

RECURRING SLOPE LINEAE (RSL) AND SUBSURFACE CHLORIDE HYDRATES ON MARS. Alian Wang¹, Yanli Lu¹, and I-Ming Chou², ¹Dept. of Earth and Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University in St. Louis, One Brookings Drive, St. Louis, MO, 63130, USA; ²U.S. Geological Survey, 954 National Center, Reston, VA 20192, USA (alianw@levee.wustl.edu).

Recurring slope lineae (RSL): RSL is an important phenomenon revealed by HiRISE-MRO observations on Mars [1]. The RSL formed and grew on some equator-facing slopes during warm seasons on Mars when $T_{\text{afternoon}}$ was in the range of ~ -23 to 27 °C (with higher T_{peak}). Thousands RSLs have been observed, and they are narrow (0.5–5 m) and long (over 100 m). They occurred repeatedly on steep slopes (>25 °) with growth rates of ~ 0 -20 m per day. RSLs were found mostly in the southern hemisphere in regions with moderate thermal inertia, but without any direct association with surface mineralogy and also rarely associated with gullies. RSL itself does not have any distinct spectral feature in the Vis-NIR range. The HiRISE team has noted that the distribution of RSL bears some similarity with putative chloride deposits in the southern hemisphere and they proposed that salty brines (chlorides or Fe sulfates) could be the source of RSL [1].

Sources of RSL: Our laboratory investigations in past few years have demonstrated that sulfates (Mg, Fe, Ca, Al, Na, K, etc.), hydrous or anhydrous, crystalline or amorphous, all have characteristic spectral peaks in Vis-NIR spectral range [2-5] that could be seen by OMEGA or CRISM, which is an obvious mismatch with the observation of “RSL does not have any distinct spectral feature in the Vis-NIR range”. Furthermore, under the current martian atmospheric conditions (low temperature [T] and low relative humidity [RH]), hydrous sulfates would dehydrate through solid-solid phase transitions [6,7], i.e., a phase with high degree of hydration transforms to the one with low degree (e.g., epsomite to starkeyite or to kieserite). Thus hydrous sulfates are unlikely to be the source of RSL.

We hypothesize that chloride hydrates (and their mixtures with water ice) may exist in the subsurface of some areas in southern hemisphere on Mars. When temperature rises during the warm season, the deliquescence of these chloride hydrates may have produced large quantity of brine that show up as RSL, while any remaining chlorides in RSL would not produce spectral peaks in Vis-NIR range detectable by CRISM.

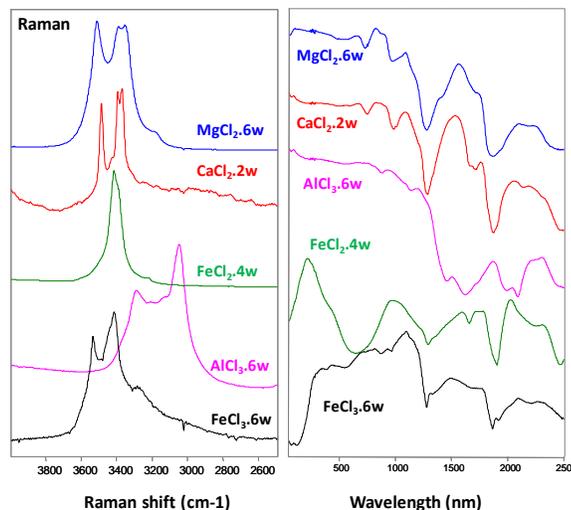
This hypothesis is based on three lines of reasoning: (1) chlorine (Cl) was found to be broadly distributed on Mars (GRS-ODY) [8] and has been detected in the chemistry of *every* surface sample during *all* Mars surface exploration missions (Vikings, Pathfinder, Spirit, Opportunity, and Phoenix). In addition, the existence of chlorides in the martian southern hemisphere was suggested by a set of THEMIS-ODY data analyses [9]. In terrestrial saline playas, large amounts of chlorides invariably appear in the precipitates from salty brines [10-11], even though the precipitation sequence of chlorides on Mars might be different from that on Earth [12-13]. (2) A subsurface layer, when enriched with ice or hydrous sulfates or chloride hydrates (all have high thermal inertia) and covered by a dry layer of surface soils (very low thermal inertia), will be able to maintain a very low T_{max} and a much smaller ΔT

