National Aeronautics and Space Administration

Europa's Habitability from Surface Mineralogy: what a Vibrational Spectrometer may find

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Program: Topical

Project Objective:

The primary goal of this research is to lay the ground work for the development of a performance model for investigating surface materials (salts) with a Raman spectrometer landed on Europa or another Ocean Worlds. This is required to understand the context of the sample(s) (Fig. 1): Was it formed from endogenic or exogenic processes? How much radiolytic processing took place after emplacement? What compositional information on the internal ocean can we derive from these analyses?

Achieving this goal requires fulfilling the following objectives:

1) Determine accurately and quantitatively the icy mineralogies, including hydration states, that result from freezing of endogenic fluids extruded to Europa's surface.
2) Investigate the influence of a Raman instrument's parameters (excitation wavelength, resolution, acquisition time, spot size), on the performance of detection and accuracy of quantification of the minerals formed.

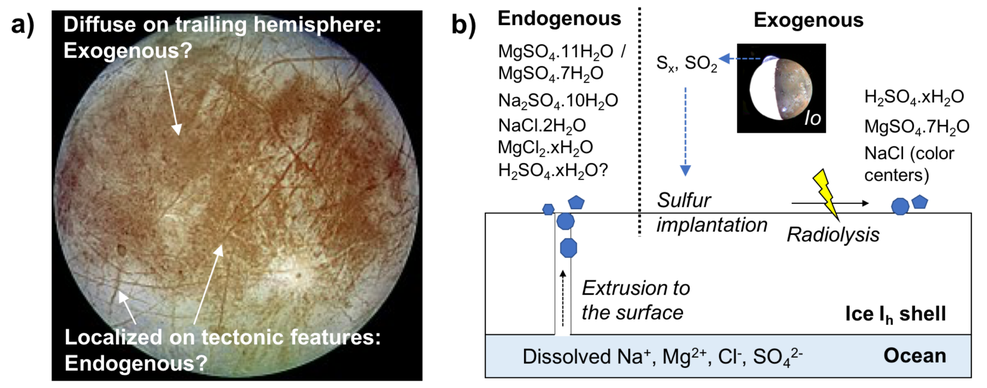

Figure 1. Non-ice materials on Europa's surface are abundant and may have various origins. *a)* Distribution of non-ice constituents (reddish-brown). *b)* Schematic illustration of likely composition of non-ice constituents, as well as the processes leading to their presence on the surface.

FY19 Results:

1. We have finished the H_2O-$MgCl_2$ investigation via XRD and are acquiring the Raman data needed to interpret them and support model testing (planned for summer FY19). Figure 2 illustrates that we resolved the debate on equilibrium hydration state of $MgCl_2$ below eutectic point, and also found out-of-equilibrium unknown phases at very low concentrations.

2. The corresponding Raman data has also been acquired. Figure 3 illustrates an additional complexity arising from freezing low-concentration solutions: a glassy behavior, which prevents identification by XRD. In FY 20 we will test whether Raman can be used to quantify the abundance of glassy materials.

3. We have developed an approach to process Raman spectra to simulate the influence of instrument parameters (e.g. spectral resolution, noise level). We have identified an existing linear mixing model (developed by the SHERLOC team) that can be used to test quantification performance.

4. We have further investigated the Mg-Na-Cl-SO_4 system via XRD, Raman spectroscopy, studying the effect of freezing rate and the capability to quantify "calibration" brines studied by XRD. Publication is submitted (Vu et al., Icarus, submitted). In this publication, we show that:
   1. Freezing rate impacts the mineralogy found at equilibrium.
   2. Even Mg sulfate forms a glass when flash-frozen, and only Mg-bearing solutions form glasses, not Na-bearing solutions.
   3. XRD quantification of mineral abundances in frozen brines has a typical ~ 10-20% uncertainty for each species, as compared to the known composition of the starting brines.
   4. Expanding this result to a 4 component mixture wherein each compound has an uncertainty on abundance of 10% implies an overall 20% uncertainty of the mineralogy mode of that sample overall.
   5. At present, the best available technique for mineral quantification will only achieve a quantification accuracy on order of 20% for mixtures. By analogy, Raman likely wouldn't be able to do better without contingencies.

