

Origin of potash salts and brines in the Qaidam Basin, China

RONALD J. SPENCER

Department of Geology and Geophysics, The University of Calgary, Calgary, Alberta T2N 1N4, Canada

TIM K. LOWENSTEIN and ENRIQUE CASAS

Department of Geological Sciences, S.U.N.Y. at Binghamton, Binghamton, New York 13901, U.S.A.

and

ZHANG PENGXI

The Institute of Salt Lakes, Academia Sinica, Xining, Qinghai, China

Abstract—The Qaidam Basin of western China (120,000 km²) is a closed, non-marine basin filled with over 10,000 metres of Jurassic and younger sediments. The Qarhan salt plain is one of the most active sites of evaporite deposition in the basin. The major source of water to Qarhan is Na⁺-HCO₃⁻ rich river water. Perennial rivers drain the Kunlun Mountains and enter the southern edge of the salt plain. The chemical composition of the river waters is similar to average world river water. Spring waters rich in Ca²⁺-Cl⁻, similar to many oil field brines and hydrothermal fluids, flow into the basin along deep seated faults at the northern edge of Qarhan.

Mixtures of different proportions of the river and spring inflow waters produce a variety of brine compositions in the lakes of Qarhan. These lakes precipitate a wide range of evaporite minerals, including mineral sequences typical of modern seawater evaporation as well as sequences similar to those found in many ancient evaporites. Lakes located along the southern margin of Qarhan, with the highest proportion of river inflow, contain Na⁺-Mg²⁺-Cl⁻-SO₄²⁻-rich brines and precipitate a mineral sequence similar to that obtained from the evaporation of modern seawater (calcite, gypsum-anhydrite, halite, polyhalite, epsomite-hexahydrate-kieserite, carnallite, bischofite). Other lakes on Qarhan do not follow the seawater evaporation sequence, because they lack MgSO₄ salts (polyhalite, epsomite, hexahydrate and kieserite) but precipitate potash salts (sylvite and/or carnallite). The major potash deposits at Qarhan are MgSO₄-free, because of a significant volume of spring inflow. These deposits are similar in mineralogy to many ancient evaporites (including the Devonian Prairie Formation). Lake and groundwater brines located along the northern edge of Qarhan contain the highest proportion of spring water inflow and precipitate salts (carnallite and tachyhydrite) which are important components of Cretaceous evaporites of the Sergipe-Alagoas basin, Brazil, Congo basin, West Africa and Khorat Plateau, Thailand.

INTRODUCTION

THE ORIGIN of ancient evaporites containing the very soluble potash salts (sylvite or carnallite) is controversial. Many of these evaporites do not contain MgSO₄-bearing salts such as polyhalite, kainite or kieserite (see HARDIE, 1990, for a compilation). The MgSO₄-bearing salts should precipitate before the potassium or magnesium chloride-bearing phases, such as sylvite, carnallite or bischofite, during the evaporation of modern seawater (HARVIE and WEARE, 1980; HARVIE *et al.* 1980; EUGSTER *et al.* 1980). These discrepancies between the mineral sequences found in many ancient evaporites and those derived from the evaporation of modern seawater have been recognised by a number of workers. BRAITSCH (1971), for example, classifies many evaporites as "MgSO₄ deficient"; VALYASHKO (1972) refers to "abnormal sea deposits"; and WARDLAW (1972) uses the term "unusual marine evaporite." There is a strong tendency to at-

tribute most ancient salt deposits to a seawater parentage and since the major element chemistry of seawater is thought to have remained nearly constant, at least during the Phanerozoic (HOLLAND, 1972; HOLLAND *et al.*, 1986), these discrepancies have led to problems in the interpretation of the potash deposits.

The Qaidam Basin is one of the few areas in the world where significant quantities of potash salts are accumulating. The Qaidam Basin is, therefore, an important natural setting in which to study the origin of potash salts and the origin of the brines which precipitate the salts. It is important to note that this is a large, non-marine basin which contains extensive salt deposits, including potash salts. Although non-marine, the processes which lead to potash salt deposition in the Qaidam Basin have application to ancient potash deposits in both marine and non-marine settings.

The Qaidam Basin is located at high altitude

(~3000 meters) on the northern edge of the Qinghai-Tibet Plateau (Fig. 1a). The 120,000 km² area is comparable in size to many ancient evaporite basins. The Qaidam Basin contains economically important oil and gas fields of continental origin, and a variety of evaporitic ore minerals, including several borates, strontianite, celestite, halite, sylvite, carnallite and bischofite. Several saline lakes and dry saline pans are located in the basin (Fig. 1b). The 6,000 km² Qarhan salt plain is one of the most active sites of evaporite deposition in the basin and contains the only significant source of potash salt fertilizer in China.

Two fundamentally different types of inflow waters feed the Qarhan salt plain. The majority of the water which flows onto the salt plain is Na⁺-HCO₃⁻-SO₄²⁻-rich river water. However, much of the salt brought onto the modern salt plain comes from Ca²⁺-Cl⁻-rich spring waters. The major potash salt on Qarhan salt plain, carnallite, forms as layered

halite-carnallite along the shores of perennial saline lakes such as Lake Dabusun. Carnallite also forms as an early diagenetic void-filling cement in Holocene-Pleistocene layered halite-siliciclastic sequences of Qarhan salt plain. The petrographic textures of the potash minerals are similar to those in many ancient evaporite deposits (for example the Permian Salado Formation, New Mexico and the Devonian Prairie Formation, Saskatchewan).

The salts found on Qarhan salt plain are, relative to the dominant inflow water (river water), deficient in MgSO₄-bearing salts, as are many ancient evaporite deposits relative to modern seawater. The lack of MgSO₄ minerals in ancient marine evaporites has been explained in several ways. Removal of sulphate by biologic reduction has been proposed (BORCHERT and MUIR, 1964; BRAITSCH, 1971; WARDLAW, 1972; SONNENFELD, 1984), as has syndepositional modification of seawater parent brines by non-marine inflow. Types of inflow include me-

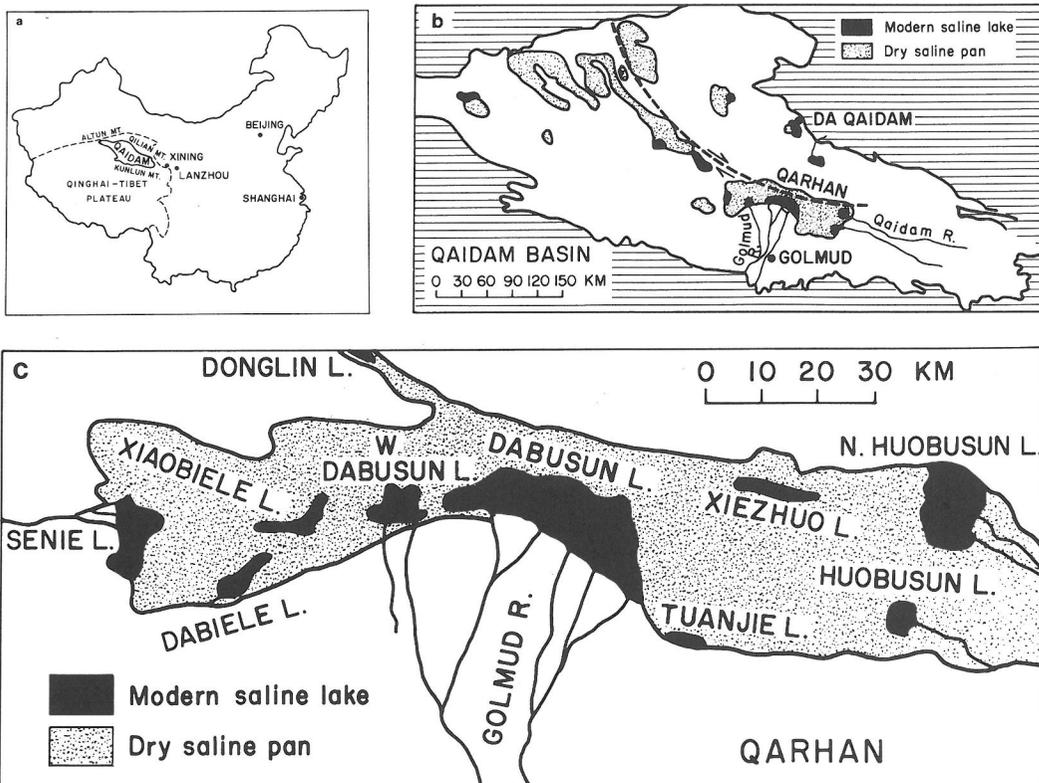


FIG. 1. a) The Qaidam Basin is located along the northern margin of the high altitude Qinghai-Tibet Plateau. The basin is surrounded by the Kunlun, Altun and Qilian Mountains. b) The Qaidam Basin has an area of about 120,000 km² and contains numerous saline lakes and dry saline pans at an average elevation of 2800 m above sea level. Dashed line through the northern margin of Qarhan and extending northwest across the Qaidam Basin is the trace of a deep seated fault zone along which springs and karst pools are found. c) Qarhan salt plain contains many modern saline lakes. Perennial rivers feed several of the lakes. Springs and karst pools are located along the north edge of Qarhan.

