern part where groundwater was located at a distance of about 3–4 m from the surface. Despite the essential differences in the salinity of the lake water, lake pH values remained steady (7.2 ± 0.1).

Tonhil-Nuur Lake is the most southern of the considered lakes. It is located to the south of Sutay-Hayrkhan Mountain and has the maximum values of TDS among sulfate type lakes in the studied area. TDS reached around 115 g/L (Rasskazov *et al.* 1991) in 1965 and by 2012 it had risen to 278 g/L. Such a large increase in salinity of the lake is due to its shrinking; the lake size was 7×4 km in 1965 (Rasskazov *et al.* 1991), but our data showed its decrease to 4.6×2.6 km (Table 3). The shore

of the lake is sandy; the floor is covered by different black clay minerals. Long-term observation has allowed the changes of chemical composition of water during evaporative concentration to be recorded: the chemical type of the lake was defined as $\text{SO}_4\text{-Mg}$ in the 20th century (Rasskazov *et al.* 1991); nowadays, it is $\text{SO}_4\text{-Cl-Na-Mg}$ type. The lake is characterized by a smaller concentration of trace elements in comparison with the lakes above ($\mu\text{g/L}$: Li 21, As 320, Mo 60, U 20).

Results of evaporation modelling

Sequential changes in the chemical composition of the lakes during the simulation of evaporation process are presented in Figure 4. The set of secondary minerals significantly varies depending on the chemical type of lake. However, all the initial solutions of the considered lakes are characterized by supersaturation with respect to calcite, strontianite and two clay minerals: illite ($\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$) or

