

**LASER RAMAN SPECTROSCOPIC STUDY OF SUBSURFACE SALTS FROM DALANGTAN ON TIBET PLATEAU – A MARS ANALOG SITE STUDY.** Alian Wang<sup>1</sup>, Pablo Sobron<sup>2</sup>, Mianping Zheng<sup>3</sup>, Fanjing Kong<sup>3</sup>, Nian Ma<sup>3</sup>, Yu-Yan Sara Zhao<sup>4</sup>, <sup>1</sup>Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis ([alianw@levee.wustl.edu](mailto:alianw@levee.wustl.edu)), <sup>2</sup>SETI ([psobron@seti.org](mailto:psobron@seti.org)), <sup>3</sup>R& D Center of Saline Lakes and Epithermal Deposits, Chinese Academy of Geological Sciences, <sup>4</sup>Dept. Geosciences SUNY.

**Missions to Mars:** *Following the water, Habitability, and Biosignature* have been the theme of US NASA's Mars exploration program that consist a series of missions to Mars, including orbital remote sensing and surface explorations. The evidences of past water activities and current H<sub>2</sub>O/OH-bearing materials were found through these missions. Among these, hydrous salts are confirmed to be one of the three types of H<sub>2</sub>O/OH-bearing materials (other two are ground H<sub>2</sub>O ice and phyllosilicates) that currently exist on Mars.

This study, as one of three investigations on a Mars analog site, reports the salt mineralogy along two stratigraphic sections in a saline playa (Da Lang Tan, DLT), that occurs in a hyperarid region (Qaidam basin) on Tibet Plateau and the implications to Mars.

**DLT Saline Playas on Tibet Plateau:** Qinghai-Tibet (QT) Plateau in southwestern part of China is the world's highest and largest plateau that stretches about 1000 kilometers north to south and about 2500 kilometers east to west. The Himalaya mountain chain has the highest average elevation in the region, ~ 6100 meters. The Qaidam basin between Altun-Qilian and Kunlun mountain chains has an average elevation, ~ 3000 meters. The Himalaya mountain chain largely blocks the pathway of humid air from the Indian Ocean, which masters the rain-fall and evaporation rate of regional lake basins, and produced large numbers of saline lakes and saline playas in the north region of QT plateau, i.e., the Qaidam basin. Based on climate classification, a hyperarid zone (<7.5% global land area on Earth) is defined by Aridity Index (AI) < 0.05. Qaidam Basin (N36-39°, E88-100°) has the highest aridity on QT-Plateau, with AI of 0.008 – 0.04 recorded at discreet locations.

Da Lang Tan (DLT) playa (N38°32', E91°25') occurs in a depression at northwest corner of Qaidam

basin, within an area of ~ 250 x 160 km (DLT area) that filled with anticlines and depressions due to tectonic activities. This area has the most ancient salt deposit (Eocene-Oligocene) in Qaidam Basin. More importantly, Mg-sulfates were reported in the evaporative salts at DLT, which mark the nearly final stage of evaporation sequence of K, Na, Ca, Mg, Fe, C, B, S, and Cl bearing brines.

The general climatic conditions on Tibetan Plateau, i.e., 50-60% of sea-level atmospheric pressure, tremendous diurnal (and seasonal) temperature swing, the high level UV radiations, the hyper aridity within Qaidam basin, and the final stage evaporative salt mineralogy within the saline playas of DLT area, all suggest that this area is an excellent Mars analog site for studying the salt (hydrous and anhydrous, sulfates and chlorides) precipitation and preservation under atmospheric conditions similar to those on Mars.

**Samples from two stratigraphic sections:** We collected 21 salt samples from two stratigraphic sections at DLT, with 5.77 m depth at north edge and with 3.05 m depth at the center. These stratigraphic sections were exposed by on-going local mining activities (Figure 1). At each sampling spot along the section, we collected only the salt samples buried deeply within the wall, to avoid the potential hydration state changes in salts due to their exposure to current atmosphere by mining activities. The samples were sealed in double layered plastic bags and shipped to US within 10-15 days then saved in a freezer at -10 °C before laboratory measurements.