Table 1. Inflow waters to the Qarhan salt plain, analyses in molalities

Type	Density	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Spring	1.058	1.207	0.007	0.072	0.137	1.580	0.026	—
Spring*	1.056	1.167	0.004	0.081	0.129	1.518	0.036	—
Spring	1.051	1.131	0.004	0.040	0.131	1.464	0.007	—
Spring	1.178	2.786	0.309	0.231	0.944	5.394	0.0005	0.0014
River	1.000	0.00474	0.00015	0.00096	0.00157	0.00384	0.00122	0.00367
River*	1.000	0.00278	0.00009	0.00093	0.00119	0.00227	0.00061	0.00364
River	1.000	0.00832	0.00025	0.00045	0.00272	0.00785	0.00148	0.00410
River	1.000	0.00232	0.00010	0.00107	0.00102	0.00158	0.00072	0.00358

* Analyses used in calculating brine evolution.

teoric (D'ANS, 1933; STEWART, 1963; VALYASHKO, 1972), diagenetic, volcanogenic or hydrothermal waters (HARDIE, 1984), and waters of uncertain origin (WARDLAW, 1972). VALYASHKO (1972) has proposed that metastable or even non-equilibrium conditions prevented deposition of a "normal" marine saline mineral assemblage. Several workers (STEWART, 1963; BORCHERT and MUIR, 1964; WARDLAW, 1968; EVANS, 1970; BRAITSCHE, 1971; HOLSER, 1979; HARDIE *et al.* 1985) suggest that the original primary evaporite mineralogy has been modified during diagenesis. HARDIE (1984) has also proposed that many of these evaporites are not of strictly marine parentage. Recent work by LOWENSTEIN and SPENCER (1990) has shown that the potash salts found in the Oligocene Rhine Graben, Permian Salado and Devonian Prairie evaporites formed from syndepositional brines which deviate from modern seawater composition. These deposits appear to be of mixed marine-non-marine or non-marine parentage.

The Qaidam Basin demonstrates that extensive non-marine potash deposits exist. The evolution of inflow waters to form these salt deposits also serves as a guide in understanding mixed-source evaporites. Below, the chemical characteristics of the inflow waters are discussed first. Theoretical evaporation paths for the two "end-member" inflows (rivers and springs) and for mixtures of these are then discussed. The compositions of brines and the minerals found on Qarhan salt plain are then compared with our theoretical predictions. The varied composition of brines of Qarhan salt plain can be produced by evaporitic concentration of mixtures of the two "end-member" inflows. Finally, possible applications of this type of mixed inflow to understanding the parent waters of ancient evaporites are discussed briefly.

INFLOW WATERS

Meteoric waters

Several perennial rivers flow onto Qarhan salt plain, including the Golmud, Wutumeiren and

Qaidam Rivers. The source areas for these rivers (and the Yellow and Yangtze Rivers) are in the Kunlun Mountains, which form the southern border of the Qaidam Basin (Fig. 1). Permanent lakes are present where rivers flow onto the Qarhan salt plain. North Huobusun Lake is fed by the Qaidam River, Senie Lake by the Wutumeiren River and Dabusun Lake by the Golmud River (Fig. 1b and c). There are several ephemeral lakes, including West Dabusun Lake; which receives inflow from the Golmud River as a result of avulsion of one of the many distributory channels of the lower alluvial fan and river delta (Fig. 1c). Many ephemeral lakes are located where dry stream beds intersect the Qarhan salt plain. These lakes appear to be fed by ephemeral streams, or by meteoric groundwater flowing below the stream beds. Xiezhuo Lake, for example, has a crescent shape defined by a deltaic fan located at the terminus of a dry river bed.

The chemical compositions of the river waters which feed the lakes on Qarhan are typical of meteoric waters derived from weathering reactions. Rivers which flow onto Qarhan are similar in composition to that of average world river water (LOWENSTEIN *et al.*, 1989). The total dissolved solid content of average world river water (LIVINGSTON, 1963) is lower than the river waters entering Qarhan (105 ppm versus >400 ppm for Qarhan rivers). The increased salinity results from evaporative concentration in this extremely arid environment and from dissolution of ephemeral salts. Evaporative concentration occurs as the rivers flow toward Qarhan, resulting in precipitation of calcium carbonate. Like average world river water, the rivers which flow onto Qarhan have molal anion abundances of HCO₃⁻ > Cl⁻ > SO₄²⁻ (Table 1). However, the relative proportion of HCO₃⁻ is smaller in these arid climate rivers than in average world river water and it decreases downstream toward the lakes. The molal abundance of the major cations in these rivers (Na⁺ > Mg²⁺ > Ca²⁺ > K⁺) also differs from average world river water which contains Ca²⁺ as the dom-

inant cation, but otherwise is similar in composition. The lower HCO_3^- and Ca^{2+} content of the river waters entering Qarhan salt plain is probably the result of CaCO_3 precipitation.

The river waters flowing onto Qarhan and average world river waters are classified as $\text{Na}^+\text{-HCO}_3^-\text{-SO}_4^{2-}$ waters (Fig. 2). This is because, on an equivalence basis, Ca^{2+} is greater than HCO_3^- . Therefore, after the precipitation of the relatively insoluble calcium carbonate minerals, Ca^{2+} is depleted in the resulting brines, and both HCO_3^- and SO_4^{2-} remain. As a consequence, sodium bicarbonate and/or sodium sulfate minerals are part of the normative mineral assemblage for these waters (see BODINE and JONES, 1986 and this volume, for explanation of normative assemblages). These salts are predicted to precipitate during the later stages of evaporative concentration of these waters (see below).

Brine springs

Groundwaters of a markedly different chemical composition reach the surface along the north edge of Qarhan as a series of springs and seeps associated with a karst zone (Fig. 1b). These groundwaters were sampled about five km west of Xiezhuo Lake, where they flow from pipes which were set several meters into the salt and mud, and which project about 50 centimeters above the salt surface. This spring inflow is undersaturated with respect to halite, even though several metres of halite are present in this area. The spring waters contain Cl^- as the dominant anion (>99%) and have molal cation abundances of $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ (Table 1). Brines in the surrounding karst pools fed by these groundwaters are saturated with respect to halite because of dissolution of halite and evaporative concentration.

The location of the karst springs and seeps may be controlled by the contrast between relatively porous sediments along the boundary of Qarhan (alluvial fan and dune deposits) and the less porous salts and muds found beneath the salt plain or by a deep seated fault which runs along the north edge of Qarhan (Fig. 1b). The trace of a deep seated fault along the northern edge of Qarhan coincides with the position of the karst.

The karst springs and seeps are classified as $\text{Ca}^{2+}\text{-Cl}^-$ type waters because the equivalents of Ca^{2+} in these waters exceed the combined HCO_3^- and SO_4^{2-} equivalents. After evaporation and precipitation of the relatively insoluble calcium carbonates and moderately soluble calcium sulfates, both HCO_3^- and SO_4^{2-} are depleted in the resulting brines.

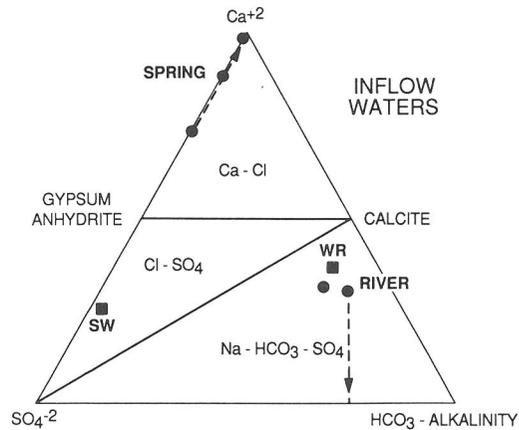


FIG. 2. Ternary $\text{Ca}^{2+}\text{-SO}_4^{2-}\text{-HCO}_3^-$ phase diagram (in equivalents) illustrates the early stage evaporation paths for river and spring inflow and chemical divides for evolved brines. The body of the diagram is the primary crystallization field for calcite. Gypsum and anhydrite crystallize along the $\text{Ca}^{2+}\text{-SO}_4^{2-}$ join. Two chemical divides, from calcite to SO_4^{2-} and from calcite to gypsum-anhydrite, separate the $\text{Na}^+\text{-HCO}_3^-\text{-SO}_4^{2-}$, $\text{Cl}^-\text{-SO}_4^{2-}$ and $\text{Ca}^{2+}\text{-Cl}^-$ brine fields. The compositions of average world river waters and sea-water are shown for comparison.

However, Ca^{2+} remains, and in the late stages of evaporation, will precipitate as a chloride salt (see below). The spring waters contain $\text{Ca}^{2+}\text{-Cl}^-$ salts as part of the normative mineral assemblage (BODINE and JONES, this volume). These waters are similar in composition to many oil field brines (GRAF *et al.*, 1966; CARPENTER *et al.*, 1974; COLLINS, 1975; CARPENTER, 1978; SPENCER, 1987) and hydrothermal brines (ROEDDER, 1972; HARDIE, 1983). No analyses of the deep formation waters which underlie Qarhan are yet available. However, deep brines from oil fields in the western portion of the Qaidam Basin are of the $\text{Ca}^{2+}\text{-Cl}^-$ type. We believe that upward movement of similar deep seated brines beneath Qarhan is responsible for the karst springs and seeps. These waters are probably diluted to different extents by mixing with meteoric groundwaters near the surface.

