

SEDIMENTARY SALTS AT DALANGTAN PLAYA AND ITS IMPLICATION FOR THE FORMATION AND PRESERVATION OF MARTIAN SALTS W. G. Kong¹, M. P. Zheng¹, F. J. Kong¹, Alian Wang², W. X. Chen¹, and B. Hu¹, ¹MLR Key Laboratory of Saline Lake Resources and Environments, Institute of Mineral Resources, CAGS, Beijing 100037, China; ²Dept Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130 USA. (Weigang.kong@gmail.com)

Introduction: The findings of widespread aqueous minerals, putative fluvial and alluvial landforms on Mars in the past decade emphasize the importance of water in its geological history [1-3]. Thick layer deposits of hydrous Mg-sulfates (up to kilometers) were identified in ILD (including in Gale Crater) [e.g. 4, 5]; variety of clays (Mg, Fe-rich smectite and Al-kaolinite) was found in wide regions [6]; putative chlorides were implied in low-land of southern hemisphere [7]. Scenarios need to be built to explain these observations and to understand the evolution of Martian aqueous environment, which relates to the evolution of Mars atmosphere. Up to now, direct deposition of hydrous minerals from open water systems is plausible among several candidate formation scenarios [8]. Furthermore, the conditions (at surface or in subsurface) that enabled the preservation of hydrous phases are of great interests since they are linked to the total water budget on Mars and the capability of hosting life in such environment.

Since 2008, we have been studying the mineralogy, geology, bio-signature, and climatic conditions of saline playas in a hyperarid region on Tibet Plateau, as a terrestrial Mars analogue site [9-15], aiming to gain understanding for the formation and preservation of Martian aqueous sediments.

Dalangtan Saline Playa on Tibet Plateau: Tibetan Plateau (or QT-Plateau) has an average elevation of ~ 4500 m (i.e., 50-60% of sea-level atmospheric pressure and high level of UV radiation). The high elevation induces a low average temperature and a tremendous diurnal (and seasonal) temperature swing. The Himalaya mountain chain (average height >6100 m) largely blocks the pathway of humid air from the Indian Ocean and produced a Hyperarid region (AI < 0.04), the Qaidam Basin (N32-35°, E90-100°), where Dalangtan (DLT) playa occurs at its north-west corner (the most ancient playas, Eocene). Climatically, the low P, T, large ΔT and high aridity all make the DLT to be one of the most Mars-like places on earth.

DLT playa formed from the dry out of a Mg-SO₄ rich salt lake, large amount of Mg-sulfates were found in the evaporative deposits, co-existing with carbonates, Ca-sulfates, Na-sulfates, chlorides and borates. In the expedition of 2012 to DLT, we have systematically sampled four vertical sections (Dp 1, 2, 3, and 4) at locations with different distance to the center of the dry playa (Fig 1, Fig. 2). During the expedition, we used a portable Raman spectrometer (iRaman 532, BW Tec)

for *in situ* characterization of the original depositional sequence of the sulfate-bearing sections (Fig. 3) where the samples were collected.

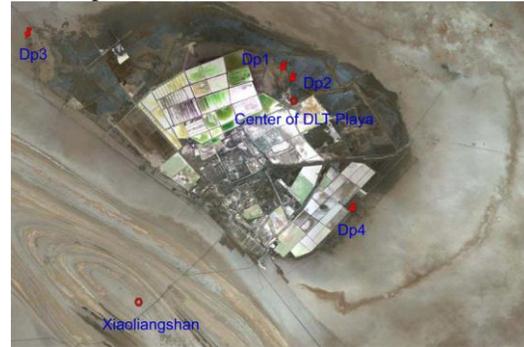


Fig. 1. Relative locations of four sampled vertical sections (Dp1, 2, 3 and 4) in the DLT Playa region.

Fig. 2 Dp2 section



Fig. 3 a portable Raman spectrometer in the field



***In situ* Raman analysis at DLT:** Fig. 4 shows the *in situ* Raman spectra of the subsurface samples exposed to the surface and the fresh subsurface samples of vertical section Dp2. The vertical sections were made during local mining activities, and were exposed to ambient atmospheric conditions for about 6 months. At the surface of salt deposits along vertical section DP2, starkeyite (MgSO₄·4H₂O) and kieserite (MgSO₄·H₂O) were identified, while epsomite (MgSO₄·7H₂O) was identified to be the only Mg-sulfate species in the subsurface salt deposit, freshly dogged out by us from this section.

Laboratory analysis of collected salt samples: For this preliminary analysis, we concentrated on the collected samples with hydrous salt minerals as major components. Laboratory laser Raman spectroscopic analysis was conducted on the collected samples from Dp2, before XRD and optical microscopy. These Raman identifications are labeled as “Lab:” in Fig. 5, to be distinguished from *in situ* Raman made in field.

