National Aeronautics and Space Administration

Europa's habitability from surface mineralogy: what a Lander "vibrational spectrometer" may find

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Program: FY21 R&TD Topics **Strategic Focus Area: Habitable Worlds**

Objectives: Understanding what materials may be formed upon freezing of ocean fluids extruded to the surface of Ocean Worlds, and how they can be best detected and their abundances quantified, is a fundamental pre-requisite to the quantitative assessment of internal ocean composition and inference of habitability from measurements that would be conducted by a landed platform on the surface of Europa or on other Ocean Worlds. The primary goal of this research is to investigate the performance of a Raman instrument at detecting and quantifying the minerals formed.

Background: The Europa Lander aims at finding evidence for life and/or habitable conditions on Europa. The Europa Lander Science Definition Team report suggested a strawman payload that would achieve these objectives; in particular, a "vibrational" spectrometer (Raman is the strawman payload instrument, infrared considered) is recommended to seek organic and inorganic traces of biological activity and characterize endogenic and exogenic non-ice constituents of the surface (including quantification of their abundances in the 0.1 to tens of percent range). Landed missions are also considered to other Ocean Worlds like Enceladus (Orbi-Lander PMCS study) and Ceres (Lander or Sample Return PMCS study). Although a body of literature exists on the Raman signature of relevant icy minerals (sulfates, chlorides, carbonates, sulfides, oxides, etc.), this literature does not investigate the minimum detection limit, accuracy of concentration determination, or most suitable instrument parameters. Filling these knowledge gaps is essential to constrain quantitatively what such an instrument may find, how well it can achieve its science objectives as function of configuration and parameters, and to prepare adequately for the analysis of scientific data.

Approach and Results: Previous Cryogenic X-ray diffraction results were published in Vu et al. (2020, **publication [A]**). In FY21 we focused on quantitative Raman spectroscopy of sodium sulfate brines, both liquid and frozen (Choukroun et al., **publication [B]**).

In aqueous solutions, we found that as the Na_2SO_4 content decreases in more and more dilute aqueous solutions, the intensity of the sulfate peaks decreases (Figure 1).

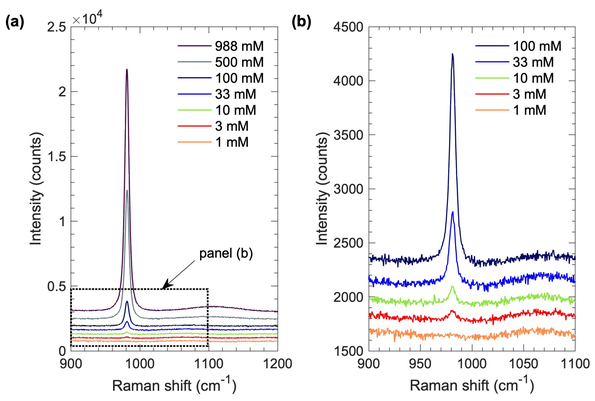

Figure 1. Dilution of Na_2SO_4 solutions results in a gradual decrease of the intensity of the SO_4 peaks. Spectra are slightly offset in intensity for clarity.

Conversely, in frozen brines, we found that the intensity of Raman peaks of Na2SO4 can vary largely within the same sample, see Figure 2. However, the ratio of peak intensities of Na_2SO_4/H_2O appears to remain correlated with concentration.

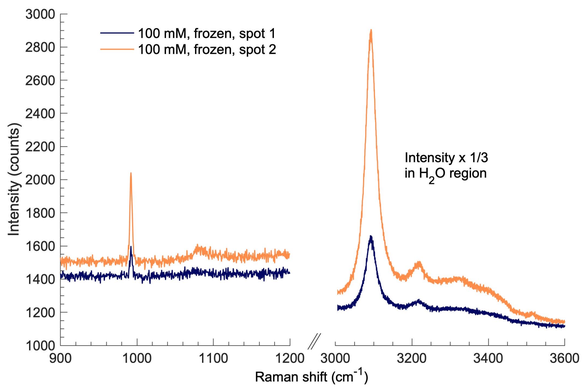

Figure 2. Raman spectra acquired at two different locations of a frozen 100 mM Na2SO4 solution illustrate the large variability in intensity of peaks in each spectral region while peak area ratios are comparable (within 15%).