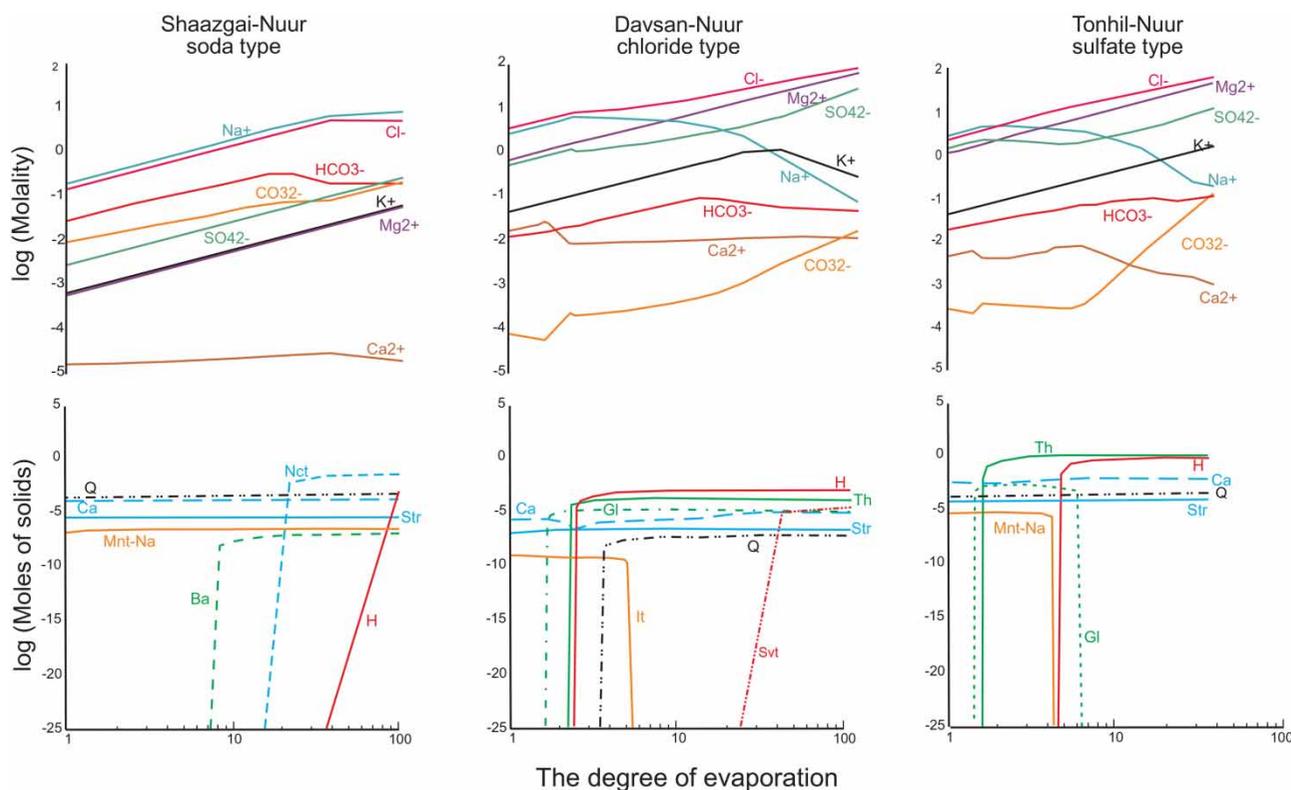


Figure 4 | Concentration of ions during evaporation of 1 kg of Shaazgai-Nuur (soda), Davsan-Nuur (chloride) and Tonhil-Nuur lake water and precipitated salts at 25 °C. The upper part represents the chemical composition change (molality) as an evaporation degree function. The lower part shows the amount of precipitated minerals (moles of solids): Ca – calcite, Q – quartz, Mnt-Na – Na-montmorillonite, Str – strontianite, Nct – nahcolite, Ba – barite, H – halite, Gl – glauberite, It – illite, K – kaolinite, Svt – sylvite, Th – thenardite.

Na-montmorillonite ($\text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$). All of these minerals remained a part of the mineral assemblages during the progressive evaporation until the complete removal of water from the solution. One more common feature for all types of lakes, discovered during the modelling, is an inevitable appearance of halite: first in chloride (33 step), next in sulfate (44 step), and only then in soda lake type (54 step), where originally there was only about 5 g/L of sodium and chloride-ion.

The results of modelling show the soda lake is characterized by a narrow range of secondary minerals – barite, nakholite and, at later stages of evaporation, halite. Moreover, it is the only lake where clay minerals, such as Na-montmorillonite, are presented at the latest stage of evaporation. The diverse mineral assemblage for the chloride lake is represented by mainly glauberite (Na_2CaSO_4) precipitated at the initial stage (TDS is 195 g/L), thenardite (Na_2SO_4), halite (NaCl), and very soluble sylvite (KCl), which precipitates only after the 25th step. The sequence of mineral deposition in sulfate lake (TDS is 278 g/L) is similar to the chloride one: glauberite (Na_2CaSO_4) appears and disappears throughout 10 steps, thenardite (Na_2SO_4) and halite NaCl appear and persist until the whole water evaporation. Note that glauberite, as a less soluble salt in comparison with thenardite, marks only the first steps of water removal in the more saline Tonhil-Nuur Lake while sodium sulfate continues precipitating until the last stage. Moreover, sodium sulfate, such as mirabilite, can be formed even at temperatures less than 25 °C that can lead to an increase of the amount of sulfate minerals above halite since solubility of the latter slightly depends on the temperature (Jones *et al.* 2009). Thus, it resulted in the fact that secondary sulfate minerals (glauberite, thenardite and mirabilite) could appear in both chloride and sulfate types of lake (the difference only in the amount); although, in Tonhil-Nuur Lake, the concentration of sulfate-ion was greater than in Davsan-Nuur Lake by three times (116 g/L in contrast with 40 g/L).

Considering the change of lake water composition in detail and in conjunction with the variety of mineral assemblages, there is one common feature for all three lakes – Mg-containing evaporitic minerals do not appear during PHREEQC-calculation and, as a result, magnesium content increases steadily in solutions.

The accumulation of main ions in the solutions is accompanied by increasing proportions of magnesium and

sodium ions in molar ratio (Ca/Mg/Na is 0.17/0.62/207, 14/533/2204 and 7.9/993/2520 accordingly to mineralization that is 13.5, 195 and 278 g/L correspondingly). However, there is significant difference between soda and sulfate/chloride types in Ca/Na ratios.

