ISOTOPIC AND CHEMICAL CHARACTERIZATION OF SALINE LAKE AND PLAYA SALTS: IMPLICATION FOR CLIMATE ON EARTH AND MARS

Y.X. Hao¹, Y.H. Qiu¹, L.X.D. Chen², J. Li^{1,3}, W.Y. Liu^{1,4}, M.J. Tang², X.Y. Zhang⁵, Z.C. Niu⁶, J.B.C. Pettersson⁷, S. Wang^{1*}, X.R. Kong^{7*}

¹Department of Environmental Sciences, College of Urban and Environmental Sciences, Northwest University, Xi'an, China, ²State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, ³Xiamen University, Xiamen, China, ⁴Beijing Normal University, Beijing, China, ⁵Key Laboratory of Salt Lake Resources and Chemistry, Key Laboratory for Salt Lake Geology and Environment of Qinghai Province, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, China, ⁶Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China, ⁷Department of Chemistry and Molecular Biology, Atmospheric Science, University of Gothenburg, SE-412 96 Gothenburg, Sweden.

Introduction: Evaporite salts from saline lakes and playas play active roles in the atmospheric cycles and the climate system. Salt particles originated from these sources can be transported together with mineral dust to long distances and further influence the atmospheric processes [1]. Also, saline lakes are continuously being desiccated and transforming to playa covered by evaporite salts, and this process is accelerated by the changing climate and the enhanced water use demand. This process has previously occurred on Mars more than three billion years ago [2]. Some terrestrial regions on Earth have similar history. One example is the Qaidam Basin located in the Qinghai-Tibet Plateau, which transformed from ancient sea and large lakes to current small saline lakes and playa, owing to the extremely low precipitation and high evaporation rates. Given the environmental conditions and chemical features, Qaidam Basin has been considered as a good terrestrial analogue for Mars [3].

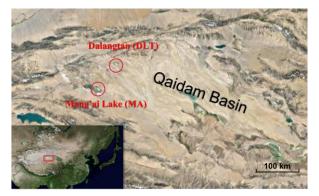


Figure 1. Sampling locations, Mang'ai Feicui Lake (MA) and Dalangtan Playa (DLT), in the Qaidam Basin.

From the chemical perspective, the Qaidam Basin and Mars have common salt evaporites, such as sulfates and chlorides [4]. These salts sampled from the Qaidam Basin are found to exist in highly hydrated forms, which have also been found in the hyper-arid Martian environment. The discovery of such hydrated salts raises the question about the presence of liquid water on Mars [5]. Various observation approaches have demonstrated that the water vapor in the Martian atmosphere is actively interacting with the Martian surface materials [6], through diurnal and seasonal RH fluctuation cycles. Such atmosphere-surface water exchange is hypothesized to be responsible for recurring slope lineae (RSL) and landslides on Martian surface.

In this study, the chemical compositions of Qaidam Basin salt samples in various forms (brines, lakebed lakes, surface salts, and layered salts) are characterized. The connection between the ionic composition and the hygroscopic properties are discussed. Isotopic analysis of two elements, sulfur and chlorine, is carried out to reveal information about the origins of the brines and the evaporites.

Methodology: The salt samples were collected from two saline lakes in the Qaidam Basin (Figure 1). The DLT playa is the second largest dried saline lake in the Qaidam Basin. The MA is a salt pond continuously recharged by underground brine.

Samples in different forms (brines, lakebed salts, crust salts, playa salts, layered salts) from MA and DLT Playa were collected. The brines were taken 2-5 cm below the lake surface; the lakebed salts were sampled directly below the brine sampling points; the crust salts and playa salts were collected from the dry lakebed; the layered hydrated salts were taken at the DLT brine extraction channel. All samples were stored in polyethylene bottles, sealed with Parafilm membranes, and stored at 4 $^{\circ}$ C.

The brines and saturated solutions of salt samples were filtered with qualitative filter paper (Beimu, GB/T1914-2017, pore size $< 20 \ \mu$ m). The saturated solutions of DLT lakebed salts and the hydrated salts of layer 3 were diluted by a factor of 2000, and other samples were diluted by a factor of 1500, so that their concentrations could within the detection limits of ion chromatography (IC). The diluted solutions were then filtered through 0.22 μ m water filter membranes. The cations and anions in the sample solutions were measured simultaneously by the Thermo Fisher Scientific IC system (DX 600). Cations were analyzed using CS12AIC column (Dionex Ion Pac. Thermo Fisher Scientific) with a 30 mmol/l methanesulfonic acid eluent. Anions were determined by AS11-HCIC

column (Dionex Ion Pac, Thermo Fisher Scientific) with a 20 mmol/l KOH eluent.

