(*30*). A range of experiments revealed a complicated bimolecular chemistry at higher desorption laser fluences and is the subject of continuing analysis.

That C_{18} (**1**) can be formed with high efficiency through this process is indicated by two other experiments: (i) detection of the He-cooled ions produced directly by ultraviolet radiation during the evaporation process, and (ii) same as (i) but without He cooling gas (*31*). In the latter case (Fig. 4c), both anthracene and C_{18}^+ ions are dominant. In the former case (Fig. 4c, inset), the C_{18}^+ ion (and $C_{18}^+ \cdot H_2O$ contaminant ion) is actually dominant over a range of heating and ionization conditions. We take these results as strong evidence that C_{18} is the terminal product of the dominant fragmentation pathway. Besides supporting the precursor status of compound **5** in chemical synthesis, these results also allow one to envisage spectroscopic experiments on the cooled C_{18} molecules in molecular beams. It should be possible to isolate preparative quantities of cyclo[18]carbon **1** from flash vacuum pyrolysis reactions (*32*).

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Origin of Ancient Potash Evaporites: Clues from the Modern Nonmarine Qaidam Basin of Western China

TIM K. LOWENSTEIN, RONALD J. SPENCER, ZHANG PENGXI

Modern potash salt deposits and associated brines of the Qaidam Basin, western China, demonstrate that some anomalous marine evaporites may have formed from nonmarine brines instead of seawater. Qaidam Basin brines are derived from meteoric river inflow mixed with small amounts of CaCl spring inflow similar in composition to many saline formation waters and hydrothermal brines. Evaporation of spring-enriched inflow yields a predicted mineral sequence including carnallite, bischofite, and tachyhydrite that is identical to several anomalous marine evaporites. Other mixtures of river and spring inflow produce the salt assemblage expected from evaporation of seawater.

EVAPORITES ARE SEDIMENTARY rocks that have formed by precipitation from waters at the earth's surface. Ancient evaporites have been used to track the chemistry of ancient surface waters, especially seawater (*1, 2*). Study of marine evaporites has led to the general, but not unanimous, consensus that the major element chemistry of seawater has not changed significantly during the Phanerozoic [the last ~600 million years (*2, 3*)]. One major problem, however, is that ancient evaporites containing soluble potash salts fail to match the mineralogical sequences predicted in the evaporation of modern seawater. For example, more than half of 50 well-known Phanerozoic potash-bearing evaporites have been called "unusual" or "$MgSO_4$-deficient" marine evaporites because they are missing $MgSO_4$ salts that are characteristic of a normal seawater evaporation sequence (*1, 4, 5*). The discrepancy between predicted versus observed potash-bearing mineral sequences has been attributed either to departures of the parent waters from seawater composition or to diagenetic alteration of the original marine mineral sequence (*1, 2, 4, 6, 7*).

The origin of ancient potash evaporites, in terms of parent waters (seawater versus nonmarine inflow), depositional environments (deep versus shallow waters), and timing of formation (primary precipitates versus diagenetic alteration products) remains controversial largely because no modern potash-bearing basins have been de-

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T. K. Lowenstein, Department of Geological Sciences and Environmental Studies, State University of New York at Binghamton, Binghamton, NY 13901.
R. J. Spencer, Department of Geology and Geophysics, University of Calgary, Calgary, Alberta T2N 1N4 Canada.
Zhang Pengxi, Qinghai Institute of Salt Lakes, Academia Sinica, Xining, Qinghai Province, People's Republic of China.

scribed in detail. One of the few places in the world where potash salts are now widely accumulating is in the Qaidam Basin of Qinghai Province, western China. We have studied the sedimentology of these modern deposits and the geochemistry of the inflow waters and subsequent brine evolution paths to resolve whether anomalous ancient potash evaporites could have formed from nonmarine brines, as do those in the Qaidam Basin.

The Qaidam Basin is a closed, nonmarine basin with an area of 120,000 km^2 (Fig. 1) (*8*). The center of the present basin, 2800 m above sea level, contains large dry areas underlain by salt and a number of shallow (<1 m deep) saline lakes that precipitate salts, including potash minerals. The largest salt deposit in the Qaidam Basin is the 6000-km^2 Qarhan Salt Lake plain (*8*). Qarhan contains ten shallow perennial and ephemeral saline lakes. The largest, Dabusun Lake, has a deposit of the potash salt carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) along its shores (*9*). The entire Qarhan plain contains a permanent ground water brine about 1 m below the surface.