To summarize, the inflow waters to Qarhan are divided into two types. Meteoric waters, especially rivers, with a $\text{Na}^+\text{-HCO}_3^-\text{-SO}_4^{2-}$ composition are the dominant source of water. The location of the lakes distributed over Qarhan is controlled by the positions of rivers which flow onto the salt plain. Groundwater inflow with a $\text{Ca}^{2+}\text{-Cl}^-$ composition emerges along the north edge of the basin. The amount of water brought in by these groundwaters is much less than the river inflow. However, these waters are much more concentrated (by about 200

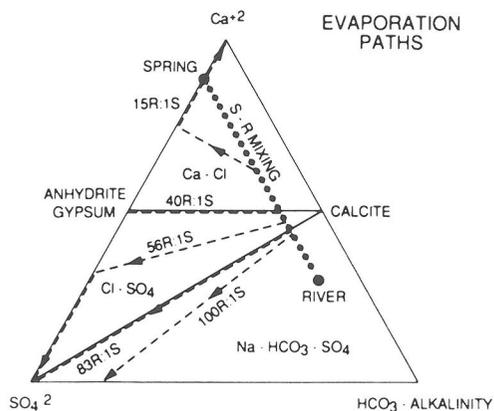


FIG. 3. The compositions of river inflow and spring inflow mixtures lie along the line S-R mixing. Evaporation paths for river waters, spring waters and several mixtures (by weight) of river inflow and spring inflow (including the mixtures for chemical divides in Fig. 2) are shown. Evaporation paths calculated using the thermochemical model of HARVIE *et al.* (1984).

times) than the river waters. Therefore, significant quantities of salt are delivered by the $Ca^{2+}-Cl^{-}$ type groundwaters.

EVAPORATION PATHS

HARDIE and EUGSTER (1970) describe the principles of brine evolution in terms of evaporative concentration and mineral precipitation. The evolution of dilute waters into different types of brines is determined early in the evaporative concentration because of chemical divides during the precipitation of calcite and gypsum. This is illustrated in Fig. 3, which is a ternary phase diagram with Ca^{2+} , SO_4^{2-} and HCO_3^{-} (all in equivalents) at the corners of the diagram. The stability field for calcite occupies the body of the diagram, with gypsum and anhydrite fields along the $Ca^{2+}-SO_4^{2-}$ join. During calcite precipitation the fluid composition moves directly away from the $CaCO_3$ (calcite) compositional point and

GOLMUD RIVER INFLOW	88 RIVER: 1 SPRING	MIXED RIVER AND SPRING INFLOW	40 RIVER: 1 SPRING	SPRING INFLOW, KARST ZONE
C C+H C+H+NaHCO ₃ - Na ₂ CO ₃ -Na ₂ SO ₄ - Assemblages	C C+H C+H+A C+H+A+Po C+H+Po C+H+Po+Hx C+H+Po+Ki C+H+Po+Ki+Car C+H+A+Ki+Car C+H+A+Ki+Car+Bi	C C+G C+A C+A+H C+A+H+Car C+A+H+Car+Bi C+A+H+Car+Bi+Ki	C C+G C+A C+A+H C+A+H+Car C+A+H+Car+Bi+Tc	
Na-HCO ₃ -SO ₄ Brine	Na-Mg-K-Cl-SO ₄ Brine		Ca-Cl Brine	
	TUANJIE L. SENIE L. DABIELE L. XIAOBIELE L. W. DABUSUN L.		DABUSUN L.	DONGLIN L. XIEZHUO L. HUOBUSUN L. N. HUOBUSUN L. KARST PONDS

FIG. 4. Calculated mineral precipitation sequences are shown from earliest (top) to latest minerals to precipitate (bottom) during evaporation for river inflow, spring inflow and mixtures of river inflow and spring inflow near the two chemical divides in Fig. 3. River inflow and mixtures of greater than 83 parts river inflow to 1 part spring inflow (by weight) evolve to $Na^{+}-HCO_3^{-}-SO_4^{2-}$ brines. Spring inflow and mixtures of less than 40 parts river inflow to 1 part spring inflow evolve to $Ca^{2+}-Cl^{-}$ brines. Several lakes on Qarhan salt plain contain $Ca^{2+}-Cl^{-}$ brines. Mixtures of between 40 and 83 parts river inflow to 1 part spring inflow evolve to $Cl^{-}-SO_4^{2-}$ brines. Mineral precipitation sequences differ for the $Cl^{-}-SO_4^{2-}$ brines (although all of these contain the same invariant mineral assemblage), depending on the particular blend of river inflow and spring inflow. The two sequences shown are for blends near the chemical divides. Minerals are calcite (C), halite (H), anhydrite (A), gypsum (G), polyhalite (Po), hexahydrate (Hx), kieserite (Ki), carnallite (Car), bischofite (Bi) and tachyhydrite (Tc).

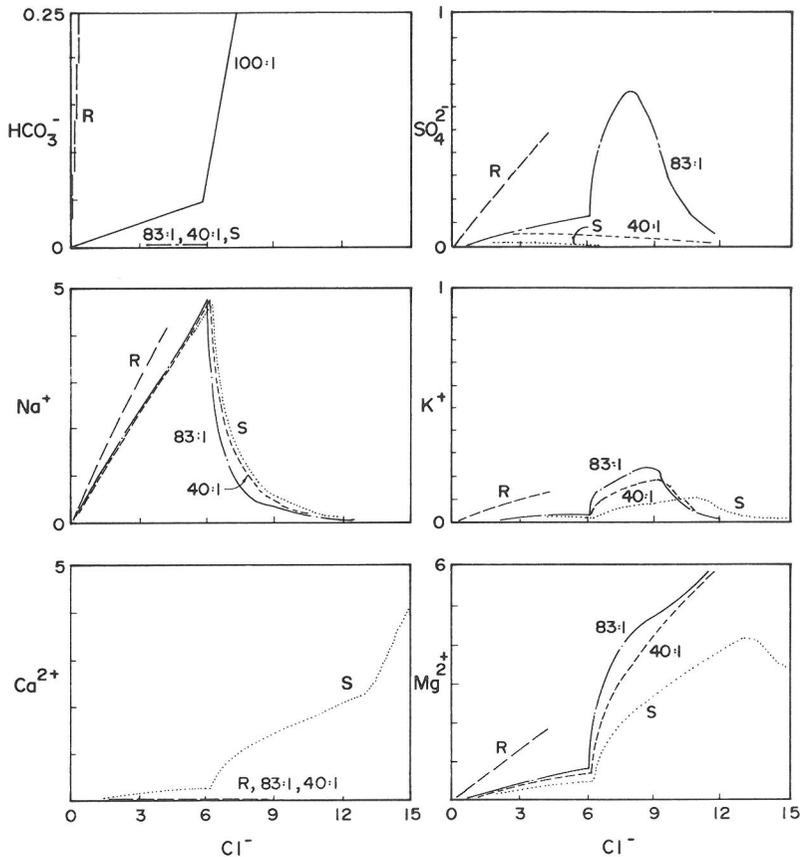


FIG. 5. Calculated evaporation paths are shown for Cl^- against the other major elements for river inflow (R, shortened to avoid crowding as none of the Qarhan brines have this type of composition), spring inflow (S) and mixtures of river and spring inflow along the chemical divides in Fig. 3 (83:1 and 40:1). Concentrations of all species are in molalities. The HCO_3^- content of mixtures with less than 83 parts river inflow to 1 part spring inflow is low during evaporative concentration and mineral precipitation. Evaporation of waters with a larger proportion of river waters (for example the 100:1 path) results in high HCO_3^- waters. Evaporation of inflow with less than 40 parts river inflow to 1 part spring inflow results in low SO_4^{2-} brines. Maximum SO_4^{2-} concentrations for the 83:1 path occur at the beginning of hexahydrate precipitation. Maximum Na^+ concentrations occur at halite saturation. The concentration of K^+ is higher in evolved brines with a larger component of river water inflow. Maxima for K^+ occur at the beginning of carnallite precipitation, which is later in the evaporation sequence for brines with a larger spring inflow. The concentration of Ca^{2+} is low for brines evolved from mixtures with greater than 40 parts river inflow to 1 part spring inflow. The Mg^{2+} content is highest for brines evolved from a larger proportion of river inflow. Brines concentrated beyond halite saturation contain Mg^{2+} as the dominant cation, except for Ca^{2+} - Cl^- brines beyond the point of bischofite saturation.

as gypsum or anhydrite precipitate, the fluid composition moves away from the CaSO_4 compositional point. Therefore, waters are divided into three fields (Ca^{2+} - Cl^- , Cl^- - SO_4^{2-} and Na^+ - HCO_3^- - SO_4^{2-}) by the two chemical divides in Fig. 3 (lines from CaCO_3 to CaSO_4 and SO_4^{2-}).