**Laser Raman Spectroscopic (LRS) Analysis:** LRS has been proposed as an in situ, non-destructive, fine-scale mineralogy tool for Mars surface exploration missions. It is the major technology that we used for phase identification and quantifications of these natural salts, helped by XRD for anhydrous chlorides ID. Two



Figure 1. One of the two vertical cross sections, 5.77 meters above the brine table at site 01, exposed by local mining activities, from which the subsurface samples were collected.

sample #	# of LRS spots	carnallite	kainite	polyhalite	MgSO <sub>4</sub> -6w	MgSO <sub>4</sub> -5w	thenardite	bloedite	gypsum	bassanite	dolomite	NaCl (XRD)
DL-01-01-08	104	2		57	7				1		3	yes
DL-01-01-07	108	2	1	103	2							yes
DL-01-01-06	209	9			130	37				2		yes
DL-01-01-05	214	3	1		208	101	16			1	1	yes
DL-01-01-04	105										1	yes
DL-01-01-03	305	1		1	6		292		1			yes
DL-01-01-02	207	1		5	102	1	6	1			1	yes
DL-01-01-01	212	26	1	7	106						1	yes

Table 1. LRS phase ID and quantifications: carnallite =  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ , kainite =  $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ , polyhalite =  $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , MgSul-6w =  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , MgSul-5w =  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ , bloedite =  $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , gypsum =  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , bassanite =  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ , dolomite =  $\text{CaMg}(\text{CO}_3)_2$ . 577-461 cm 231-121 cm 121-0 cm from bottom

types of LRS measurements were made: (1) 5-10 point-check on individual grains of salt samples with the purpose to get best S/N Raman spectra from typical salt minerals; (2) >100 points in LRS 2-3 cm line scan on powdered salt. The purpose was to detect the major, minor, and trace mineral phases as complete as possible, and at the same time, to obtain a rough estimation of the mineral modes of each sample along the section. **Salts, carbon, and perchlorate:** About 20 salt minerals were found in the collected samples, classified into four categories: chlorides, sulfates, chloride-sulfates, and carbonates. Within both chloride and sulfate groups, there are single cation salts and multi-cation salts. Within each single-cation sulfate sub-group, there are sulfate hydrates with different hydration degrees. Among the hydrous Mg-sulfates, mostly identified phases are  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ , and in some cases,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . We anticipate that all of these Mg-sulfates are originated from epsomite based on our study of the stability fields and dehydration/rehydration rates of Mg-sulfates [1-3]. Among Na-sulfates, only thenardite  $\text{NaSO}_4$  was identified. Based on the powdery appearance of this mineral, we anticipate it is originated from the dehydration of morabolite  $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$  for two reasons: (1) full dehydration of morabolite was observed to complete in a few minutes under laboratory conditions (20.3 °C and 42%RH) with the appearing change from transparent crystal to white powder; (2) when thenardite  $\text{NaSO}_4$  forms directly from brine at  $T > 33^\circ\text{C}$ , it appears as mm to cm transparent crystals. The mineralogy of these salts indicates a brine system of K, Na, Mg, Ca, Cl,  $\text{SO}_4$ , mixed with local silicates, carbonates, oxides. XRD analysis suggests the existence of NaCl in all 21 samples.

Within a few samples, reduced carbon was detected.  $\text{ClO}_4$  were detected in the salt samples near surface with substantial content (~51 ppb in soluble proportion of the solid sample).

**Multiple events of brine intrusion and salt precipitations:** Phase IDs of salts, their encountering fre-

quencies among the total number of LRS spectra collected in line scans of eight samples along the stratigraphic section at site 01 are listed in Table 1.

The major salts (with high encountering frequency in LRS linear scans) from these eight samples revealed at least three events of brine intrusion happened, accompanied by salt precipitations, apparently separated by the enrichment of hydrous Mg-sulfates at individual sampled layers (01, 02, 05, 06). In addition, the changes in salt mineral assemblages among the sampled layers reflect the changes in the chemistry of brines, with Mg, Na, Cl,  $\text{SO}_4$  throughout the whole section, but higher K in early event, and higher Ca in later event (Table 1).

**Subsurface salts with high hydration degrees:** Within two studied stratigraphic sections at DLT, we have identified Mg-sulfates and KMg-chlorides with very high degrees of hydrations ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ) within shallow subsurface (< 1 meter). In laboratory, these minerals would dehydrate very quickly at mid-low relative humidity (e.g.,  $\leq 33\% \text{RH}$ ). During our expedition in 2008, the on-site atmospheric RH measurements were <10%RH during day-time and were 26-36%RH during night-time, confirmed the hyperaridity of Qaidam basin.

The finding of subsurface salts with high hydrations in a hyperarid region on Earth supports a hypothesis, i.e. the existence of mineralogical water reservoir in the subsurface on Mars [4, 5, 6].

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**References:** [1] Wang et al., 2006, GCA, V70, 6118-6135; [2] Wang et al., 2009, JGR, doi:10.1029/2008JE003266; [3] Wang et al., 2011, JGR, doi:10.1029/2011JE003818; [4] Feldman et al., 2004, JGR, doi:10.1029/2003JE002160 [5] Jakosky et al., 2005, Icarus, doi:10.1016/j.icarus.2004.11.014; [6] Wang et al., 2013, Icarus, 226, 980-991.