Qarhan is underlain by about equal amounts of salt and siliciclastic sediments, which reach thicknesses of up to 70 m (*8, 9*). On the basis of radiocarbon dating, the base of the salt was deposited about 25,000 years ago (*10*). More than 40 m of halite and siliciclastic mud are deposited in the Dabusun Lake area, and carnallite also occurs in the top 10 m. Halite layers consist of a framework of halite crystals that have been modified in texture by early diagenetic dissolution, cementation, and displacive growth. Anhedral crystals of carnallite commonly fill voids between halite crystals. On the basis of its texture and the occurrence of large deposits near the surface, we interpret the carnallite as an early diagenetic cement. Texturally similar carnallite and sylvite (KCl) cements are also common in ancient potash evaporites such as the Permian Salado salts in New Mexico and the Devonian Prairie Formation in Saskatchewan (*11*).

A major question, then, concerns how inflow waters to the Qaidam Basin evolve into brines capable of precipitating potash salts. In the Qarhan area, inflow consists of perennial river water, for example, the Golmud River, and spring waters (Fig. 1), which emerge at the surface at the northern margin of Qarhan along a linear fault zone (*9*). Solution associated with these waters has formed a zone of karst along the fault.

The river waters entering Qarhan are enriched in $NaHCO_3$ and are not unlike average world river composition except that Qarhan river waters contain relatively more Na and Cl and less Ca (Fig. 2). The waters are meteoric in origin and contain solutes derived from low-temperature weathering reactions between bedrock and rainwater (*12*). The spring inflow is quite different in composition (Fig. 2). The cations are dominated by Na, with lesser Ca, Mg, and K; Cl is the only significant anion; the waters contain little SO_4 and virtually no HCO_3. Spring waters contain more Ca on an equivalent basis than $SO_4 + HCO_3 + CO_3$. These waters belong to a special class of waters called CaCl brines because part of their Ca is balanced by Cl. Other CaCl brines with similar chemical compositions include saline formation waters and hydrothermal brines (*1, 4, 13, 14*). Most CaCl brines are produced by circulation and interaction of hot ground water with sediments or rocks at diagenetic to low-grade metamorphic conditions (*1, 4, 14*). Based on their composition, the spring waters of Qarhan are interpreted as deep subsurface brines that have risen to the surface along faults.

Various mixtures of river and spring inflow, followed by evaporative concentration, can produce the variety of saline lake brines found at Qarhan (Fig. 3). River waters, with SO_4 and HCO_3 in excess of Ca, would, upon precipitation of calcite, evolve into calcium-depleted, Na-HCO_3-SO_4 brines. Spring waters, with Ca equivalents greater than SO_4 and HCO_3, evolve into CaCl brines, virtually free of SO_4 and HCO_3. On mixing, the chemical divide separating waters that evolve into CaCl brines is about 40 parts river water to 1 part spring water. Mixtures between about 40 and 83 parts river water to 1 part spring water produce Na-Cl-SO_4–rich brines after precipitation of calcite and gypsum; Na-HCO_3-SO_4 brines form from mixtures with a ratio of river to spring water greater than 83:1.

The lakes of Qarhan have brine compositions that lie along predicted evaporation

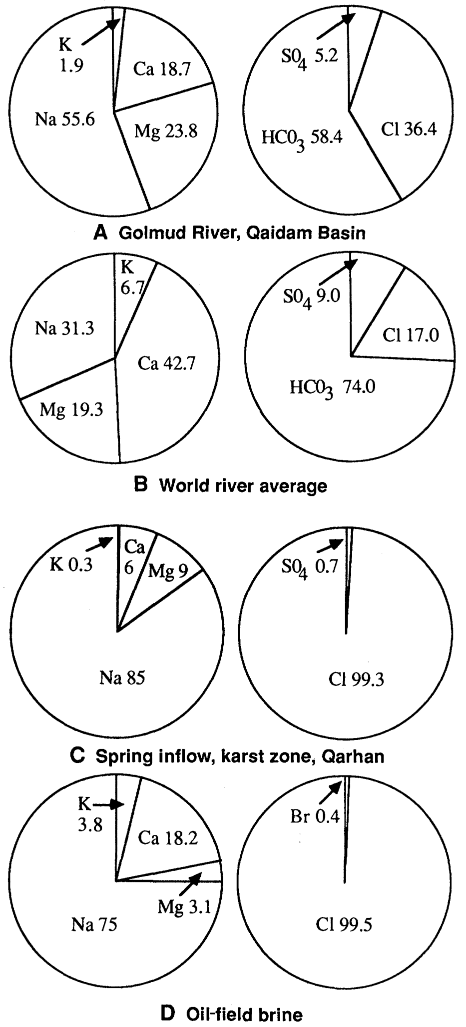

Fig. 2. Chemical composition of inflow waters, Qarhan (in molal percent cations and molal percent anions). (**A**) Golmud River (500.3 ppm TDS) compared with (**B**) average world river composition (105.1 ppm TDS) (*17*). (**C**) Spring inflow (80,900 ppm TDS) compared with (**D**) saline formation water (248,000 ppm TDS), Smackover Formation, Mississippi Salt Dome Basin (84-MS-13) from (*13*); TDS, total dissolved solids, in parts per million.