that are not affected by the large temperature variations at the surface during diurnal and seasonal cycles [14]. (3) Chloride hydrates (such as $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, etc.) formed from Cl-bearing brine at low T contain large amounts of H_2O (up to 69 wt%), and they are stable in median T range (some $>$ room T) until deliquescence commences abruptly at an elevated temperature, as indicated by the laser Raman studies of briny fluid inclusions in terrestrial minerals [15].

To test this hypothesis, we need to investigate the pathway of phase transformations of various chloride hydrates (and their mixtures with water ice) under the environmental conditions relevant to Mars subsurface.

Feasibility of experimental investigation: Most chlorides have no Vis-NIR, MIR, or Raman peaks, because of the metal-Cl ionic bonding in their structures. However, the vibrational modes of H_2O in chloride-hydrates do contribute Vis-NIR, MIR, and Raman peaks. Figure 1a shows the Raman active modes of H_2O in five chloride hydrates; Figure 1b shows the overtone and combinational modes of these H_2O in Vis-NIR spectral range.

Figure 1. Chloride hydrates have distinctive Raman, MIR, Vis-NIR spectra



We have been using two non-invasive tools, gravimetric measurements and laser Raman spectroscopy, to monitor the phase transitions of hydrous salts. We anticipate the application of these tools will make the experimental study on the phase transition pathway of chloride hydrates feasible.

Experimental study of chloride hydrates: We have started a systematic laboratory investigation on the thermodynamic and kinetic properties of chloride hydrates. The goals are to determine: (1) the stability fields of Mg-, Fe²⁺-, Fe³⁺-, Ca-, Al-, Na-chloride hydrates in RH-T space, specifically the boundaries of hydrate-deliquescence; (2) the rate of their dehydration and deliquescence as function of T, P, and P_{H2O}; (3) the RH level that each chloride hydrate can maintain in an enclosure at Ts relevant to those within the martian subsurface. We report here some preliminary results.

Bonding strength of metal-H₂O in chloride hydrates: We conducted a set of dehydration experiments of six chloride hydrates, including MgCl₂·6H₂O, AlCl₃·6H₂O, KMgCl₃·6H₂O, CaCl₂·2H₂O, FeCl₂·4H₂O, and FeCl₃·6H₂O, at 52 °C and 9 (±3) % RH. Figure 2 shows the results from gravimetric measurements, the remaining % of structural water in each chloride hydrate vs. experimental duration. These data revealed how tightly the water molecules are held in the structure of each chloride hydrate, i.e. the bonding strength of metal-H₂O. We found the rate of dehydration is directly linked to the size of octahedra of M-(H₂O)₆. MgCl₂·6H₂O, AlCl₃·6H₂O, and KMgCl₃·6H₂O show great resistance to dehydration because of the small sizes of Al-(H₂O)₆ and Mg-(H₂O)₆. For the same reason, CaCl₂·6H₂O shows a moderate resistance, FeCl₂·4H₂O and FeCl₃·6H₂O have very low resistance, and KCl hydrate does not exist.

