

**SURFACE SOLVATION OF MARTIAN SALT ANALOGUES AT LOW RELATIVE HUMIDITIES.** X. R. Kong<sup>1</sup>, S.Y. Zhu<sup>2</sup>, A. Shavorskiy<sup>2</sup>, J. Li<sup>3</sup>, W.Y. Liu<sup>3</sup>, P. Corral Arroyo<sup>4</sup>, R. Signorell<sup>4</sup>, S. Wang<sup>3</sup> and J. B. C. Pettersson<sup>1</sup>, <sup>1</sup>Department of Chemistry and Molecular Biology, Atmospheric Science, University of Gothenburg, SE-41296 Gothenburg, Sweden, <sup>2</sup>MAX IV Laboratory, Lund University, SE221-00 Lund, Sweden, <sup>3</sup>Shaanxi Key Laboratory of Earth Surface System and Environmental Carrying Capacity, Northwest University, Xi'an 710127, China, <sup>4</sup>Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland.

**Introduction:** As one of the largest regions of saline lakes and playas on Earth, Qaidam (meaning *salt flat* in Mongolian) Basin is considered as a good terrestrial analogue for Mars.[1] The Qaidam Basin is located in the Qinghai-Tibet Plateau, and the specific geographic conditions make the location extremely sensitive to climate change. Recent explorations and studies revealed that the Martian crusts have similar compositions. Sulfates, chlorides and carbonates are the common salt compositions deposited both in the Qaidam Basin and on Mars.[2] Sulfate and chloride components sampled from the Qaidam Basin exist in a highly hydrated form in spite of the hyper-arid conditions, similar to the Martian environment.[3] Highly hydrated salts have been identified on Mars, which raises the question about the presence of liquid water on Mars. Also, the hydrated forms of sulfate might be the cause of present-day topographic changes observed on Mars.

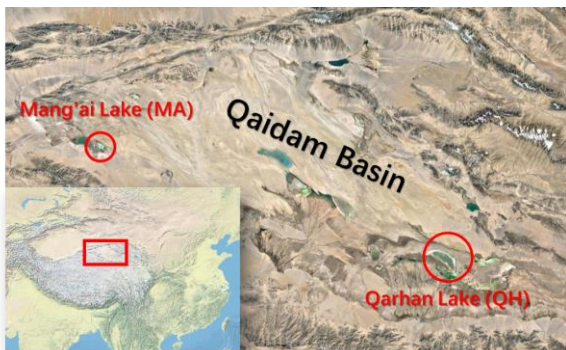


Figure 1 Sampling locations, Mang'ai Lake (MA) and Qarhan Lake (QH), in the Qaidam Basin.

Another recently discovered phenomenon on Mars is the recurring slope lineae (RSL), which is hypothesized to be mainly caused by hydrous chlorides and oxychlorine salts through deliquescence. However, the water vapor levels required for deliquescence are much higher than those in the present Martian atmosphere, thus the RSL formation mechanism and the roles of salts need to be further understood. The knowledge gap of salt-water interactions has limited our understandings on the Martian environment, and a more comprehensive picture on the governing mechanisms may greatly enhance our understanding and accelerate the Martian exploration.

Given these aspects, the Qaidam salts can be regarded as proxies for inland-originated atmospheric

salt particles on Earth and salts on Mars. A better understanding of the interactions between gas phase water and the Qaidam salts will shed lights on the roles of salt mixtures in the environments on both Earth and Mars. Another merit of studying saline lake salts is that these salts are relatively simple in terms of low biogenic activities and low levels of organics, which serves as an excellent bridge between laboratory pure systems and realistic complex systems. In this study, we use a state-of-the-art experimental approach, ambient pressure X-ray photoelectron spectroscopy (APXPS), to study the influence of relative humidity (RH) on the surface chemical environment of Qaidam salts. The near-edge X-ray absorption fine structure (NEXAFS) approach is also used to probe the local environment on the salt surface under interactions with water vapor. Such synchrotron-based surface-sensitive approach has shown promising capacity in probing detailed and novel physicochemical processes on salt surfaces.[4, 5]

**Methodology:** The salt samples were collected from two saline lakes in the Qaidam Basin (Figure 1). The Qaidam paleolake was migrating from west (the Mang'ai Pond, MA) to east (the Qarhan Lake, QH), and salt mixtures from these two lakes are selected to represent lakes in different development stages. The Qarhan (QH) Lake is located in the south-central part of the Qaidam Basin. It is one of the largest inland saline lakes in the world and the largest soluble potassium magnesium salt deposit in China. The Mang'ai (MA) Pond is located on the western edge of the Qaidam Basin, lying on the Kunlun Mountain in the south and Altun Mountain in the north. It is a salt pond continuously recharged by underground brine.

The acquired brines were taken 2-5 cm below the lake surface, and then filtered by filter papers (Beimu, GB/T1914-2017, pore size < 20  $\mu\text{m}$ ) within 48 hours after sampling. The lakebed salts were collected at the same sampling points as brines. The salt crusts were collected from nearby playa fields. All samples were stored in polyethylene bottles and sealed with Parafilm membrane, and then stored in fridge at 4  $^{\circ}\text{C}$ .