The same set of collected samples from Dp2 has also been characterized by powder XRD and optical microscopy. For XRD analysis, the salt sample was grinded into powder and then made XRD measurement immediately. A Zeiss petrographic microscope was used to determine the optical mineralogy, and different

hydrated mg-sulfates can be distinguished on the basis of their different optical properties. The minerals identified by XRD analysis and by optical microscopy are listed in Fig. 5 together with their depositional depth.

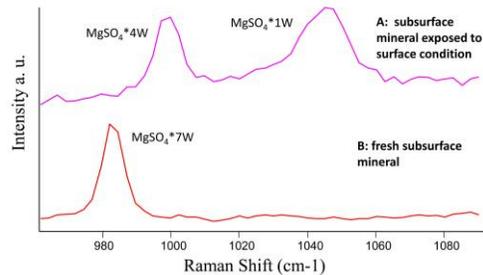


Fig. 4. In situ Raman spectra of minerals from Dp2 section.

Depth (m)	Layer number	Layer thickness (cm)	Rock Types	Salt Mineralogy (XRD)	Mineralogy (Raman)	Optical Mineralogy
-0.2	4	70	+	Halite Hexahydrate Pentahydrate Carnallite Bischofite	Lab: Epsomite Pentahydrate	Siliciclastics Carnallite Picromerite Clays Halite
-0.4			+			
-0.6			+			
-0.8			+			
-1.0	3	50	+	Halite Hexahydrate Pentahydrate Bischofite	Lab: Epsomite Pentahydrate	Halite Epsomite Carnallite Siliciclastics Clays
-1.2			+			
-1.4			+			
-1.6	2	60	+	Halite Hexahydrate Pentahydrate	In situ: Epsomite Lab: Epsomite Hexahydrate Pentahydrate	Halite Epsomite Siliciclastics Clays Carnallite Gypsum
-1.8			+			
-2.0	1	30	+	Halite		Clays Halite Siliciclastics

Fig. 5. Mineralogy of the fresh subsurface rocks from Dp2 section.

Discussion #1 – dehydration of subsurface epsomite: Hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) and pentahydrate ($\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$) has been identified in the laboratory Raman and XRD analyses in the samples where epsomite was the only (or major) Mg-sulfate phase by *in situ* Raman, thus these two Mg-sulfates should be the dehydration products from the original epsomite during the delivery (one week) and the storage (several weeks). In addition, the dehydration of epsomite can happen during the grinding before the powder XRD measurement. These observations are consistent with the results from the study on the stability field and phase transition pathway of epsomite [16, 17].

It is important to note that similar phase transitions of hydrated minerals can happen on Mars during the exploration of Curiosity rover, e.g., “drilling” into a salt sample, as well as sieving and delivering the fine powder to a XRD system (MinChem).

Discussion #2 – Occurrence of kieserite: Starkeyite, and especially, kieserite were identified by *in situ* Raman analysis at the exposed surface of vertical section DP2, while the fresh subsurface rocks (of same area) host epsomite as the only Mg-sulfate.

In a laboratory experiments, the dehydration of epsomite or hexahydrate stop at starkeyite under Mars relevant temperatures, but kieserite could form under similar conditions when epsomite co-existing with Fe- or Ca-sulfates. Hence it was suggested that other sul-

fates might catalyze the dehydration process of epsomite [18]. Therefore, the experiments are consistent with our field observation that the kieserite in the outermost surface of the Dp2 section comes from the dehydration of epsomite hosted in the fresh subsurface rocks after its exposure to the surface environment (mean annual T 3-5 °C and relative humidity < 30%) at DLT region.

Can kieserite direct precipitate from aqueous solution, on Mars and on Earth? Laboratory experiments found that kieserite forms from pure Mg-SO₄ brine only at temperature >70 °C, much higher than those of current and historical Mars surface temperatures (<50 °C). On the other hand, geochemical modeling has suggested that kieserite can deposit directly from SO₄-Cl mixed brines at Mars-like temperature [19]. Because the higher magnesium concentration induced by Cl anion will reduce the water activity of the brines, thus would facilitate the formation of kieserite.

Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was found to co-exist with epsomite in many collected Dp2 subsurface samples. It tells us that the coexistence of chloride is not the sufficient condition to form primary kieserite. There may be need for the co-precipitation of other chlorides (e.g. bischofite, an indicator of much lower water activity, [20]) for the direct precipitation of kieserite from brines.

Needless to say that to understand the origin of kieserite at DLT (a Mars like environment) is important to explain the widespread kieserite in ILD on Mars.

Future work: The other three vertical sections (Dp1, 3, and 4) will be studied later, and further field trips at Dalangtan playa will focus on the secondary processes of Martian related salts at different seasons.

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