As can be seen from Figure 4, Shaazgay-Nuur soda lake does not change its type during the evaporation process; however, Ca concentration in the solution remains stable (because of carbonate precipitation) while Na concentration increases constantly (until saturation with nahcolite). As a result, Ca/Na ratio changes from 1,220 to more than 500,000. The lake is specified by a gradual increase of concentrations of all components (Figure 4(a)), only the content of carbonate-ion is stabilized after $\text{NaHCO}_{3(s)}$ precipitation, as well as the content of Na^+ and Cl^- after reaching saturation state with respect to halite. After removal of 7% water from solution there is a saturation of lake water with respect to barite; however, it does not reflect on the SO_4^{2-} concentration because the content of barium is insignificant (0.017 mg/L). Thereby, high molal ratio of Na/Ca (1,220) and low SO_4/HCO_3 ratio (0.09) of lake water can lead to precipitation of carbonate-clay sediments with quartz, in which both nakholite and halite correspond with the latest stage of evaporative concentration.

The chemical composition of Davsan-Nuur chloride lake more clearly responds to mineral deposition (Figure 4(b)). First, water saturation with glauberite $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ leads to a reduction of calcium concentration in the solution, which evokes its stable equilibrium with calcium. The precipitation of sodium minerals – glauberite, thenardite and halite – induces gradual depletion of Na^+ resources (Ca/Na ratio changes from 158 at the beginning to 65.5 at the last stage). Against this, the concentration of Cl^- continues to increase even after sylvite formation due to the lack of K^+ concentration (1.37 g/L) in solution. This corresponds to the ‘chemical divide’ concept of Hardie & Eugster (1970), which was clearly manifested in the studied lakes mostly for sodium and chlorine. The sharp drop in sodium content leads to the substitution of lake water chemical type from Cl-Na to Cl-Mg. Thus, if the initial Cl-Na solution is characterized by high salinity (about 200 g/L), high sodium concentration and low SO_4/Cl (0.17) ratio, then bottom sediments of such lake will be specified by typical Na-evaporitic minerals as halite (mainly) and thenardite, small amounts of glauberite and calcite, and insignificant content of

quartz. According to our result, it is the only lake where minerals containing potassium can precipitate (illite at the early stages and sylvite at the latest stage of evaporation). The first one crystallizes instead of montmorillonite because of a shortage of silicon (in this lake it is much less than in the other two), and the second mineral forms due to high concentrations of chlorine and potassium in the solution. Our previous research (Kolpakova *et al.* 2014) has shown that the upper part (0–5 cm) of the Davsan-Nuur Lake sediments is composed of quartz, calcite, muscovite, halite and thenardite, which agrees with the modelling results.

For the sulfate lake Tonhil-Nuur (Figure 4(c)) a similar change of mineral association with the chloride lake can be observed and, therefore, the composition of solutions: they both are neutral and highly mineralized, but SO_4/Cl ratio is much higher (0.37) in the sulfate lake than in the chloride one (0.11). There is a similarity in opposite changes of Na^+ and Cl^- concentrations and in the HCO_3^- and CO_3^{2-} increase due to the calcite (carbonates) amount reduction and clay minerals dissolution. One interesting feature is the deposition and then dissolution of glauberite (Na_2CaSO_4) at the later stages of evaporation that lead to steadily decreasing Ca^{2+} concentration in the solution and, as a result, the molar ratio of Ca and Na stays nearly stable (318/546) during the whole process whereas intensive precipitation of halite and thenardite removes all Na from the solution.

Thus, there are three main minerals – NaHCO_3 , NaCl and Na_2SO_4 – according to the final stages of evaporation, which define the considered lakes respectively, as soda, chloride and sulfate types.