Mineral precipitation sequences and brine evolution are more difficult to predict from simple phase diagrams during the later stages of evaporative concentration. Evaporation paths and mineral pre-

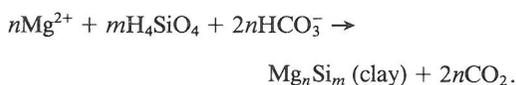
cipitation sequences at 25°C for river and spring inflow, and mixtures of the two, are calculated using the thermochemical model of HARVIE *et al.* (1984). A number of solid phases have been withheld from the model including dolomite and other MgCO_3 minerals, Mg-oxides and Mg-hydroxides. These phases are predicted to form at low temperatures, but have not been observed. Additional mineral precipitation sequences are calculated at temperatures other than 25°C using the variable tempera-

ture thermochemical model of SPENCER *et al.* (1990).

Evaporative trends for river inflow

Calculated evaporation paths for the river inflow yield mineral precipitation sequences as indicated in Fig. 4. All of the river waters are calculated to precipitate calcite, followed by halite. The mineral precipitation sequence beyond the point of halite saturation varies slightly from one river analysis to another. All calculated river evaporation sequences contain sodium sulfate (mirabilite), one or more of the sodium carbonate or sodium bicarbonate minerals and magnesium sulfate minerals. The minerals precipitated vary depending on the partial pressure of CO₂ and as a function of temperature. Because the equivalents of HCO₃⁻ are greater than the equivalents of Ca²⁺ in these waters, they evolve into Na⁺-HCO₃⁻-SO₄²⁻ brines (Fig. 3), and HCO₃⁻ increases during evaporative concentration and calcite precipitation (Fig. 5). It is important to note that no sodium carbonate or bicarbonate minerals or sodium sulfate minerals have been reported from Qarhan. Furthermore, the present-day lakes on the salt plain do not contain the concentrations of HCO₃⁻ expected from evaporative concentration of the river waters.

The model used for the evaporation of the river waters does not take into account the possible precipitation of Mg as a carbonate or a clay mineral. The carbonate minerals reported from Qarhan do not contain high Mg, but Mg-rich clay minerals do occur. The formation of Mg-rich clays can be described schematically by the following reaction:



This reaction consumes HCO₃⁻ in the same manner as occurs during the precipitation of a carbonate mineral. The precipitation of Mg-rich clay minerals may therefore lead to a brine depleted in HCO₃⁻. Removal of Mg²⁺ from solution to form clays in the lacustrine brines of the Great Salt Lake, Utah, has a pronounced influence on the brine evolution (SPENCER, 1982). Diagenetic formation of Mg-rich clays in the Great Salt Lake system has removed up to three fourths of the long term Mg input to the system (SPENCER *et al.*, 1985b), where the resulting clays are highly enriched in Mg (SPENCER *et al.*, 1984). The removal of Mg in the Great Salt Lake system is not apparent in the short term (SPENCER *et al.*, 1985a). The river waters which flow onto Qarhan may become depleted in HCO₃⁻

through the precipitation of Mg-rich clay minerals. Removal of all HCO₃⁻ requires about three fourths of the Mg²⁺ entering the system to also be removed. This process leads to the evolution of high Cl⁻-SO₄²⁻ brines. The resulting paragenetic mineral sequence includes the minerals halite, glauberite, polyhalite, bloedite, epsomite, hexahydrate and kieserite in addition to calcium carbonate and Mg-silicate.

Evaporative trends for spring inflow

Calculated evaporation paths for the most Ca²⁺-rich of the karst springs and seeps are given in Fig. 4. However, all spring waters modeled yielded the same mineral precipitation sequence. The order of precipitation, calcite-gypsum-halite-carnallite-bischofite-tachyhydrite is not strongly influenced by temperature. However, antarcticite, rather than tachyhydrite, is predicted to form below 18°C. Spring waters evolve to precipitate Ca²⁺-Cl⁻ salts (antarcticite or tachyhydrite) in the latest stages of evaporation because the equivalents of Ca²⁺ in the inflow waters exceed the combined equivalents of HCO₃⁻ and SO₄²⁻ (Fig. 3). Therefore, precipitation of the calcium carbonate and calcium sulfate salts exhausts HCO₃⁻ and SO₄²⁻ in solution. The remaining brine contains Ca²⁺ and Cl⁻ is the only anion present in significant quantities (Fig. 5). Several lakes on Qarhan contain Ca²⁺-Cl⁻ brines (see below).

Evaporative trends for mixtures of river and spring water

The evaporation paths for mixtures of the two "end member" inflow waters (rivers and springs) have been calculated. Mixtures of about 83 parts river water to one part spring water by weight contain equivalents of Ca²⁺ equal to equivalents of HCO₃⁻ and are, therefore, along the Cl⁻-SO₄²⁻ and Na⁺-HCO₃⁻-SO₄²⁻ chemical divide in Fig. 3 (proportions will vary slightly depending on which river and spring analyses are used; the analyses of the Golmud River and karst spring asterisked in Table 1 are used for the calculations here and below). Mixtures with a higher proportion of river water evolve into Na⁺-HCO₃⁻-SO₄²⁻ brines. The phases to form upon evaporation of the Na⁺-HCO₃⁻-SO₄²⁻ waters are the same as for the river waters (Fig. 4). A higher proportion of sodium sulfate and magnesium sulfate salts are precipitated and these salts precipitate earlier in the evaporation sequence as the chemical divide is approached. However, all brines of this type contain sodium carbonate or bicarbonate phases in the final invariant assemblages.

The chemical divide between $\text{Ca}^{2+}\text{-Cl}^-$ and $\text{Cl}^- \text{-SO}_4^{2-}$ brines is defined by waters in which the equivalents of Ca^{2+} equal the total equivalents of HCO_3^- plus SO_4^{2-} (Fig. 3). Mixtures of about 40 parts river water to one part spring water fall along this divide. Mixtures with a higher proportion of spring water evolve into $\text{Ca}^{2+}\text{-Cl}^-$ brines. The spring waters are high in Ca^{2+} relative to HCO_3^- and SO_4^{2-} , so that mixtures with a larger proportion of spring water will contain Ca^{2+} in solution after HCO_3^- and SO_4^{2-} are depleted in the brines during evaporation and precipitation of calcium carbonate and calcium sulfate. The sequence of minerals formed during evaporation of all mixtures of inflow resulting in $\text{Ca}^{2+}\text{-Cl}^-$ brines (greater than 1 part spring inflow to 40 parts river inflow by volume) is the same as for the spring water (Fig. 4).

Mixtures of between 40 and 83 parts river water to one part spring water evolve into $\text{Cl}^- \text{-SO}_4^{2-}$ brines (Fig. 3). All of the $\text{Cl}^- \text{-SO}_4^{2-}$ brines modeled contain the invariant assemblage of calcite, anhydrite, halite, carnallite, bischofite and kieserite (Fig. 4). The sequence of minerals precipitated from these brines varies depending on the specific mixture. The $\text{Cl}^- \text{-SO}_4^{2-}$ brines that originate from a larger proportion of spring inflow produce a mineral sequence similar to that formed by evaporation of spring inflow, except that kieserite instead of tachyhydrite (or antarcticite) is the final phase to crystallize (Fig. 4). Those $\text{Ca}^{2+}\text{-Cl}^-$ brines that originate from larger proportions of river inflow produce a distinctly different mineral sequence on evaporation. These brines are modeled to precipitate calcite, halite, anhydrite, polyhalite (with anhydrite reacting out of the solid assemblage), hexahydrite, kieserite (replacement of hexahydrite), carnallite, anhydrite (with polyhalite reacting out of the solid assemblage) and bischofite (Fig. 4).

Other mixtures of inflow waters evolve into $\text{Cl}^- \text{-SO}_4^{2-}$ brines with additional mineral sequences (between the two sequences given in Fig. 4). Brines formed from a larger proportion of spring inflow precipitate gypsum and anhydrite at earlier stages of evaporation and the magnesium sulfate salts polyhalite and hexahydrite do not appear in these evaporation sequences. The larger the proportion of spring water inflow, the later the magnesium sulfate salts (polyhalite, hexahydrite and kieserite) precipitate. Mixtures formed from a larger proportion of river inflow result in mineral precipitation sequences which are similar to that of modern seawater. A small range of river and spring inflow mixtures have mineral precipitation sequences identical to the seawater sequence given by HARVIE *et al.* (1980), which is calcite, gypsum replaced by anhydrite, halite, polyhalite, epsomite replaced by

hexahydrite and then kieserite, carnallite (with polyhalite reacting out of the solid assemblage) and bischofite.

Calculated evaporation paths of river and spring water, and mixtures of river and spring inflow defining the chemical divides in Fig. 3 are given for the major elements, HCO_3^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} against Cl^- in Fig. 5 (note the differences in scale for the various plots). Trends for all mixtures of river and spring inflow that produce $\text{Ca}^{2+}\text{-Cl}^-$ brines lie between the spring and 40:1 curves, $\text{Cl}^- \text{-SO}_4^{2-}$ brines lie between the 40:1 and 83:1 curves and $\text{Na}^+ \text{-HCO}_3^- \text{-SO}_4^{2-}$ brine trends lie between the river and 83:1 curves for all species in Fig. 5. The content of HCO_3^- is low for all $\text{Cl}^- \text{-SO}_4^{2-}$ and $\text{Ca}^{2+}\text{-Cl}^-$ brines. The HCO_3^- content of brines with even a slight excess of river inflow (for example the 100 river inflow to one spring inflow curve for HCO_3^- in Fig. 3) becomes large during evaporation. None of the modern brines on Qarhan contain high HCO_3^- , so this type of brine is not discussed further.

