The Geochemical Characterization of Planetary Analog Sites Using *in situ* Raman and Reflectance Spectroscopy: Lessons from Field Work in Iceland

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July 28th-August 10th, 2018, Team Ice undertook an expedition to Europa analog sites around Kverkfjoll volcano, Iceland. One of the goals was to test portable Raman and relfectance spectroscopy instrumentation to guide instrument development for in situ planetary science and life detection missions, particularly in icy Europa-like environments. Dr. Bower was the Raman lead, using a Delta Nu Rockhound 785nm hand held Raman instrument. Dr.'s Hewagama and Nixon lead the reflectance, fluorescence, and IR measurements using a Stellar-RAD handheld spectroradiometer and portable IR/NIR spectrometers, FLIR camera, and field portable optical-fluorescence microscope. One task was to make correlative measurements for each target, however, instrument malfunctions and logistical issues prevented the completion of this task. Here we discuss some of the data from in situ Raman measurements in Iceland along with data from Raman, relflectance, and optical microscopy measurements done in the laboratory at GSFC using the same field portable instruments. For comparison, included here also is some data collected from the Iceland samples using a newly acquired TSI EZRaman 532nm portable Raman instrument.

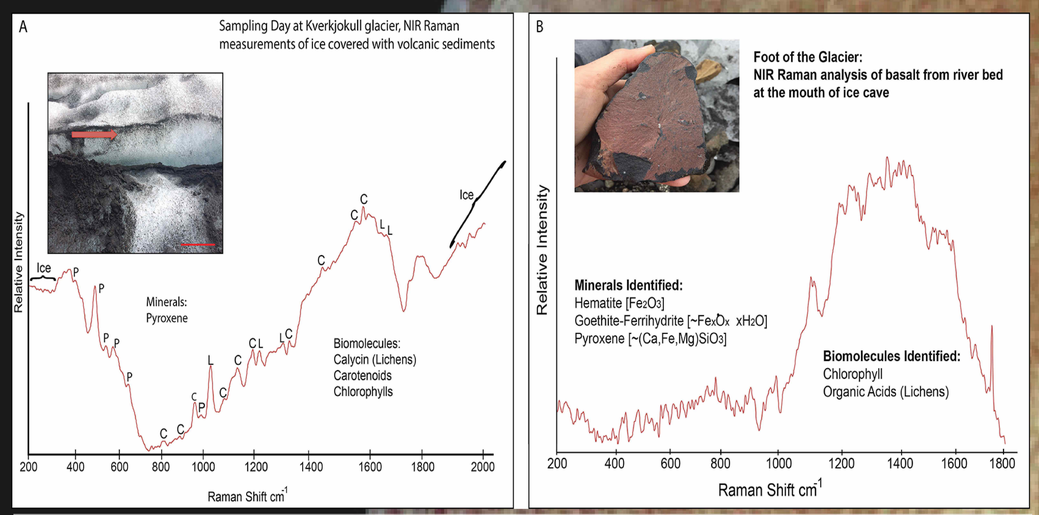

Figure 1 Raman spectra collected *in situ* with the Rockhound at Kverkjokull glacier. A) Measurements of ice coated in volcanic sediment detect a mixture of biomolecules and a pyroxene mineral, ice peaks are outside the bounds of the NIR spectral range. B) Measurements of river rocks also detect mixtures of biomolecules, a pyroxene mineral and mixed Fe-oxides. Spectra are not baseline corrected. Acquisitions 7-10s, high power.

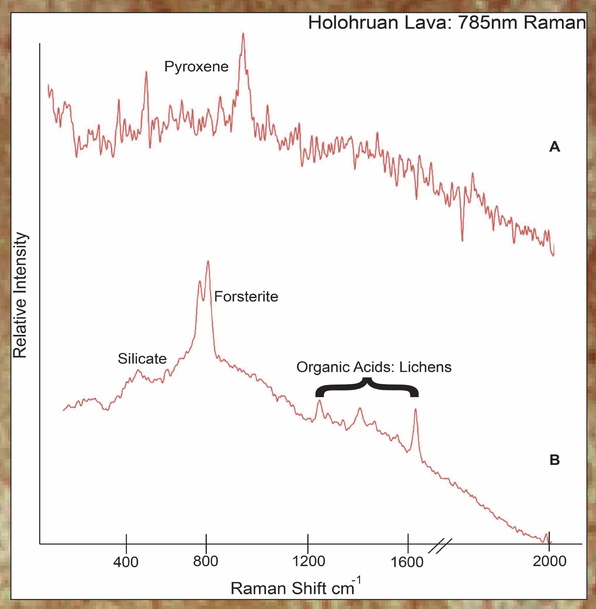

Figure 2. Laboratory measurements using the Rockhound on lava samples collected from Holohruan lava field. A) Raman measurement of rock surface detects a pyroxene mineral. B) Scan of powdered lava sample reveals a specific olivine, forsterite, a silicate, and lichen-derived organic acids. Spectra are not baseline corrected. Acquisitions 5-7s, Med high power.