Saturated solutions of lakebed and crust salts were prepared by dissolving them in ultrapure water. These saturated solutions, including sampled brines, were diluted by a factor of 1000 to meet the upper detection limits of ion chromatography (IC). The diluted solutions were then filtered through 0.22  $\mu\text{m}$  water filter membranes. The cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) and anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) were measured by the Dionex

AQUION IC system (Thermo Scientific, USA). Cations were analyzed using CS12A IC columns (Dionex IonPac, ThermoFisher) with 30 mmol L<sup>-1</sup> methanesulfonic acid eluent. Anions were determined by AS11-HC IC columns (Dionex IonPac, ThermoFisher) with 20 mmol L<sup>-1</sup> KOH eluent.

Ambient pressure X-ray photoelectron spectroscopy (APXPS) experiments were performed at the HIPPIE beamline of MAX IV in Sweden.[6] Before and between measurements, the experimental cell was kept under high vacuum ( $1 \cdot 10^{-10}$  mbar base pressure). The salt samples were dissolved in ultrapure water and deposited onto the sample holder by drop-cast. The solutions of the crust samples had a brownish color, due to some suspension of soil and dust particles. The lakebed and crust salt solutions were not filtered. After the samples had dried, they were transferred into the vacuum chamber. Water vapor was introduced from a glass water reservoir via a leak valve. The water source (Fluka TraceSelect Ultra; Water ACS reagent) was degassed using 3 freeze-pump-thaw cycles. During experiments, the RH was varied by regulating the leak valve to change the water vapor partial pressure. The sample temperature was kept at 16°C.

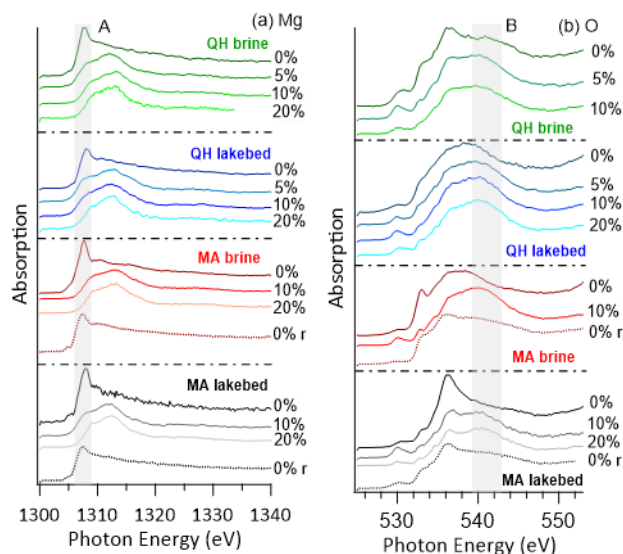


Figure 2 NEXAFS of Mg K-edge and O K-edge of brine and lakebed samples. The *r* in the brackets indicates that the RH was reversed to 0% from high RHs.

**Results:** The XPS results shows general agreements with the ion chromatograph results, with the exception that some elements (Na<sup>+</sup> and K<sup>+</sup>) are absent in the surface-sensitive XPS spectra, likely due to their low photoionization cross sections and surface depletion. Specifically, element-selective surface enhancement of Cl<sup>-</sup> is likely caused by the relatively high level of SO<sub>4</sub><sup>2-</sup> in the samples. Another interesting phenomenon is that Mg<sup>2+</sup> is seemingly enhanced at the presence of Na<sup>+</sup>, which is repelled to the bulk. No major spectral changes

were observed, except for the growth of the oxygen component indicating condensed H<sub>2</sub>O with increasing RH. The NEXAFS spectra reveal that the Mg and Na spectra change immediately as RH increases slightly (Figure 2 and Figure 3), implying that the surface is solvated already when trace levels of condensed water are available. All samples show high sensitivity to RH, *i.e.*, no major differences are seen depending on sample types and sampling locations. Thus, the highly RH-sensitive surface is a common feature for these salts, indicating that under the typical environmental conditions on Earth and Mars the salt mixtures commonly have surface-solvated surfaces.

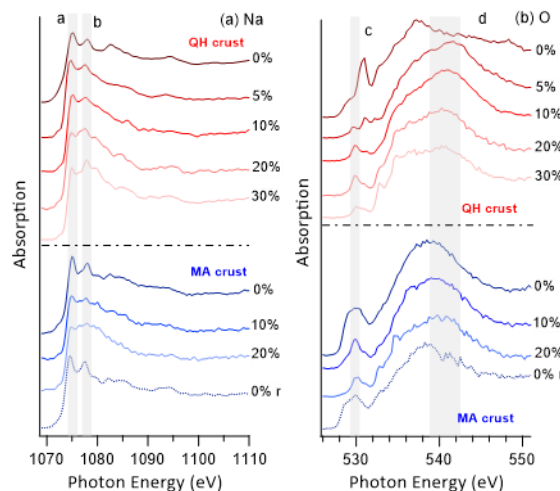


Figure 3 NEXAFS of Na K-edge and O K-edge of crust samples. The *r* in the brackets indicates that the RH was reversed to 0% from high RHs.

**Acknowledgement:** We acknowledge MAX IV Laboratory for time on Beamline [HIPPIE] under Proposal [20200271]. Research conducted at MAX IV, a Swedish national user facility, is supported by the Swedish Research council under contract 2021-04042 and 2015-04212. This work was also supported by the National Natural Science Foundation of China (41975160), the European Union's Horizon 2020 research and innovation program from the European Research Council under grant agreement 786636 and from the Swiss National Science Foundation (200020\_200306). X.K. acknowledges the support from the Swedish Foundation for International Cooperation in Research and Higher Education (CH2019-8361).

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