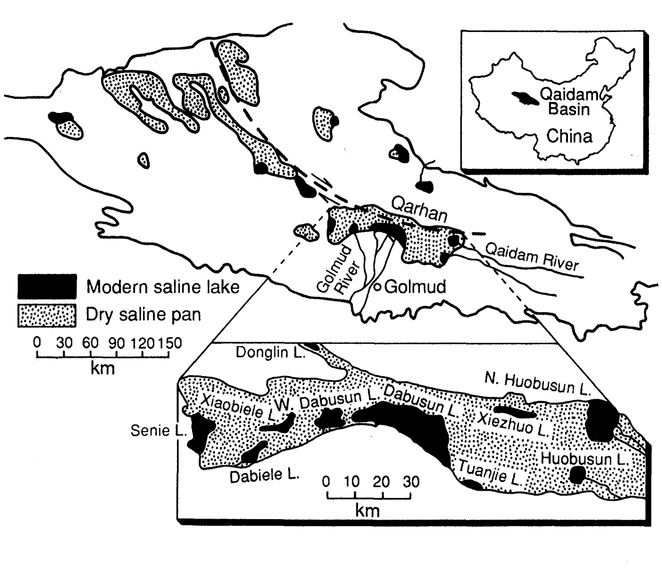

Fig. 1. The Qaidam Basin is located along the northern margin of the Qinghai-Tibet-Plateau. The surrounding mountains are between 4000 and 5000 m above sea level (*8*). Modern saline lakes and dry saline flats occur in the center of the Qaidam Basin. Dashed line through northern margin of Qarhan and extending northwest across the Qaidam Basin is the fault zone along which springs are found. Alluvial fans and dunes occupy much of the marginal area (*8, 9*); L., lake.

paths for mixtures of river inflow and spring inflow (Fig. 3C). Brines formed from mixtures with a relatively large proportion of spring inflow evolve into CaCl brines. Such CaCl-rich lake waters and ground waters are all located near the karst zone where spring waters emerge at the surface (Fig. 1). The Na-Cl-SO_4–rich brines form from mixtures dominated by river inflow, between about 40 and 100 parts river water to 1 part spring inflow. Lakes with this brine composition are located near major river inflow and far from the CaCl spring inflow at the karst zone. Dabusun Lake apparently contains brines derived from a blend of about 40 parts river water to 1 part spring water. In this 40:1 mixture, Ca equivalents are about equal to HCO_3 plus SO_4 equivalents. Therefore, evaporation and precipitation of calcite and gypsum leaves the evolved brines depleted in Ca, HCO_3, and SO_4. It appears that the evolved brines are quite scattered in composition, but all the Dabusun brines are Na-Mg-Cl–rich, with subordinate Ca or SO_4.

Mineral precipitation sequences predicted to form from equilibrium evaporation of Qarhan waters at 25°C vary, depending upon the particular blend of river and spring inflows. River waters evolve into Na-HCO_3-SO_4 brines that should produce a $NaHCO_3$-Na_2CO_3-Na_2SO_4 salt assemblage. The lack of such brines or mineral assemblages at Qarhan supports the observation that in order to precipitate potash evaporites in the Qaidam Basin, some spring inflow is required. Addition of small amounts of spring inflow, as little as 1 to 2%, exerts a significant influence over brine evolution paths and saline mineral sequences. Evaporative concentration of between 40 and 83 parts river water to 1 part spring water yields a Na-Mg-K-Cl-SO_4 brine. The mineral sequences predicted to form contain calcite, gypsum-anhydrite, halite, the sulfate salts polyhalite ($2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$) and kieserite ($MgSO_4 \cdot H_2O$), and the late-stage chlorides carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) and bischofite ($MgCl_2 \cdot 6H_2O$). These particular sequences are similar to those predicted to form from evaporation of modern seawater and they contain the identical final invariant salt assemblage (*1, 5*). Thus, determining the parent waters of ancient evaporites, based upon saline mineral sequences, may be complicated by the possibility that an entirely nonmarine brine can produce a salt assemblage characteristic of modern seawater.