However, widespread sulfate minerals with calcium and magnesium (gypsum, kieserite $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, hexahydrate $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, etc.) were not detected during simulation of the evaporation process. As was shown earlier (Kolpakova & Gaskova 2015), the mobility of chemical elements in Western Mongolian lakes and water–rock interaction process are greatly influenced by the geochemical environment. Migration species of Ca and Mg in water solution depend on the chemical type of lake because of the great stability of their carbonate, sulfate and chloride complexes (Figure 5). For example, a high concentration of chloride-ion provides that up to 80% of magnesium and calcium bound to MgCl^+ and CaCl^+ complexes at pH less than 7.5. Furthermore, $\text{Mg}(\text{SO}_4)_2^{2-}$ complex which sometimes reaches 90% with an average of 40% also plays a significant role in reactivity of Mg^{2+} .

Unlike calcium and magnesium, Na^+ and K^+ migrate primarily in the ion forms (about 95%). For example, the soda type lakes (HCO_3^- -Na) are characterized by their binding to NaCO_3^- and KCO_3^- complexes (average 2.8 and 1.4%, respectively) and the sulfate type – in to NaSO_4^- and KSO_4^- (2.5 and 6.4%, respectively). Therefore, it can be possible for chloride and sulfate lakes to reach the saturation state with respect to thenardite, glauberite and halite. Thus, the complexation could provide an explanation of precipitation sequence in closed surface basins of different types because it is one of the leading geochemical processes during evaporative concentration.

We consider to be interesting to show the effect of solution salinity on gypsum (as an example) precipitation to bottom sediments (Table 5). The increasing salinity along

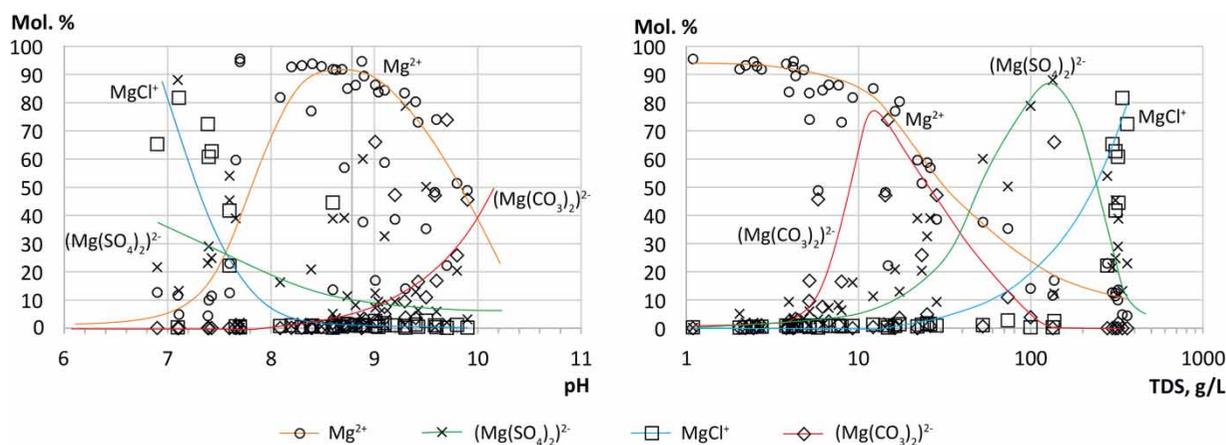


Figure 5 | Magnesium migration complexes depending on pH (a) and TDS (b) values (Kolpakova & Gaskova 2015).

Table 5 | Gypsum solubility via NaCl molality, where '0' corresponds to its solubility in pure water at 25 °C

NaCl, mol/L	Ion activity products (IAP)	(CaCl ⁺), mol/L	log SI
0	0.000031	0	0.01 (equilibr.)
1	0.0000067	0.0006189	-0.67 (undesat.)
2	0.0000044	0.001505	-0.89 (undesat.)
3	0.0000035	0.006651	-1.02 (undesat.)

The initial condition is equilibrium of gypsum with pure water.

with increasing amounts of calcium chloride species lead to *log SI* lowering, up to -1.02. Ion activity coefficients (γ) and ion activity products (*IAP*), i.e., $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$, have been calculated using Pitzer equations.

