

**FORMATION OF CHLORIDE HYDRATES VIA VAPOR-SOLID REACTION AT LOW-T -- IMPLICATION FOR A H<sub>2</sub>O-RICH CRYOSPHERE IN MARS SUBSURFACE AND ON OTHER ICY PLANETARY BODIES.** Alian Wang, Jie Wei, Lily Lu, and Kathryn Connor, 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), Rudolph Hall, One Brookings Drive, St. Louis, MO, 63130, USA).

**A H<sub>2</sub>O-Rich Cryosphere:** On Mars, ground ice was identified in Polar Region by Phoenix lander [1], and was implied at high latitude region by the color change of “white” impact ejecta through orbital imaging [2]. In equatorial region, a H<sub>2</sub>O-rich cryogenic environment in subsurface sulfate-rich layer was suggested through the observed color change of subsurface ferric sulfates (Tyrone site at Gusev Crater), which indicates dehydration happened after excavation and exposure to Mars current surface condition [3, 4].

Cl was found existing in every sample of every surface exploration mission to Mars [5]. Putative chlorides were suggested to exist in broad region of southern hemisphere on Mars [6]. Similar to sulfates, a thick layer of chlorides at subsurface could maintain a low-temperature environment because their high thermal inertia, on the basis of a thermal profile model [7]. Furthermore, chloride hydrates are the stable forms of chlorides at low temperature, such as CaCl<sub>2</sub>·6H<sub>2</sub>O (antarticite) [8].

We would hypothesize a H<sub>2</sub>O-rich cryosphere within the subsurface of Mars, made of ground ice layer at polar and high latitude regions, and of salt- or salt-enriched-regolith-layers at low latitude regions. One piece of puzzle in this hypothesis is the source materials of Reoccurring Slope Lineae (RSL) that has been observed during local summer season with large quantity and broad spreading at low-latitude region and equatorial area on Mars [9, 10].

We report here the results from a set of experiments that has proved a critical concept in above RSL related study, i.e., the recharging of RSL source material at low-temperature (T) during local winter on Mars. These results have significant implication for the process that might happen on all low-T planetary bodies, i.e., Mars, Moon, icy satellites, asteroids, and comets.

**RSL & 1<sup>st</sup> set of Experiments:** Based on the observations made by HiRISE and CRISM, i.e., the tight correlation of RSL occurrence with temperature (T), the time duration of its occurrence and annually recurrences, the regional correlation with putative chloride deposits, and the lack of VIS-NIR spectral features at RSL sites [9, 10, 11], we hypothesized the source materials of RSL to be the subsurface chloride hydrates [12]. To test this hypothesis, we

designed and conducted two sets of experiments. The results from first set of experiment was reported early [13], which demonstrated: (1) the deliquescence of Mg-, Ca-, Fe-, Al-chloride hydrates are heavily dependents of temperature; (2) under the T and partial water pressure (P<sub>H<sub>2</sub>O</sub>) relevant to Mars subsurface, the rates of deliquescence of these chloride hydrates allow the process to begin and to accomplish (to exhaust the tested quantity of chloride hydrates) within hours and days. These results support that *the deliquescence of chloride hydrates can generate RSL phenomena within the time duration of RSL observed on Mars* [14].

This abstract reports the second set of experiments, that was designed to test if the rehydration of chlorides can happen through vapor-solid reaction at low-T relevant to Mars subsurface, i.e., if the recharging of RSL source materials can happen during a local winter period on Mars.

**Vapor-solid reaction at -78 °C:** The experimental setup is shown in Figure 1. MgCl<sub>2</sub>·6H<sub>2</sub>O was used as the starting material. It was baked in a 200 °C oven for 48 hours. Gravimetric measurements before and after baking confirmed the loss of 6.5 H<sub>2</sub>O per molecule (including adsorbed H<sub>2</sub>O). Raman spectroscopic measurements before and after baking confirmed the total transformation from MgCl<sub>2</sub>·6H<sub>2</sub>O to MgCl<sub>2</sub>, shown as the loss of Raman spectral features in 3000-4000 cm<sup>-1</sup> for hydrates. Visually, original transparent MgCl<sub>2</sub>·6H<sub>2</sub>O grains (Fig. 2a) all transformed to opaque-white grains of MgCl<sub>2</sub> (Fig. 2b) after baking.