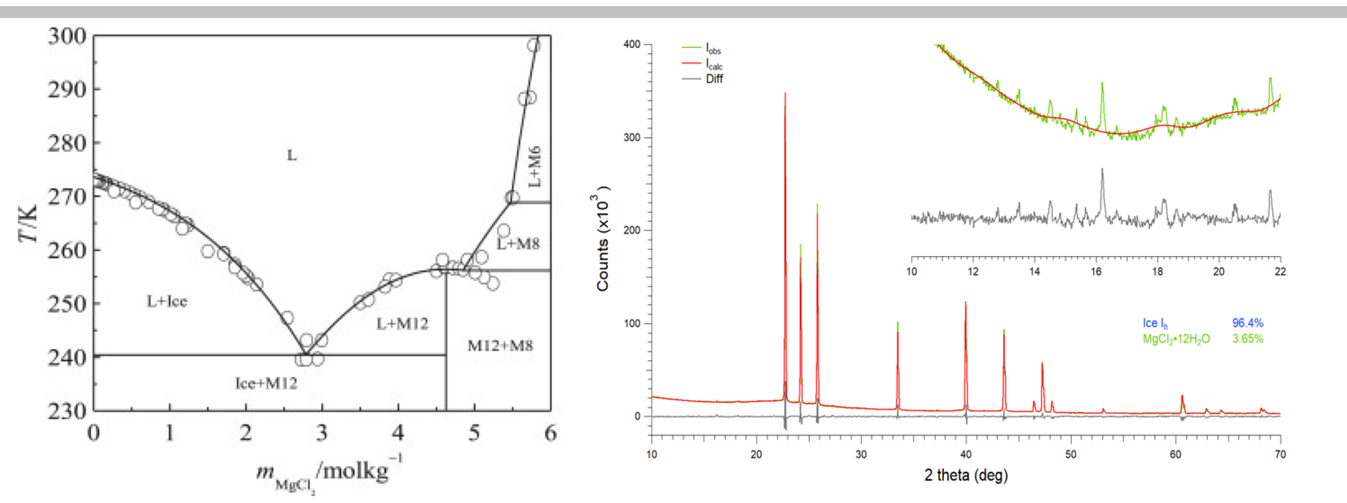

Figure 2. *Left:* In the first year of this project, we have demonstrated that the equilibrium state for $MgCl_2$ below eutectic temperature is $MgCl_2$.12 H_2O. *Right:* At very low concentrations, freezing resulted in the formation of unknown phases that remain to be identified (none of the known hydration states of $MgCl_2$).

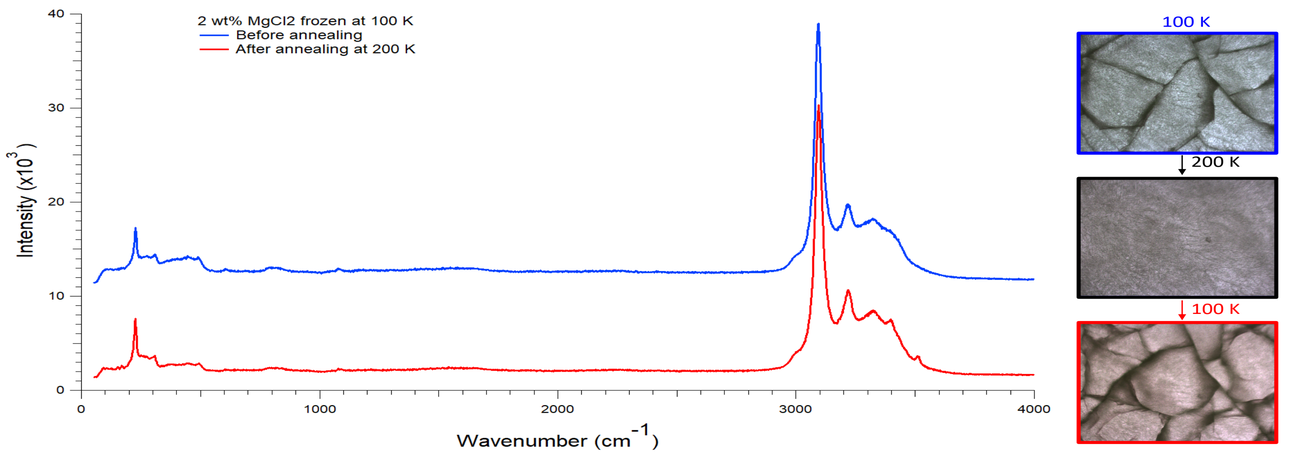

Figure 3. Raman spectra of a 2 wt% $MgCl_2$ solution frozen to 100 K. on first freezing, only water ice can be seen. Annealing to 200 K is needed for the $MgCl_2$ to crystallize. This suggests glassy materials could be present on Europa and hide the presence of some salt species (chlorides in particular).