Discussing the results of calculations performed for the same lakes using 'HCh' code, it is necessary to emphasize that UNITHERM thermodynamic database is more broad ranging. It concerns especially aluminium silicates and solid solutions of magnesium calcite. As a result, trona ($\text{Na}_3\text{CO}_3 \cdot (\text{HCO}_3)_2 \cdot 2\text{H}_2\text{O}$), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, 0.0001 mol/L) and Mg-chlorite (3.48×10^{-6} mol/L) appear in sediments of the Shaazgay-Nuur soda lake instead of nahcolite NaHCO_3 . If nesquehonite was removed from the database, Mg calcite would be formed and thenardite could be expected to precipitate (*log SI* is -0.199). The remaining minerals are the same, including the appearance of halite. In the work of Kolpakova *et al.* (2014), it is shown that bottom sediments of Shaazgay-Nuur Lake truly contain quartz, calcite ($\text{Mg}_{0.03}\text{Ca}_{0.97}\text{CO}_3$), Mg-chlorite (a member of the mica group of minerals, sheet silicate), montmorillonite and optionally kaolinite.

Let us consider the Tonkhil-Nuur sulfate lake as an example. Table 6 shows the number and order of evaporated minerals' appearance (not shown calcite, quartz, barite and strontianite), as well as changes of their saturation indexes (*log SI*). Mg-chlorite is stable over the entire range of the evaporation process regardless of the amount of evaporated water, and glauberite appears in the medium stage of evaporation and does not disappear from mineral assemblages until the end. The precipitation of thenardite and halite is reached after 90% evaporation of water; the different sulfates are very close to saturation - mirabilite, syngenite and bloedite (marked by *). The HCh modelling results have confirmed that lake water undersaturates with respect to simple sulfates of Ca and Mg. These alkali metals migrate

Table 6 | Precipitated minerals (mol/L) during water evaporation (in bold) and *log SI*

Mineral	1 kg H ₂ O	0.5 kg H ₂ O	0.1 kg H ₂ O	0.05 kg H ₂ O
Mg-chlorite	0.000004	0.000004	0.000004	0.000004
Glauberite $\text{Na}_2\text{Ca}(\text{SO}_4)_2$	-0.544	0.005	0.007	0.007
Thenardite Na_2SO_4	-0.89	-0.133	0.4	0.4
Halite NaCl	-1.30	-0.61	1.11	1.44
Syngenite $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	-2.14	-1.67	-0.53	-0.06 ^a
Bloedite $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	-1.41	-0.49	-0.09 ^a	-0.11
Eugsterite $\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$	-1.38	-0.15	-0.19	-0.33
Epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	-0.83	-0.79	-0.77	-1.00
Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-0.38	-0.67	-0.97	-1.11
Mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	-0.38	-0.01 ^a	-0.73	-1.42

^aThese minerals are very close to saturation.

primarily in the form of sulfate complexes in lake water. Although, gypsum is very often the precursor of glauberite, as well as thenardite being the precursor of bloedite.

DISCUSSION

Due to the discussed problems of the sequence of mineral precipitation from solutions of different types, it is interesting to consider the experimental data (Lopez & Mandado 2007). Solutions, coming from two natural playa-lake saline systems located in Spain, were evaporated in the laboratory in order to obtain the precise path of chemical evolution followed until high concentration stages. The lakes belong to two chemically different neutral brines: Na-Cl solution and Na-Mg-SO₄ solution (Shaazgai-Nuur and Tonhil-Nuur lakes). Experimental evaporation was carried out at 25 °C until total dryness, and samples collected during the experiment were analysed for their major components. The mineral precipitation sequence for Na-Cl brines following the saturation data is gypsum, halite, thenardite and epsomite. Brines reach saturation almost simultaneously with respect to both halite and thenardite, but halite precipitates more massively and

hence the solid samples collected after total desiccation were composed mainly of halite. In the case of Na-Mg-SO₄ brines, the order of precipitation is somewhat different and is as follows: gypsum, mirabilite, thenardite and bloedite. Solid samples consisted of bloedite and thenardite here.