The SO_4^{2-} concentration is low in all $\text{Ca}^{2+}\text{-Cl}^-$ brines, but increases sharply for $\text{Cl}^- \text{-SO}_4^{2-}$ brines during the initial precipitation of halite and prior to the precipitation of the magnesium sulfate salts hexahydrite or kieserite. The concentration of Na^+ is larger relative to Cl^- , prior to halite precipitation, for brines with a higher proportion of river inflow. The Na^+ content of the brines decreases sharply during halite precipitation because the equivalents of Na^+ are less than the equivalents of Cl^- for both $\text{Ca}^{2+}\text{-Cl}^-$ and $\text{Cl}^- \text{-SO}_4^{2-}$ brines. Brines derived from a larger proportion of river inflow are modeled to contain relatively higher concentrations of K^+ , except during the later stages of evaporation because the potassium salts polyhalite and carnallite precipitate earlier in these brines. The Ca^{2+} concentration is low for all of the $\text{Cl}^- \text{-SO}_4^{2-}$ brines. High levels of Ca^{2+} are generated during the later stages of evaporation of the $\text{Ca}^{2+}\text{-Cl}^-$ brines; at the invariant point the Ca^{2+} is greater than 5 molal. The Mg^{2+} molality is modeled to increase sharply after the initial precipitation of halite; Mg^{2+} is the dominant cation in most concentrated $\text{Cl}^- \text{-SO}_4^{2-}$ and $\text{Ca}^{2+}\text{-Cl}^-$ brines.

LAKE BRINES

The modern lake brines found on Qarhan are discussed in three groups. Lakes and groundwaters located along the northern edge of the salt plain associated with the karst springs and seeps are $\text{Ca}^{2+}\text{-Cl}^-$ brines. Lakes along the southern edge of the salt plain contain $\text{Cl}^- \text{-SO}_4^{2-}$ brines. The largest lake on Qarhan, Lake Dabusun, contains brines depleted in Ca^{2+} , HCO_3^- and SO_4^{2-} . All of the lake brines analysed in this study, as well as those reported by Zhang (1987) contain less than 0.04 molal

Table 2. Modern lake brines, Qarhan salt plain, analyses in molalities

Lake	Year	Density	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Donglin	1966	1.37	0.0822	0.0006	1.510	4.530	12.02	0.0002	—
Xiezhuo	1980	1.248	0.782	0.222	0.495	2.990	7.989	0.0023	—
N. Huobusun	1980	1.1995	4.082	0.085	0.104	0.981	6.302	0.0182	0.004
Karst pool	1987	1.202	4.588	0.014	0.277	0.457	6.059	0.0063	—
Karst pool	1987	1.200	3.904	0.048	0.318	0.885	6.171	0.0097	—
Karst pool	1987	1.207	3.709	0.041	0.390	1.021	6.251	0.004	—
Karst pool	1987	1.205	3.798	0.042	0.403	1.063	6.448	0.004	—
Karst pool	1988	1.291	0.307	0.232	0.929	3.962	9.601	—	0.0026
Karst pool	1988	1.263	0.634	0.144	0.859	3.175	8.345	0.0001	0.0028
Karst pool	1988	1.317	0.166	0.081	1.388	4.096	10.301	—	0.0039
Senie	1980	1.2144	4.628	0.209	0.0077	0.565	6.006	0.265	0.0054
Dabiele	1980	1.2419	4.062	0.247	0.0288	1.452	5.703	0.749	0.021
Dabiele	1980	1.2402	1.151	0.672	0.0123	2.990	7.667	0.079	0.0051
Xiaobiele	1980	1.2626	0.544	0.553	0.0024	3.834	8.449	0.147	0.032
Tuanjie	1980	1.3023	0.288	0.211	—	4.632	8.801	0.469	0.030
W. Dabusun	1981	1.24	2.536	0.0629	0.0105	2.915	8.262	0.090	0.0124
W. Dabusun	1982	1.07	0.633	0.0330	0.0087	0.104	0.874	0.0008	0.0003
W. Dabusun	1988	1.257	0.872	0.554	0.0097	3.387	7.727	0.115	0.038
W. Dabusun	1988	1.257	2.120	0.365	0.0192	1.910	6.158	0.087	0.018
Dabusun	1958	(1.19)	3.081	0.187	—	1.136	5.540	—	—
Dabusun	1959	1.195	3.626	0.239	—	1.510	6.884	—	—
Dabusun	1959	(1.19)	2.187	0.218	—	1.919	6.243	—	—
Dabusun	1960	1.220	3.698	0.226	—	1.301	6.525	—	—
Dabusun	1960	1.203	3.241	0.290	—	1.937	7.405	—	—
Dabusun	1964	1.220	1.152	0.577	—	2.717	7.164	—	—
Dabusun	1965	1.213	2.904	0.372	—	1.873	7.021	—	—
Dabusun	1966	1.228	1.800	0.444	—	2.465	7.174	—	—
Dabusun	1966	1.246	0.734	0.592	—	3.638	8.602	—	—
Dabusun	1980	1.3186	0.007	0.022	—	5.840	11.53	0.0813	0.031
Dabusun	1980	1.3186	0.041	0.021	0.0025	5.755	11.40	0.0806	0.016
Dabusun	1980	1.2196	2.051	0.549	0.062	2.156	6.979	0.0273	0.004
Dabusun	1987	1.239	1.219	0.524	0.023	3.131	7.700	0.176	—
Dabusun	1987	1.281	0.264	0.157	0.002	4.731	9.492	0.197	—
Dabusun	1988	1.256	0.832	0.471	0.021	3.392	7.592	0.055	0.042
Dabusun	1988	1.255	0.897	0.486	0.021	3.237	7.594	0.051	0.041
Dabusun	1988	1.256	0.883	0.462	0.022	3.257	7.471	0.060	0.041

Analyses from 1987 and 1988 this study. All others from ZHANG (1987).

HCO₃⁻. All of the brines lie along the evaporation paths for Na⁺ and Cl⁻ in Fig. 5.

Ca²⁺-Cl⁻ brine lakes

Brines from Donglin, Xiezhuo and North Huobusun Lakes (analyses from ZHANG; 1987) and brines from the karst pools and springs (this study) along the northern edge of Qarhan (Fig. 1c) have a Ca²⁺-Cl⁻ composition. They are all low in SO₄²⁻ and high in Ca²⁺ (Tables 1 and 2). The spring waters are dilute relative to the lake and karst pool brines. The less concentrated brines in the karst pools fall along the evaporation path of the spring waters (Fig. 6). All of the Ca²⁺-Cl⁻ waters modeled precipitate the same sequence of minerals on evaporation as is precipitated by the spring waters (Fig. 4). How-

ever, simple evaporation and mineral precipitation of the spring waters does not fully account for many of the more concentrated brines.

The more concentrated brines are lower in Ca²⁺ (Fig. 6) and higher in Mg²⁺ (Fig. 7) than is predicted for evaporation of the spring inflow. The deviation from the spring inflow evaporation path is exactly that expected for mixtures of spring and meteoric inflow for both elements. North Huobusun Lake receives inflow from the Qaidam River in addition to the spring inflow. Xiezhuo Lake is located at the mouth of a dry river channel, a likely conduit for meteoric groundwater. Additional meteoric water inflow is also likely along the entire North edge of Qarhan. Still, the major element composition of these brines appears to be strongly influenced by input of spring inflow.

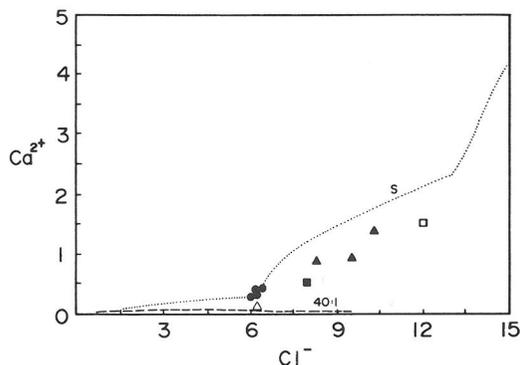


FIG. 6. Calculated evaporation paths for Ca^{2+} against Cl^- (in molalities) for the chemical divides bounding the Ca^{2+} - Cl^- brine field and the concentrations of these ions in the Ca^{2+} - Cl^- lakes and karst pools. Donglin Lake—open square, Xiezhuo Lake—filled square, North Huobusun Lake—open triangle, karst pools north of Dabusun Lake—filled triangles, karst pools near springs (west of Xiezhuo Lake)—filled circles.