We conducted a weighted linear regression of SO_4 peak area in liquid solutions and of SO_4/H_2O peak area ratio in both liquid and frozen solutions, and SO_4/H_2O peak area ratio in frozen solutions, see Figure 3.

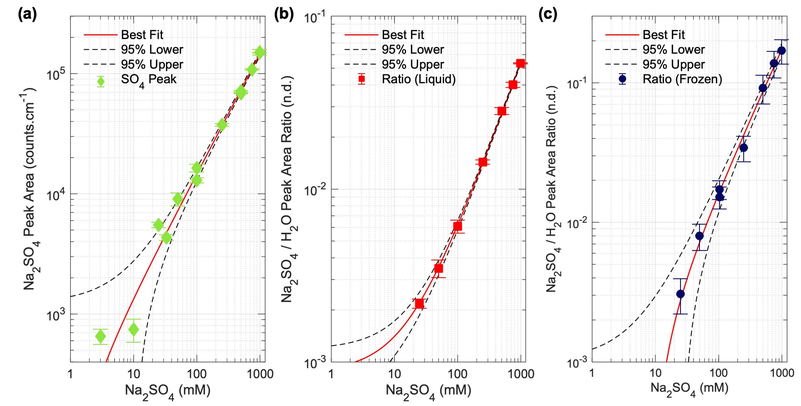

Figure 3: Log-log representations of linear regressions of the liquid and frozen solution datasets, including 95% confidence intervals, showing good quality fits.

We then evaluated the uncertainty of concentration estimates of an unknown Na_2SO_4 solution based on our results and the weighted fits obtained, see Figure 4. The uncertainty varies substantially with concentration. The relative uncertainty also improves drastically as concentration in Na_2SO_4 increases, although the absolute uncertainty increases.

The most important result of this study is that the abundance of Na_2SO_4 in an icy sample can be quantified via Raman spectroscopy down to concentration levels equivalent to the salinity of highly saline terrestrial water environments and sea ice (~ 1 wt% salt), as well as oceanic water (~ 3.5 wt% salt). These results are in publication at time of writing (Choukroun et al., under revisions **[publication B]**).

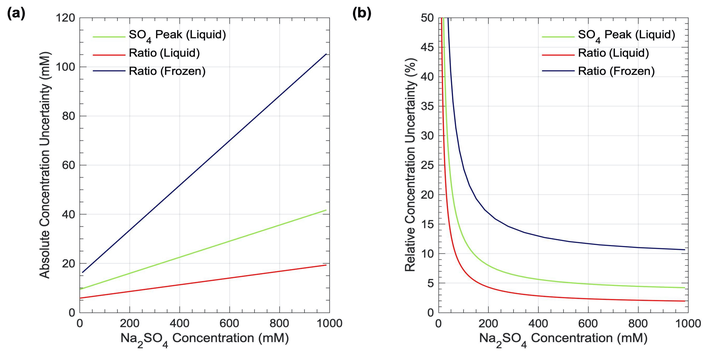

Figure 4. Estimated absolute (left) and relative (right) concentration estimate uncertainty at the 95% confidence level using the linear regressions from the datasets.

Significance/Benefits to JPL and NASA:
This research is the first step towards establishing a leading edge in the definition of science requirements, performance modeling, and scientific data analysis, for a Raman instrument on Ocean World landers.

This research provides robust grounds towards instrument performance assessment in a future proposal in response to a future Ocean Worlds Lander instruments AO, and/or would contribute significantly to the analysis and interpretation of the data obtained by such an instrument.

Publications:

A. Vu, T.H., Choukroun, M., Hodyss, R. and Johnson, P.V., 2020. Probing Europa's subsurface ocean composition from surface salt minerals using in-situ techniques. *Icarus*, *349*, p.113746.
B. Choukroun, M., Mahjoub A., Razzell Hollis J., Sanghavi S., Vu, T.H., Abbey, W.J., Hodyss, R., Johnson, P.V.. "Quantitative Raman spectroscopy of icy materials on Ocean Worlds - an initial assessment from frozen sodium sulfate brines." *Planetary Science Journal*, under minor revisions.

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