Significance of results:

1. Our experiments enabled the development of a roadmap for qualitative analysis of Europa surface materials in order to constrain endogenic formation processes (plume activity vs. diapirism) as well as ionic composition of the internal ocean, see Figure 4. Achieving this distinction requires first analysis of the sample while it is held at a 100 K temperature, not compatible with the proposed Europa Lander architecture described in the Europa Lander SDT report. This has implications for the operations plan of a Europa Lander and its thermal design for sample analysis.

2. Quantifying mineral abundances via Raman spectroscopy appears at first sight unlikely to reach the level recommended by the Europa lander SDT report (0.1% = 1 part per thousand for salt species) if calibrated only from X-ray diffraction. To be investigated further in FY20:
   1. Whether other salt species may be more amenable to quantification.
   2. Whether improved sample preparation can enable better quantification.
   3. Whether complementary techniques could reduce uncertainty.
   4. Test Raman quantification of crystalline/glass proportions and nature.

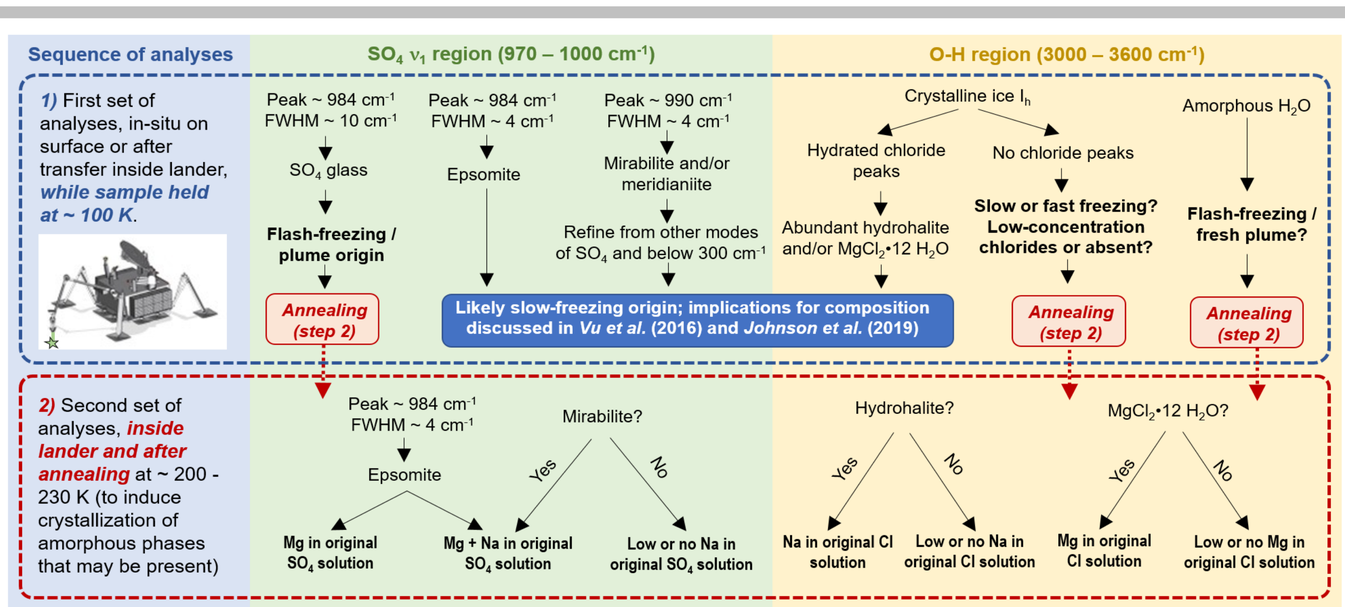

Figure 4. Roadmap for analysis and qualitative interpretation of Raman data of recently exposed areas on Europa surface in terms of hydrated mineral compositions and likely emplacement mechanisms.

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Publications:

Vu T.H., Choukroun M., Hodyss R., Johnson P.V. Probing Europa's Subsurface Ocean Composition from Surface Salt Minerals Using in-situ Techniques. Submitted to *Icarus.*

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