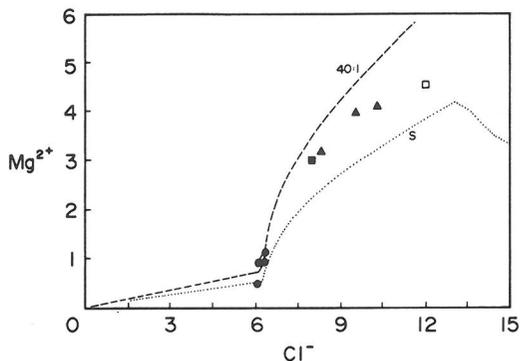


FIG. 7. Calculated evaporation paths for Mg^{2+} against Cl^- (in molalities) for the chemical divides bounding the Ca^{2+} - Cl^- brine field and the concentrations of these ions in the Ca^{2+} - Cl^- lakes and karst pools. Donglin Lake—open square, Xiezhuo Lake—filled square, North Huobusun Lake—open triangle, karst pools north of Dabusun Lake—filled triangles, karst pools near springs (west of Xiezhuo Lake)—filled circles.

The K^+ content of North Huobusun and Xiezhuo Lakes, and of some of the more concentrated brines from the karst zone is somewhat higher than expected for evaporation of the spring waters or spring water-river water mixtures (Fig. 8). We interpret this to result from recycling of carnallite. The influence of carnallite dissolution is relatively large for K^+ in solution, though it amounts to less than 0.2 m. Increases of this magnitude in Mg^{2+} or Cl^- (expected for the dissolution of carnallite, $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) are not apparent because of the relatively high background for these ions in solution.

Cl^- - SO_4^{2-} brine lakes

Xiaobiele, Dabiele, Senie and Tuanjie Lake brines all contain equivalents of SO_4^{2-} in excess of Ca^{2+} . The HCO_3^- alkalinity for each of these lakes reported by ZHANG (1987) is low as is the Ca^{2+} molality of these waters (Table 2). The SO_4^{2-} content of these lake brines varies, and Cl^- is the major anion in solution (Fig. 9). Based on their chemical compositions, these lakes are grouped together as Cl^- - SO_4^{2-} brines. Their brine compositions indicate a larger proportion of river water inflow relative to spring inflow (greater than 40 parts river to 1 part spring inflow) as discussed above under evaporation paths. These lakes are located along the southern edge of Qarhan, near the Kunlun Mountains, and away from the spring inflow (Fig. 1).

The composition of Tuanjie Lake is very close to that predicted for evaporation of waters along the Cl^- - SO_4^{2-} and Na^+ - HCO_3^- - SO_4^{2-} chemical divide (a ratio of about 83 parts river to 1 part spring

inflow). The Tuanjie brines are quite concentrated, and calculated to be at or near saturation with respect to calcite, halite, polyhalite, kieserite and carnallite. The SO_4^{2-} , Mg^{2+} and K^+ concentrations are all along the 83:1 evaporation path as shown in Figs. 9, 10 and 11. The SO_4^{2-} (Fig. 9) and Mg^{2+} (Fig. 10) concentrations in the Senie Lake brines also lie along the 83:1 evaporation path. However, K^+ is somewhat higher than the model value (Fig. 11). Senie Lake brines are less concentrated than Tuanjie Lake brines. They are at or near saturation with respect to only anhydrite and halite. The high K^+

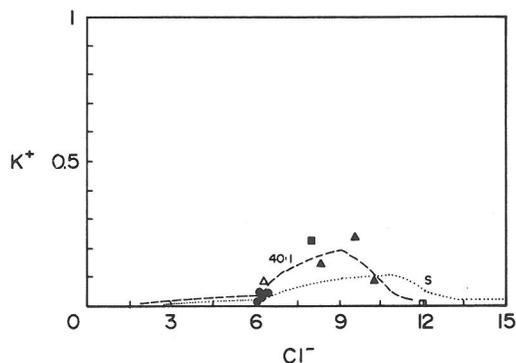


FIG. 8. Calculated evaporation paths for K^+ against Cl^- (in molalities) for the chemical divides bounding the Ca^{2+} - Cl^- brine field and the concentrations of these ions in the Ca^{2+} - Cl^- lakes and karst pools. Donglin Lake—open square, Xiezhuo Lake—filled square, North Huobusun Lake—open triangle, karst pools north of Dabusun Lake—filled triangles, karst pools near springs (west of Xiezhuo Lake)—filled circles.

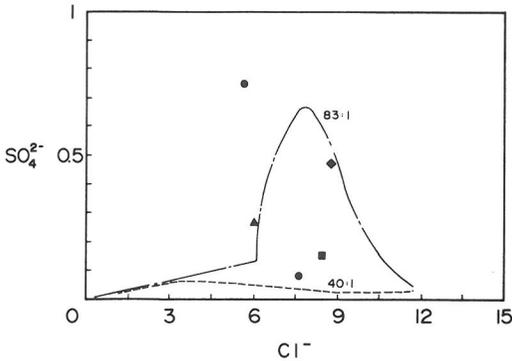


FIG. 9. Calculated evaporation paths for SO_4^{2-} against Cl^- (in molalities) for the chemical divides bounding the Cl^- - SO_4^{2-} brine field and the concentrations of these ions in the Cl^- - SO_4^{2-} lakes. Tuanjie Lake—diamond, Xiaobie Lake—square, Senie Lake—triangle, Dabiele Lake—circles.

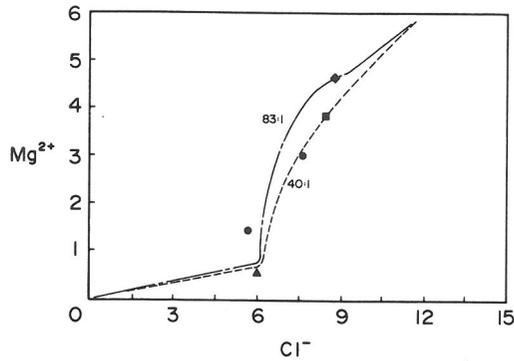


FIG. 10. Calculated evaporation paths for Mg^{2+} against Cl^- (in molalities) for the chemical divides bounding the Cl^- - SO_4^{2-} brine field and the concentrations of these ions in the Cl^- - SO_4^{2-} lakes. Tuanjie Lake—diamond, Xiaobie Lake—square, Senie Lake—triangle, Dabiele Lake—circles.

content for Senie Lake may result from recycling of polyhalite or carnallite, formed when the lake was more concentrated, and later dissolved during dilution of the lake brines.

Brines from Xiaobie and Dabiele Lakes fall within the Cl^- - SO_4^{2-} field (between the 83:1 and 40:1 chemical divides) for SO_4^{2-} (Fig. 9). Both lake brines are close to saturation with respect to calcite, anhydrite, halite and carnallite. The Mg^{2+} concentrations of these lake waters are along the Cl^- - SO_4^{2-} and Ca^{2+} - Cl^- chemical divide (40:1 curve on Fig. 10), slightly lower than expected from the SO_4^{2-} . Both lake brines are highly enriched in K^+ relative to the model evaporation paths (Fig. 11). The high K^+ and low Mg^{2+} may result from recycling of carnallite, and the precipitation of MgSO_4 salts such as epsomite, hexahydrate or kieserite. If this were the case, a proportionately larger decrease in SO_4 would be expected (SO_4^{2-} is present in lower amounts than Mg^{2+} , and therefore precipitation of MgSO_4 salts should be more apparent in the SO_4^{2-}). Another possibility is that these brines may have a higher than estimated proportion of river inflow. Formation of significant quantities of Mg-rich clays could alter the evaporation paths, resulting in higher K^+ and lower Mg^{2+} in the brines.

Lake Dabusun

The brines from Lake Dabusun reported by ZHANG (1987) and in this study are highly concentrated (at or beyond halite saturation) and contain low concentrations of HCO_3^- , SO_4^{2-} and Ca^{2+} (Table 2). Lake Dabusun brines appear to have evolved from source waters along the Ca^{2+} - Cl^- and Cl^- - SO_4^{2-} chemical divide, indicating a ratio of about

40 parts river water to one part spring water (Fig. 3). The Golmud River flows into the lake providing Na^+ - HCO_3^- - SO_4^{2-} waters. Groundwaters, derived from the karst zone springs, also enter the lake along its north edge, providing Ca^{2+} - Cl^- brine input. These two inflow types mix in proportions such that the equivalents of Ca^{2+} are nearly equal to the combined equivalents of HCO_3^- and SO_4^{2-} . Therefore, nearly all of the Ca^{2+} , HCO_3^- and SO_4^{2-} precipitate as CaCO_3 and CaSO_4 salts at relatively low brine concentrations.