For the low-T experiment, a reaction vial containing about 100 mg of MgCl<sub>2</sub> was buried in dry ice (-78 °C) in a foam box. This box-vial set was put into a

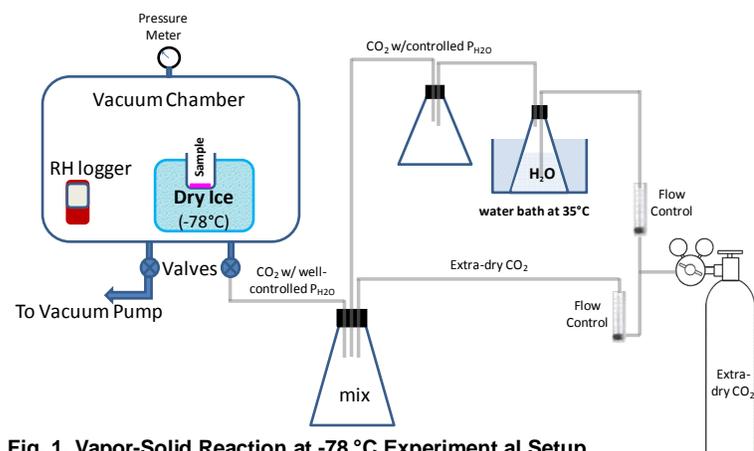
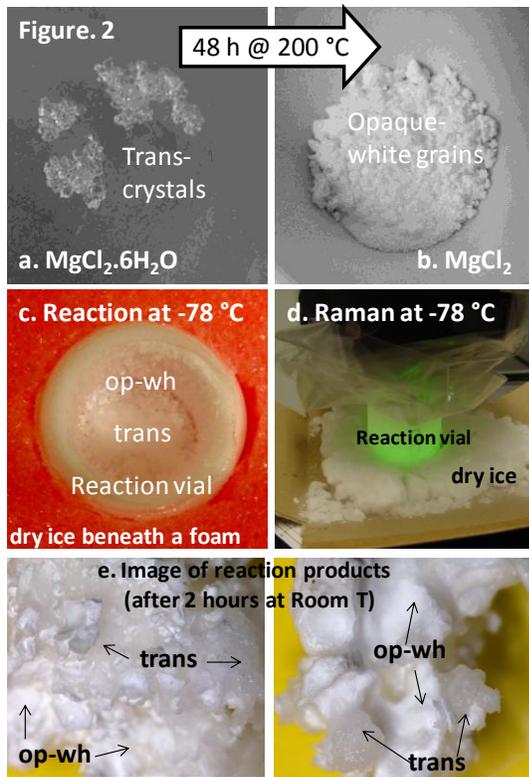


Fig. 1. Vapor-Solid Reaction at -78 °C Experimental Setup

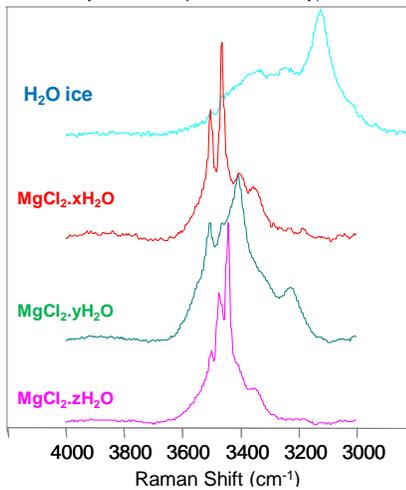


vacuum chamber where a low vacuum near  $P_{\text{Mars}}$  was maintained.  $\text{H}_2\text{O}$  vapor generated from a  $\text{H}_2\text{O}$  bath (maintained at  $35^\circ\text{C}$ , thus a controlled  $P_{\text{H}_2\text{O}}$ ) was mixed with a flow of dry  $\text{CO}_2$  and was input into the chamber. A delicate balance between the chamber pressure  $P$  and  $P_{\text{H}_2\text{O}}$  was maintained. A logger for temperature and relative humidity (RH) was kept in the chamber during the whole experimental duration.