For sulfur isotope measurement, 5-gram solid salt samples were dissolved in 10 ml ultrapure water. The brines and salt solutions were filtered with filter papers and then filtered through 0.22 µm filter membranes. Each sample was taken 3 ml filtered solution, added 2 ~ 3 drops of hydrochloric acid solution (1:1), shaken well and stood for 30 min, then the pH was detected with pH test paper to ensure the pH is lower than three. 5-ml barium chloride solution (250 g/l) was added to the salt solutions and shaken with a shaker for about 1h to completely mix sulfate and barium ions. After standing for 24 h, white powder was observed at the bottom of the bottle. The solutions were filtered through the cellulose acetate filter membrane by a suction filter pump to obtain a barium sulfate precipitate, which was then repeatedly washed with deionized water. The filter membranes were transferred to clean crucibles and calcined in an 800°C-muffle furnace for 2 hours to obtain pure barium sulfate powder for sulfur isotope determination.

The brine samples of MA and DLT were filled with 50 ml, and the solid salt samples were weighed 50 g to measure the chlorine isotope. The determination of chlorine isotope was completed by Qinghai Salt Lake Institute, Chinese Academy of Sciences.

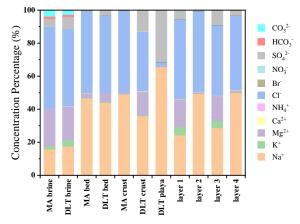


Figure 2. Normalized ionic molar compositions of all samples.

Results: The Hygroscopic results of solid salts show strong connections between the ionic composition and hygroscopic properties though discrepancy exists (Figure 2 and Figure 3), indicating that the hygroscopicity is sensitive to the molecular forms and the hydrate degrees of salts. The δ^{34} S values of samples from MA and DLT show great difference (Figure 4a). The δ^{34} S values of MA samples are comparable to previously reported fresh water, brines and local precipitation, indicating that the MA samples are strongly influenced by materials exchanged from local environments. The DLT samples have higher δ^{34} S

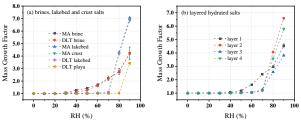


Figure 3. Mass growth factor (m/m_0) as a function of RH. (a) brines, lakebed salts and crust salts, (b) layered hydrated salts. values, which suggest that the material exchanges with surrounding environments are limited. The δ^{37} Cl values are confined within a relatively narrow window compared to literature values. A trend is that the δ^{37} Cl values vary with sample types, i.e., crust > lakebed > brine (Figure 4c). This is likely caused by the isotopic fractionation during evaporite precipitation, where the heavier 37 Cl isotope is preferably precipitated.

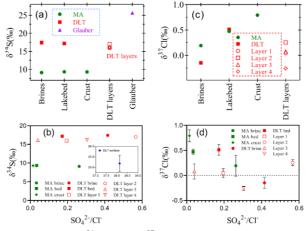


Figure 4. (a) δ^{34} S and (c) δ^{37} Cl values of different sample types collected in MA and DLT. (b) δ^{34} S and (d) δ^{37} Cl values as a function of SO₄²⁻/Cl⁻ ratio.

Acknowledgement: This work is supported by the National Natural Science Foundation of China (41975160), and the Swedish Research Council (2021-04042). X.K. and X.Y.Z. acknowledges the supports from STINT (CH2019-8361) and the Science and Technology Plan Project of Qinghai Province (Grant No. 2021-ZJ-T07), respectively. The sulfur isotopic analyses were conducted in State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences.

References: [1] Gaston, C.J., et al. (2017) EST, 51, 1348-1356. [2] Rapin, W., et al. (2019) NAT GEOSCI, 12, 889-895. [3] Xiao, L., et al. (2017) EARTH-SCI REV, 164, 84-101. [4] Osterloo, M.M., et al. (2010) JGR, 115, E10. [5] Wang, A., et al. (2016) J GEOPHYS RES-PLANET, 121, 678-694. [6] Gough, R.V., et al. (2019) Icarus, 321, 1-13.