The K^+ content of most Lake Dabusun brines analysed is much higher than that predicted along the Ca^{2+} - Cl^- and Cl^- - SO_4^{2-} chemical divide (the 40:1 curve in Fig. 12). This may be the result of recycling of K^+ from carnallite deposits along the lake

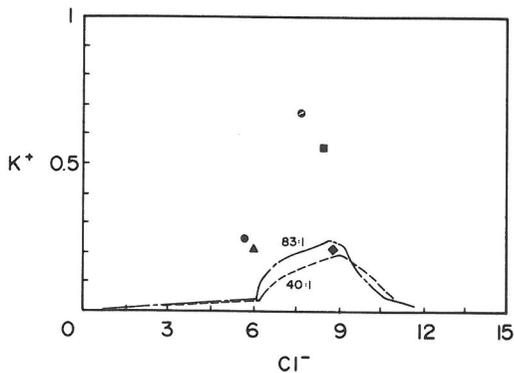


FIG. 11. Calculated evaporation paths for K^+ against Cl^- (in molalities) for the chemical divides bounding the Cl^- - SO_4^{2-} brine field and the concentrations of these ions in the Cl^- - SO_4^{2-} lakes. Tuanjie Lake—diamond, Xiaobie Lake—square, Senie Lake—triangle, Dabiele Lake—circles.

shore. Carnallite was present in salt flats along the north shore of the lake in 1987, and along both the north and south shores of the lake in 1988. The extent and thickness of the carnallite beds has varied over the past few decades, with complete dissolution of the carnallite beds occurring during some years (ZHANG, 1987). However, the Mg^{2+} concentrations of Lake Dabusun brines are lower in Mg^{2+} than predicted, especially if recycling of carnallite occurs (Fig. 13). Based on the excess of K^+ in the brines relative to the predicted evaporation path, carnallite dissolution should result in an elevation of the Mg^{2+} in the brines of up to 0.4 m. The majority of the Lake Dabusun brines are near the evaporation curve for the Ca^{2+} - Cl^- and Cl^- - SO_4^{2-} chemical divide, but the Mg^{2+} contents are mostly lower than predicted, not higher. The discrepancy may indicate significant removal of Mg^{2+} from solution (possibly 20% or more of the total input) to form Mg-rich clays.

SUMMARY OF LAKE BRINE ORIGIN

The Qaidam Basin, located at high elevation on the Qinghai-Tibet Plateau, contains the largest modern accumulations of potash salts found anywhere in the world. These deposits leave no doubt as to the possibility of forming large, non-marine potash deposits. Potash salts develop because of the mixed inflow parent waters. "Normal" meteoric waters flow into the basin from the surrounding mountain ranges. The rivers are the major source of water to the basin, and control the position of the many lakes located on the Qarhan salt plain. The chemical evolution of the river waters is altered because of the inflow of Ca^{2+} - Cl^- spring waters. The

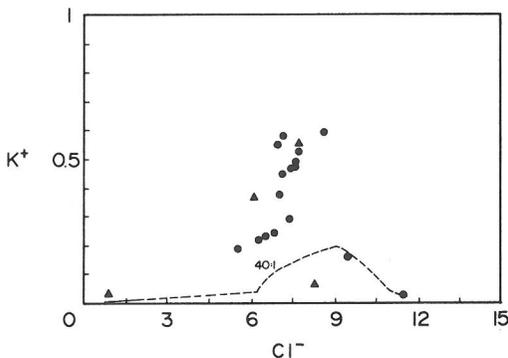


FIG. 12. Calculated evaporation paths for K^+ against Cl^- (in molalities) for brines along the Ca^{2+} - Cl^- and Cl^- - SO_4^{2-} chemical divide and the concentrations of these ions in Lake Dabusun (circles) and West Dabusun Lake (triangles) brines. Brines at carnallite saturation (above about 9 m Cl^-) are along the calculated trend, less concentrated brines are generally higher in K^+ than predicted.

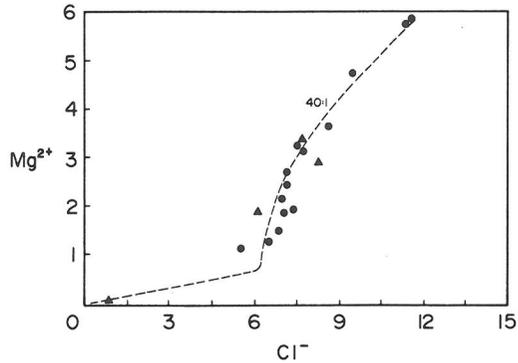


FIG. 13. Calculated evaporation paths for Mg^{2+} against Cl^- (in molalities) for brines along the Ca^{2+} - Cl^- and Cl^- - SO_4^{2-} chemical divide and the concentrations of these ions in Lake Dabusun (circles) and West Dabusun Lake (triangles) brines. Brine analyses scatter along the calculated 40:1 evaporation path (as do Na^+ , Ca^{2+} , HCO_3^- and SO_4^{2-} , not shown), unlike K^+ in Fig. 12.

amount of water brought in by these springs is small, relative to the river inflow. However, the spring waters are far more concentrated than the river waters and contribute significant quantities of dissolved solutes.

Addition of small amounts of Ca^{2+} - Cl^- spring waters produce evolved brines which are depleted in HCO_3^- relative to evolved river inflow. The HCO_3^- precipitates early in the evaporation sequence as a calcium carbonate, rather than remaining in solution and precipitating as sodium carbonate or sodium bicarbonate during the later stage of evaporation. Mixed inflow brines may evolve to yield mineral paragenetic sequences very similar to the seawater sequence.

Slightly higher proportions of spring inflow produce evolved brines depleted in both HCO_3^- and SO_4^{2-} relative to evolved river waters. Progressive increase in the proportion of Ca^{2+} - Cl^- spring inflow results in the precipitation of HCO_3^- and SO_4^{2-} early in the evaporation sequence as calcium carbonate and calcium sulfate. The $MgSO_4$ -bearing salts precipitate at increasingly later stages of evaporation, and finally evolved brines form no $MgSO_4$ -bearing salts. These brines produce "MgSO₄ deficient" mineral sequences, and may precipitate CaCl₂-bearing salts upon extreme evaporation.

The modern lake brines and salts found on the Qarhan salt plain can be accounted for by mixing varying proportions of Na^+ - HCO_3^- - SO_4^{2-} river water and Ca^{2+} - Cl^- spring water. Lakes located along the north edge of Qarhan, in the area of spring inflow, have the highest proportion of spring water input, and contain Ca^{2+} - Cl^- brines. Lakes along the

south edge of Qarhan, away from the spring inflow, have the highest proportion of river water input, but are influenced by spring inflow. These lakes contain Cl^- - SO_4^{2-} brines. A simple evaporation-mineral precipitation model accounts for most of the observed brine compositions. Recycling of salts and the formation of Mg-rich clays may also influence lake brine compositions.

IMPLICATIONS FOR ANCIENT EVAPORITES

Many ancient evaporites, thought to have a seawater parentage, are deficient in MgSO_4 salts (BORCHERT and MUIR, 1964; BRAITSCH, 1971; VALYASHKO, 1972; HARDIE, 1990). The potash deposits of the Qaidam Basin may be used to develop two possible explanations for these MgSO_4 deficient evaporites. First, the deposits may be non-marine, and have formed in a similar manner to the Qaidam Basin evaporites with mixed river water and spring water inflow. Second, these deposits may have had a mixed seawater and spring water parentage, with or without significant meteoric water influence.

Mixed-source evaporites may be difficult, or impossible, to identify in the geologic record. In part, this is because the water and solutes may be predominantly derived from one, or more than one source. For instance, at Qarhan the major source of water, HCO_3^- and SO_4^{2-} is meteoric, whereas spring inflow is the major source of Cl^- and a significant source of the major cations. Therefore, the stable isotopes (H, O, C, S) in these mixed source brines are dominated by the meteoric source. However, the major element composition and mineral precipitation sequence is strongly influenced by the spring water input. Great Salt Lake, Utah, has a similar mixed source inflow, with nearly all of the water from Na^+ - HCO_3^- - SO_4^{2-} meteoric sources and a significant input of Ca^{2+} - Cl^- spring water (SPENCER *et al.*, 1985b). Great Salt Lake contains Cl^- - SO_4^{2-} brines.

Modification of the saline mineral sequence in seawater-sourced evaporite deposits may occur from the input of similar types of spring waters as are present at Qarhan. As is true for non-marine systems, relatively small proportions of highly concentrated Ca^{2+} - Cl^- waters may significantly alter the composition of evolved brines. Higher proportions of Ca^{2+} - Cl^- waters mixed with seawater yield MgSO_4 -bearing salts later in the evaporation sequence. Evolved brines, deficient in MgSO_4 -bearing salts, can be generated by addition of a few percent of these waters to seawater. Because only small amounts of Ca^{2+} - Cl^- spring waters are necessary to alter the paragenesis, the water isotopes (H and O)

may retain the seawater signal. Waters rich in Ca^{2+} - Cl^- , in general, contain only small quantities of HCO_3^- and SO_4^{2-} , therefore, isotopes of C and S from mixed source brines may also give a seawater signal. Trace elements may also have a dominant seawater or spring water source in such mixed source brines. The salts found in mixed source evaporites, especially the highly soluble chloride salts, may come dominantly from the spring water source.

Mixtures of small quantities of Ca^{2+} - Cl^- spring waters to seawater can explain the mineralogy of the MgSO_4 deficient class of ancient evaporites. Many large ancient evaporites belong to this class. The proportion of spring to seawater in the inflow could determine the saline mineral paragenesis. Evaporites such as those found in the Early Cretaceous rift deposits of Brazil and the Congo Basin (WARDLAW, 1972) or the Late Cretaceous of the Khorat Plateau of Thailand (HITE and JAPAKESETR, 1979), which contain the CaCl_2 -bearing salt tachyhydrite, appear to evolve from inflow with a relatively large proportion of non-marine, Ca^{2+} - Cl^- waters. The MgSO_4 deficient Devonian Prairie Evaporite of Canada, along with many other deposits with a similar mineral assemblage, can be derived by a smaller influx of Ca^{2+} - Cl^- water added to a seawater source. Evidence for circulation of Ca^{2+} - Cl^- hydrothermal waters in western Canada during the Devonian is given by AULSTEAD and SPENCER (1985), SPENCER (1987) and AULSTEAD *et al.* (1988). Therefore, the Prairie Evaporite appears to have a mixed seawater-hydrothermal water parentage. Deposits such as the Permian Salado Formation of New Mexico, which contain MgSO_4 salts, but in smaller amounts than expected from the evaporation of seawater, may also have received inflow from Ca^{2+} - Cl^- waters.