Large field of deliquescence of chloride hydrates: A set of stability field experiments on the

Figure 2. Comparison of dehydration rates of different chloride hydrates (52°C, 9±3% RH)

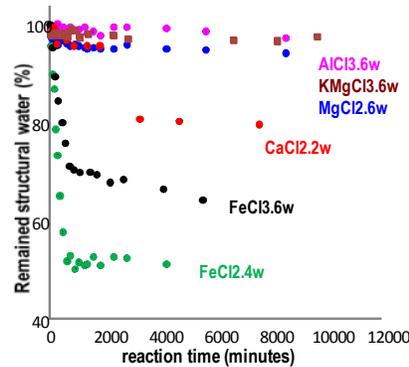


Figure 3. Large field of CaCl₂·2H₂O deliquescence

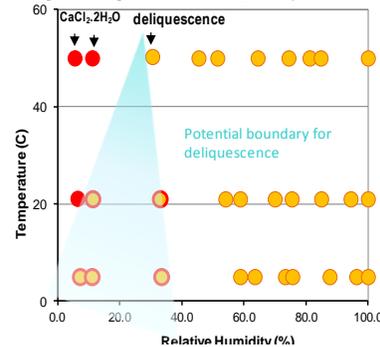
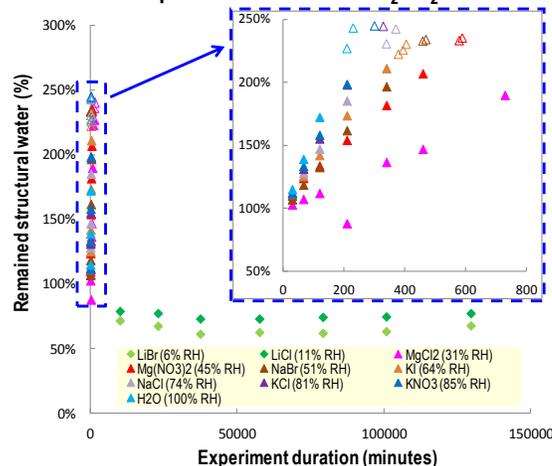


Figure 4. Comparison of dehydration and deliquescence rates of CaCl₂·2H₂O



above chloride hydrates at three temperatures (50, 21, and 5 °C) and ten RH levels (from 6 to 100%) has been run for 90 days. One primary finding is the extremely large deliquescence field of chloride hydrates compared with those of hydrous sulfates. We found that deliquescence can happen at quite low RH level, some < 20% RH at 5 °C. Figure 3 shows a potential range for solid-deliquescence boundary of CaCl₂·2H₂O, located at quite low RHs in 50 to 5 °C range. RSL were observed on Mars at T_{afternoon} ~-23 to 27 °C. Longer durations of above experiments and additional low T experiments are needed to define the trend of deliquescence as function of temperature.

High deliquescence rates of chloride hydrates compared with the rates of dehydration: Figure 4 shows the deliquescence of a CaCl₂·2H₂O sample completed (shown as hollow triangles) in 4 - 25 hours (RH>31%, 50 °C) whereas dehydration during 90 days (5-11% RH) only lost 32 - 23% of structural water (shown as solid diamonds). The rate ratios of deliquescence over dehydration of other chloride hydrates at similar conditions are in the same order of magnitude.

Conclusion: Preliminary results from a systematic experimental investigation support our hypothesis that subsurface chloride hydrates could possibly be the source of water for RSL.

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References: [1] McEwen et al., 2011, *Science*; [2] Wang et al., 2006, *GCA*; [3] Ling & Wang, 2010, *ICARUS*; [4] Liu & Wang, 2009, *LPSC*; [5] Zhou & Wang, 2012, *LPSC*; [6] Wang et al., 2009, *JGR*; [7] Wang et al., 2012, *Icarus*; [8] Keller et al., 2007, *JGR*; [9] Osterloo et al., 2008, *Science*; [10] Zheng & Wang, 2009, *LPSC*; [11] Wang & Zheng, 2009, *LPSC*; [12] Tosca et al., 2008, *JGR*; [13] McLennan et al., 2011, *MEPAG*; [14] Mellon et al., 2004, *JGR*; [15] Baumgartner & Bakker 2009, *Chem. Geology*; and many other papers.