It is obvious that the deposition sequence for Cl-Na solution described in this article does not correspond to mineralogy assemblage (Lopez & Mandado 2007), with the exception of halite appearance during evaporation modelling and, in the case of SO₄-Na-Mg solution, bloedite, thenardite and halite. This corresponds to the starting point that 'because of the multiple equilibria involved, simple inspection of a water analysis does not reveal its eventual fate upon evaporation' (Hardie & Eugster 1970). The exact initial composition of water and the ratio of major ions are the important factors of evaporite formation. Migration species depend on the specific geochemical environment and are able to dramatically change the direction of evolution.

In addition to this, precipitation of certain salts occurs due to their reduction in solubility with temperature decrease (positive temperature coefficient of solution). The resultant minerals, like epsomite, sylvite and hexahydrate, are called cryophilic salts (Herrero *et al.* 2015). Attempts to classify evaporitic minerals by their formation temperature was proposed by Zheng *et al.* (2000), with mirabilite Na₂SO₄·10H₂O being the typical product of cool periods, bloedite Na₂Mg(SO₄)₂·4H₂O for slightly warm phases, and thenardite Na₂SO₄ being formed under warm conditions. We confirm that our findings support the conclusions of Lopez & Mandado (2007) and Zheng *et al.* (2000). For example, from Table 6 one can see that in the Tonhil-Nuur Lake mirabilite is near saturation ($\log SI = -0.01$) in the first step of evaporation (0.5 kg H₂O), then bloedite is near saturation ($\log SI = -0.09$ at 0.1 kg H₂O) and in the third step of evaporation (0.05 kg H₂O) thenardite prevails. In the sequence of mineral formation inferred for the basin, sodium bicarbonate NaHCO_{3(s)}, sodium-calcium sulfate Na₂CaSO₄ and sodium sulfate Na₂SO₄ are formed instead of calcium or magnesium sulfates.

CONCLUSION

The evaporation models of saline lakes with three different types of chemical composition were studied: Shaazgay-

Nuur (soda), Davsan-Nuur (chloride) and Tonhil-Nuur (sulfate). The obtained data were closely related to the real composition of bottom sediments. The modelling was performed for these natural objects for the first time, and subsequently, can be used for estimation of their state in the future for the sharply continental climate area.

In this article we supposed that 'evaporative concentration is the dominant mechanism effecting mineral formation and solute evolution in closed basin systems' (Jones 1966). The completed physical-chemical calculation showed that formation of autigenic minerals in lakes plays a significant role in their chemical evolution, which is presented as a number of sequential equilibrium and nonequilibrium states.

According to a classical concept (Hardie & Eugster 1970) and our model calculations, high alkalinity $\text{HCO}_3^- + \text{CO}_3^{2-} > \text{Ca}^{2+}$ of lakes determines gypsum absence in the solid phase of the studied lakes. The evolution of the Shaazgay-Nuur soda lake is probably in the initial carbonate stage (according to Strakhov (1962)), neither soda minerals (geylussit, nahcolite) nor halite were found in the bottom sediments (Isupov *et al.* 2013). Shaazgay-Nuur Lake is the largest lake among the considered lakes and it does not change its chemical type during evaporation. On the contrary, the smallest Davsan-Nuur and Tonhil-Nuur lakes undergo a change of chemical type and become clearly Cl-Mg.

According to our results, the exact composition of the lake water (not only the chemical type) and the ratio of major ions in it, as well as migration species of chemical elements that can significantly change the direction of solution evolution, are important factors in the study of the evaporation processes.

As magnesium content in the studied chloride and sulfate lakes is much higher than HCO_3^- , it should result in Mg-sulfates precipitation. Nevertheless, due to strong calcium and magnesium complexation in Cl-SO₄-brines and ionic strength influence, glauberite and thenardite precipitated instead. This process leads to the changes of the main cations in solution ($\text{Mg} > \text{K} > \text{Na}$) that is a sign of a significant brine metamorphism. The possible presence of K-bearing evaporites in the model core sediments (Davsan-Nuur Lake) suggests that the evaporation of brine could exceed the halite saturation stage. Thus, regardless of the specific composition, saline waters can be cross-compared in terms of the total salt assemblage expected after complete evaporation on the base of the current ion-ion ratio and the possibility of solution species calculation.

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