Acknowledgements—We are indebted to Hans Eugster, who kindled our interest in the potash deposits of Qarhan after his visits in the early 1980's and for his assistance in setting up our cooperative research. Comments by Blair Jones and Wayne Nesbitt improved the manuscript. This work is supported by grants from the Petroleum Research Fund, administered by the American Chemical Society (PRF-18652-G2 and 21130-AC2), the National Science Foundation (U.S.A.), the Natural Science and Engineering Research Council (Canada) and Academia Sinica (China).

REFERENCES

- AULSTEAD K. L. and SPENCER R. J. (1985) Diagenesis of the Keg River Formation, northwestern Alberta: fluid inclusion evidence. *Bull. Can. Petrol. Geol.* 33, 167-183.

- AULSTEAD K. L., SPENCER R. J. and KROUSE H. R. (1988) Fluid inclusion and isotopic evidence on dolomitization, Devonian of western Canada. *Geochim. Cosmochim. Acta* **52**, 1027–1035.
- BODINE M. W. and JONES B. F. (1986) The salt norm: a quantitative chemical-mineralogical characterization of natural waters. U.S. Geol. Surv., Water Res. Invest. Rep. 86-4086.
- BODINE M. W. and JONES B. F. (1990) Normative analysis of groundwaters from the Rustler Formation associated with the waste isolation pilot plant (WIPP), southeastern New Mexico. In *Fluid-Mineral Interactions: A Tribute to H. P. Eugster* (eds. R. J. SPENCER and I-MING CHOU), Spec. Publ. No. 2, pp. 213–269. The Geochemical Society.
- BORCHERT H. and MUIR R. O. (1964) *Salt Deposits: The Origin, Metamorphism and Deformation of Evaporites*. 300 pp. D. Van Nostrand Co., Princeton, New Jersey.
- BRAITSCH O. (1971) *Salt Deposits, Their Origin and Composition*. 279 pp. Springer-Verlag, New York.
- CARPENTER A. B. (1978) Origin and chemical evolution of brines in sedimentary basins. *Oklahoma Geol. Surv. Circ.* **79**, 60–77.
- CARPENTER A. B., TROUT M. L. and PICKETT E. E. (1974) Preliminary report on the origin and chemical evolution of lead- and zinc-rich oil field brines in central Mississippi. *Econ. Geol.* **69**, 1191–1206.
- COLLINS A. G. (1975) *Geochemistry of Oilfield Brines*. 496 pp. Elsevier.
- D'ANS J. (1933) *Die Losungsgleichgewichte der Systeme der Salze Ozeanischer Salzblagerungen*. 245 pp. Kall-Forschungsanstalt, Verh. Gesel. Ackerbau, Berlin.
- EUGSTER H. P., HARVIE C. E. and WEARE J. H. (1980) Mineral equilibria in a six-component seawater system, Na-K-Mg-Ca-SO₄-Cl-H₂O, at 25°C. *Geochim. Cosmochim. Acta* **44**, 1335–1347.
- EVANS R. (1970) Genesis of sylvite and carnallite-bearing rocks from Wallace, Nova Scotia. In *Third Symposium on Salt* (eds. J. L. RAU and L. F. DELLWIG), pp. 239–245. Northern Ohio Geol. Soc., Cleveland, Ohio.
- GRAF D. L., MEENTS W. F., FRIEDMAN I. and SHIMP N. F. (1966) The origin of saline formation waters., III: Calcium Cl⁻ waters. *Illinois State Geol. Surv. Circ.* **397**.
- HARDIE L. A. (1983) Origin of CaCl₂ brines by basalt-seawater interaction: Insights provided by some simple mass balance calculations. *Contrib. Mineral. Petrol.* **82**, 205–213.
- HARDIE L. A. (1984) Evaporites: marine or non-marine? *Amer. J. Sci.* **284**, 193–240.
- HARDIE L. A. (1990) Potash evaporites, rifting and the rôle of hydrothermal brines. *Amer. J. Sci.* **290**, 43–106.
- HARDIE L. A. and EUGSTER H. P. (1970) The evolution of closed-basin brines. *Mineral. Soc. Amer. Spec. Paper* **3**, 273–290.
- HARDIE L. A., LOWENSTEIN T. K. and SPENCER R. J. (1985) The problem of distinguishing between primary and secondary features in evaporites. In *Sixth International Symposium on Salt* (eds. B. C. SCHREIBER and H. L. HARNER), pp. 11–39. Salt Institute, Washington D.C.
- HARVIE C. E., MOLLER N. and WEARE J. H. (1984) The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-H₂O system to high ionic strengths at 25°C. *Geochim. Cosmochim. Acta* **48**, 723–751.
- HARVIE C. E. and WEARE J. H. (1980) The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO₄-H₂O system from zero to high concentration at 25°C. *Geochim. Cosmochim. Acta* **44**, 981–997.
- HARVIE C. E., WEARE J. H., HARDIE L. A. and EUGSTER H. P. (1980) Evaporation of seawater: calculated mineral sequences. *Science* **208**, 498–500.
- HITE R. J. and JAPAKSETR T. (1979) Potash deposits of the Khorat Plateau, Thailand and Laos. *Econ. Geol.* **74**, 448–458.
- HOLLAND H. D. (1972) The geologic history of sea water—an attempt to solve the problem. *Geochim. Cosmochim. Acta* **36**, 637–651.
- HOLLAND H. D., LAZAR B. and MCCAFFREY, M. (1986) Evolution of the atmosphere and oceans. *Nature* **320**, 27–33.
- HOLSER W. T. (1979) Trace elements and isotopes in evaporites. In *Marine Minerals* (ed. R. G. BURNS), Short Course Notes 6, Ch. 9, pp. 295–346. Mineral. Assoc. Amer.
- LOWENSTEIN T. K. and SPENCER R. J. (1990) Syndepositional origin of potash evaporites: Petrographic and fluid inclusion evidence. *Amer. J. Sci.*, **290**, 1–42.
- LOWENSTEIN T. K., SPENCER R. J. and ZHANQ PENGXI (1989) Origin of ancient potash evaporites: Clues from the modern nonmarine Qaidam Basin of western China. *Science* **245**, 1090–1092.
- ROEDDER E. (1972) The composition of fluid inclusions. U.S. Geol. Surv. Prof. Paper 440-JJ.
- SONNENFELD P. (1984) *Brines and Evaporites*. 613 pp. Academic Press Inc., Orlando, Florida.
- SPENCER R. J. (1982) *Geochemical Evolution of Great Salt Lake, Utah*. Ph.D. Dissertation, The Johns Hopkins University, Baltimore, Maryland. 309 pp.
- SPENCER R. J. (1987) Origin of Ca-Cl brines in Devonian formations, western Canada sedimentary basin. *Appl. Geochem.* **2**, 373–384.
- SPENCER R. J., BAEDECKER M. J., EUGSTER H. P., FORESTER R. M., GOLDBABER M. B., JONES B. F., KELTS K., MCKENZIE J., MADSEN D. B., RETTIG S. L., RUBIN M. and BOWSER C. J. (1984) Great Salt Lake, and precursors, Utah: the last 30,000 years. *Contrib. Mineral. Petrol.* **86**, 321–334.
- SPENCER R. J., EUGSTER H. P., JONES B. F. and RETTIG S. L. (1985a) Geochemistry of Great Salt Lake, Utah, I: Hydrochemistry since 1850. *Geochim. Cosmochim. Acta* **49**, 727–737.
- SPENCER R. J., EUGSTER H. P. and JONES B. F. (1985b) Geochemistry of Great Salt Lake, Utah, II: Pleistocene-Holocene Evolution. *Geochim. Cosmochim. Acta* **49**, 739–747.
- SPENCER R. J., MOLLER N. and WEARE J. H. (1990) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO₄-H₂O system at temperatures below 25°C. *Geochim. Cosmochim. Acta* **54**, (in press).
- STEWART F. H. (1963) Marine evaporites. U.S. Geol. Surv. Prof. Paper 440-Y.
- VALYASHKO M. G. (1972) Playa lakes—a necessary stage in the development of a salt-bearing basin. In *Geology of Saline Deposits* (ed. G. RICHTER-BERNBURG), Earth Sciences Series 7, pp. 41–51. UNESCO, Paris.
- WARDLAW N. C. (1968) Carnallite-sylvite relationships in the Middle Devonian Prairie Evaporite Formation Saskatchewan. *Geol. Soc. Amer. Bull.* **79**, 1273–1294.
- WARDLAW N. C. (1972) Unusual marine evaporites with salts of calcium and magnesium chloride in Cretaceous basins of Sergipe, Brazil. *Econ. Geol.* **67**, 156–168.