Finally, evaporative concentration of spring inflow or any water with greater than 2.5% spring inflow (a ratio of river to spring inflow less than 40:1) generates a CaCl brine. The mineral sequence predicted to form is calcite, gypsum-anhydrite, halite, followed by carnallite, bischofite, and finally the Ca-Mg-Cl salt tachyhydrite. This is the mineral sequence found in Lower Cretaceous rift evaporites of Brazil and the Congo Basin of west Africa (*15*), as well as in Upper Cretaceous evaporites of the Khorat Plateau of Thailand (*16*). These so-called anomalous potash deposits may have formed from nonmarine parent waters. Other ancient potash evaporites deposited in marine settings but which lack the mineral sequences predicted by the evaporation of modern seawater, for example, the Permian Salado salts and the Devonian Prairie evaporites (*7, 11*), may have had small additions of nonmarine waters similar in composition to the CaCl spring inflow of the Qaidam Basin.

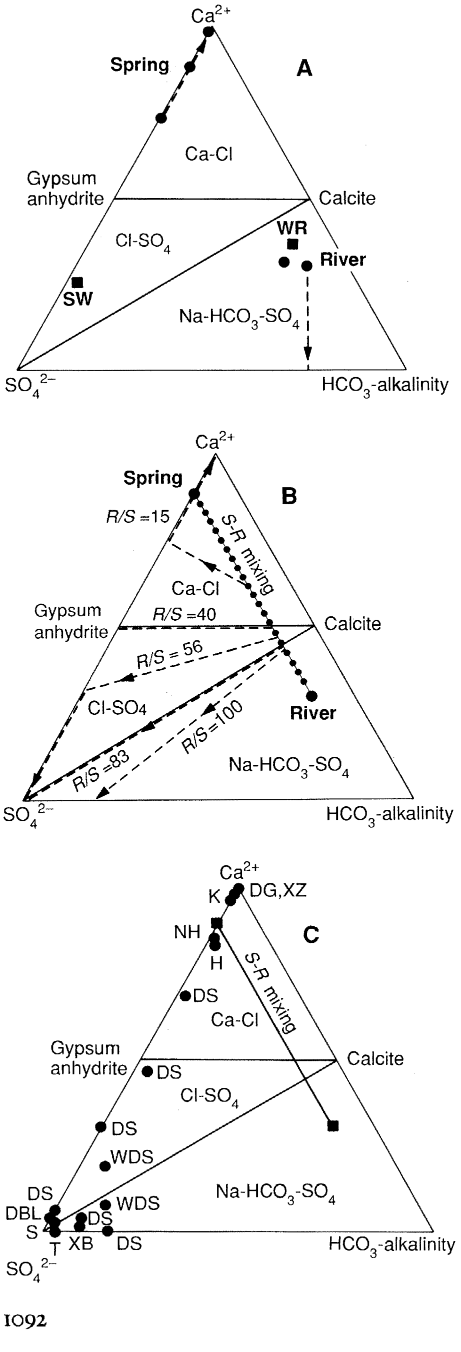

Fig. 3. Ternary Ca-SO_4-HCO_3 phase diagrams illustrating how inflow waters evolve into brines. Calcite is the primary crystallizing phase in virtually the entire space, and the gypsum-anhydrite field hugs the Ca-SO_4 side of the triangle. Two chemical divides (lines from Calcite to SO_4 and Calcite to Gypsum-anhydrite) segregate waters that will evolve, upon evaporation and precipitation of calcite and gypsum, into Ca-Cl brines, Cl-SO_4–rich brines, and Na-HCO_3-SO_4–rich brines. These divides are based on the equivalents of Ca in the inflow waters relative to equivalents of HCO_3 and SO_4. (**A**) Inflow waters of the Golmud River and the karst-zone springs (in equivalents); also shown are average world river composition (WR) (*17*) and seawater composition (SW). (**B**) Evaporation paths for varying mixtures, by weight, of river (*R*) inflow and spring (*S*) inflow (*S-R* mixing line). (**C**) Surface brine compositions at Qarhan (in equivalents); lakes are: DG, Donglin; XZ, Xiezhuo; H, Huobusun; NH, North Huobusun; S, Senie; DBL, Dabiele; XB, Xiaobiele; T, Tuanjie; DS, Dabusun; WDS, West Dabusun; K, karst brine ponds.

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