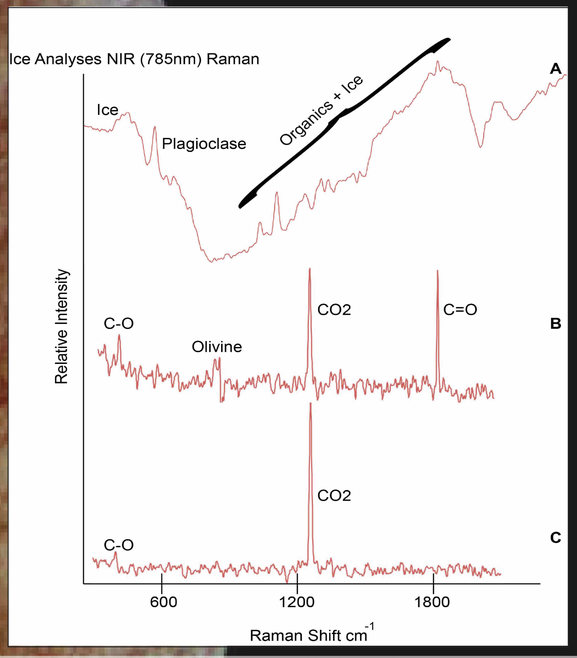

Figure 3. Raman spectra of ice samples as measured by the Rockhound NIR system. A) Spectrum acquired in situ at the foot of the glacier (also shown in Fig. 1), where the ice peak shifts are not apparent due to an excessive signal from biota. B) Spectrum acquired in the laboratory from tap water ice mixed with glacial sediment where some of the gases present in the ice are detected along with olivine. C) Spectrum acquired in the laboratory from tap water ice where two of the peaks were identified. Spectra not baseline corrected.

Note: the 785nm system has a limited spectral range (200 - 2000 cm-1), which prevents the identification of Nitrogen species, OH or H2O peaks that occur in the higher spectral range >2000 cm-1.

Figure 4. Lichens on rock surfaces (white). There are over 400 types of lichens in Iceland!

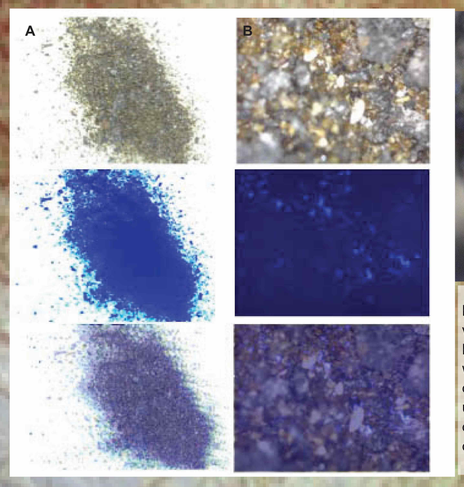

Figure 5. Microscopy images of powdered volcanic sediment and a piece of lava. A) Powder as viewed at low magnification with broadband visible light, UV, and an overlay of the two . B) Higher magnification using same method show more correlation of structure with UV active areas. C) Close-up of lava surface showing Fe-oxide encrustation.