The vapor ( $\text{H}_2\text{O}$ )-solid ( $\text{MgCl}_2$ ) reaction was conducted for about 6 hours, and repeated three times in three days. Similar results were obtained each day, which include: (1) the visual observation during the experiment at  $-78^\circ\text{C}$  through the transparent wall of vacuum chamber that indicated the formation of some transparent grains at the surface of  $\text{MgCl}_2$  grains in the reaction vial (Fig. 2c); (2) Raman spectroscopic measurements at  $-78^\circ\text{C}$  (Fig. 2d) of the reaction products that show various Raman peaks of chloride hydrates ( $\text{MgCl}_2 \cdot x\text{H}_2\text{O}$ ,  $x=\text{TBD}$ , Fig. 3); (3) gravimetric measurements of the reaction products that indicate the gaining of 0.7 to 1.3  $\text{H}_2\text{O}$  molecule per  $\text{MgCl}_2$  molecule from three repeating experiments; (4) optical microscopic images of reaction products (after keeping at room T for two hours) that show mixtures of transparent grains with opaque-white grains (Fig. 2 e).

*These results demonstrated the formations of chloride hydrates via a vapor-solid reaction at a temperature within the T range that can be maintained by a thick layer of salt at nowadays Mars subsurface.*

Fig. 3 Raman spectra of reaction products at  $-78^\circ\text{C}$  ( $\text{MgCl}_2 \cdot x\text{H}_2\text{O}$ , where  $x$  can be 2, 4, 6, 8, 12 that needs a systematic experimental study)



period on Mars. This vapor-solid reaction would rehydrate the chlorides, which were formed during the local summer period on Mars by dehydration. The chloride hydrates formed in such way will be the source materials for RSL to reoccurring in next local summer.

**Future works:** These two sets of experiments are proof-of-concept studies, which demonstrated the correctness of our hypothesis, and the feasibility of our experimental design. A detailed systematic experimental investigation is designed and will be proposed. It will concentrate on the thermodynamics and kinetics properties of specific chloride hydrates that are stable at lower T thus having even higher hydration degrees. The study on reaction rates (for deliquescence and rehydration) will be emphasized. Furthermore, experiments to reveal the  $P_{\text{H}_2\text{O}}$  values (i.e.,  $\text{H}_2\text{O}$  availability) at low-T within an environment filled with chloride hydrates and sulfate hydrates will be conducted, for the purpose to evaluate the habitable potentials of icy-salt-environments, within Mars subsurface and on other icy planetary bodies as well.

**Acknowledgements:** Thanks for NASA funds, #1295053 & NNX13AM22G, and for the discussion with A. McEwen, J. Head, J. Dubessy, I-Ming Chou.

**References:** [1] Smith et al., (2009) *Science*, 325, p58. [2] Byrne et al., (2008) *Science*, 325, p1674. [3] Wang et al., (2008) *JGR*, 113, E12S40. [4] Wang and Ling (2011) *JGR*, 116, E00F17. [5] Clark et al., (1978) *JGR*, 87, p10059. [6] Osterloo et al., (2008) *Science*, 319, p1651. [7] Mellon et al., (2004) *ICARUS*, 169, p324. [8] Dubessy et al., (1982) *Chem. Geology*, 37, p137. [9] McEwen et al., (2011) *Science*, 333, p740. [10] McEwen et al., (2013) *Nature GeoScience*, DOI:10.1038; [11] Ojha et al., (2013) *GRL*, 40, p5621. [12] Wang et al., (2013) 44<sup>th</sup> LPSC, abs #2606. [13] Wang (2014) 8<sup>th</sup> Mars, abs #1058. [14] Wang et al., (2014) *GSA*, abs # 248005.

Thus, the recharging of RSL source materials annually during local winter period is allowed by thermodynamics and kinetics. It means that the subsurface salt- or salt-rich-regolith layers could function like a “cold-trap”, to react with atmospheric  $\text{H}_2\text{O}$  vapor that is moving from polar region to mid-low latitude regions during local winter