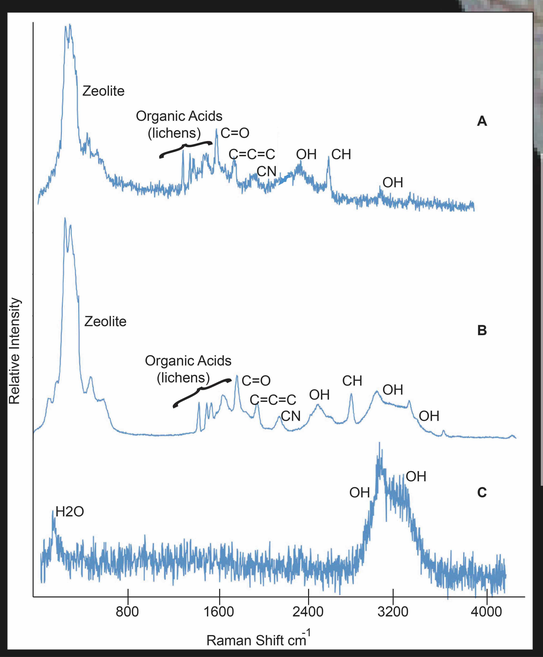

Figure 6. Laboratory measurements using the EZRaman 532nm portable system. A) Lava sample from Holohruan, spectra show a mix of organic acids and a zeolite mineral. B) Ice mixed with powdered lava from Holohruan, same rock features identified with ice peaks. C) Tap water ice. Spectra are not baseline corrected. Acquisitions 2-5s, low power.

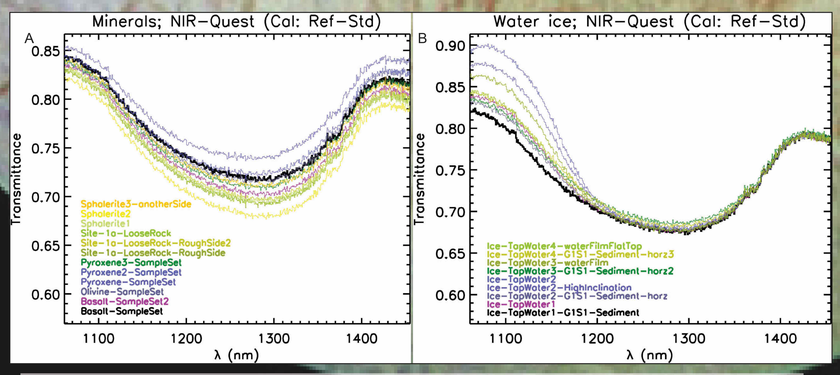

Figure 7. Laboratory NIR reflectance measurements of returned samples, ice, and relevant standards using a portable NIRQuest spectrometer. A) Spectra collected from Holohruan lava samples, basalt standard, and pyroxene, olivine, and sphalerite standards showing similar structure for all samples. B) Spectra collected from plain tap water ice, and tap water ice with added volcanic sediment showing slight differences in structure between samples.

Conclusions and Future Directions

In situ Raman measurements can yield a wealth of information on the composition of ice and rocks and on the predominant types of colonizing biota as demonstrated in Iceland.

- Using a portable NIR (785nm) Raman system it is possible to acquire useful data, however, a VIS (532nm) Raman system offers a wider range of spectral signatures including those necessary to detect water or hydrated chemical species.
- Reflectance spectroscopy has a long legacy with planetary science, and in situ, tightly focused measurements will become more important as future planetary missions evolve.
- Icy environments can make field logistics difficult, especially when multiple instruments are used to study the same target. For future investigations, instruments will be packaged to accomodate slippery and windy conditions, higher efficiency, and ease of use.
- Acclimation to different lithologies and ice variations can be challenging at each site, but is essential for more representative data sets; future field measurement preparations and calibrations will relflect this.
- There is no shortage of biology in the glacio-volcanic environments of Iceland, which can pose a problem for Raman measurements to identify specific inorganic compounds in these materials; future targets will be from the subsurface
- Co-located Raman, reflectance, fluorescence, and optical microscopy measurements were not possible due to instrument limitations; with lessons learned from the field, we are moving forward to develop a portable Raman-reflectance-optical microscopy system for field work and for instrument development/planetary science missions.

Acknowledgements

Team Ice: Conor Nixon (GSFC), Tilak Hewagama (UMCP), Dina Bower (UMCP), Jennifer Eigenbrode (GSFC), Jennofer Stern (GSFC), Aaron Regberg (JSC), Claire Cousins (Andrews Uni), Molly Wasser (ADNET)

Team Fire: Patrick Whelley (UMCP), Jacob Richardson (UMCP), Chris Hamilton (ASU), Sarah Sutton (ASU), Stephen Scheidt (ASU) Joana Voigt (ASU)

Team JS: Amy McAdam (GSFC), Kelsey Young (GSFC), Christine Knudson (UMCP), Cherie Achilles (NPP,GSFC)

And...GIFT, FLaRe, Jake Bleacher, Jamie Elsila Cook, Christine Whelley, Bjorn Oddsson, Sigrun, Stymir, Andrew Steele, Shahid Aslam