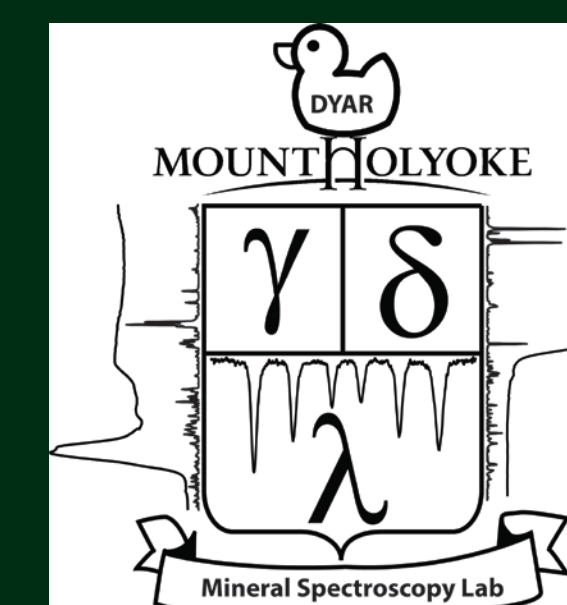


INTERLABORATORY AND CROSS-INSTRUMENT COMPARISON OF RAMAN SPECTRA OF 96 MINERALS



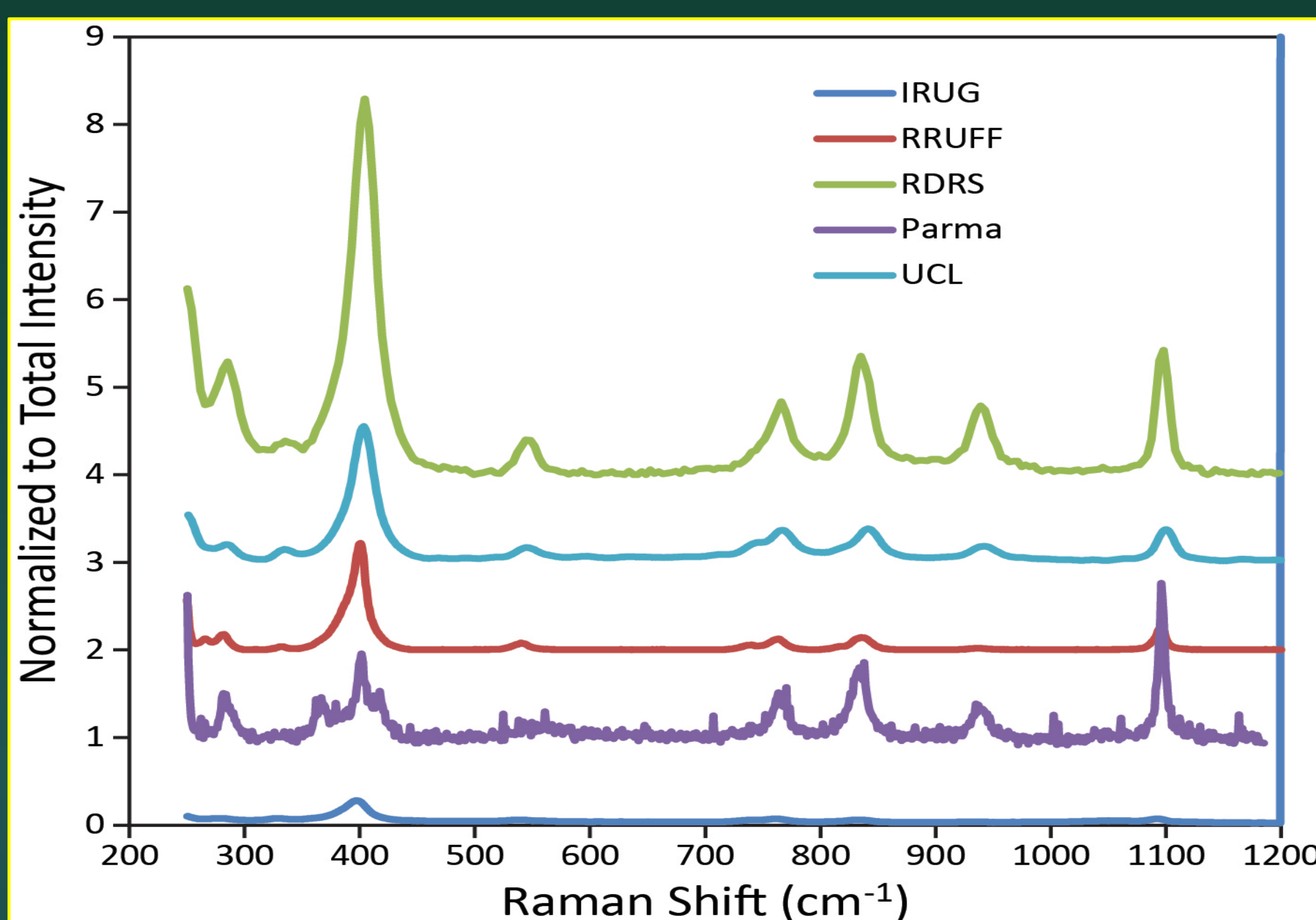
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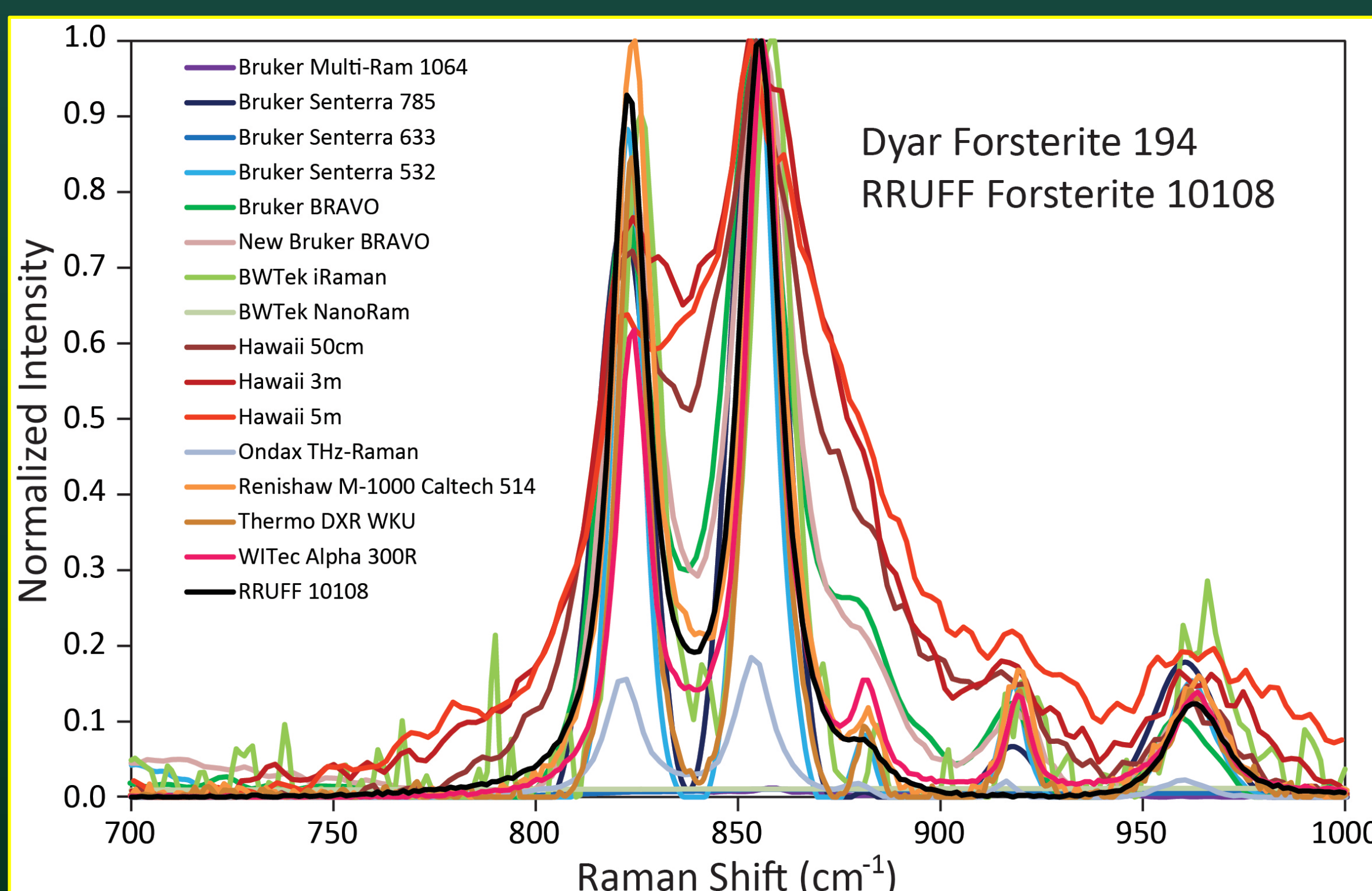
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Overview

The emerging importance of Raman spectroscopy for *in situ* planetary exploration requires an infusion of work into development of databases for mineral identification. Key to that endeavor is an understanding of the characteristics of various commercial and built-from-scratch instruments, their data processing software, and the presumption of consistency of spectra from identical minerals across varying instruments and platforms. This study tests the latter of these assumptions by presenting comparative results on a suite of 96 pure mineral powders from 15 different instrument/laser combinations using an array of geometries and laser energies. Our results assess the usefulness of existing databases built on powder or single crystal data and suggest work needed to align datasets from varying instruments to provide the deepest possible databases for impending Mars exploration use.



Raman spectra of azurite from five different on-line databases: RDRS: <http://rdrs.uaic.ro/>, UCL: <http://www.chem.ucl.ac.uk/resources>, RRUFF: rruff.info, IRUG: <http://www.irug.org/search-spectral-database>, and Parma: <http://www.fis.unipr.it/pheviz/ramandb.html>. All data were normalized to total intensity over this wavelength range. There are clear differences in instrument sensitivity at the various institutions, but the diagnostic peaks associated with azurite are present in all cases. Variations in peak intensities, peak intensity ratios, presence/absence of peaks, and signal to noise are all apparent.



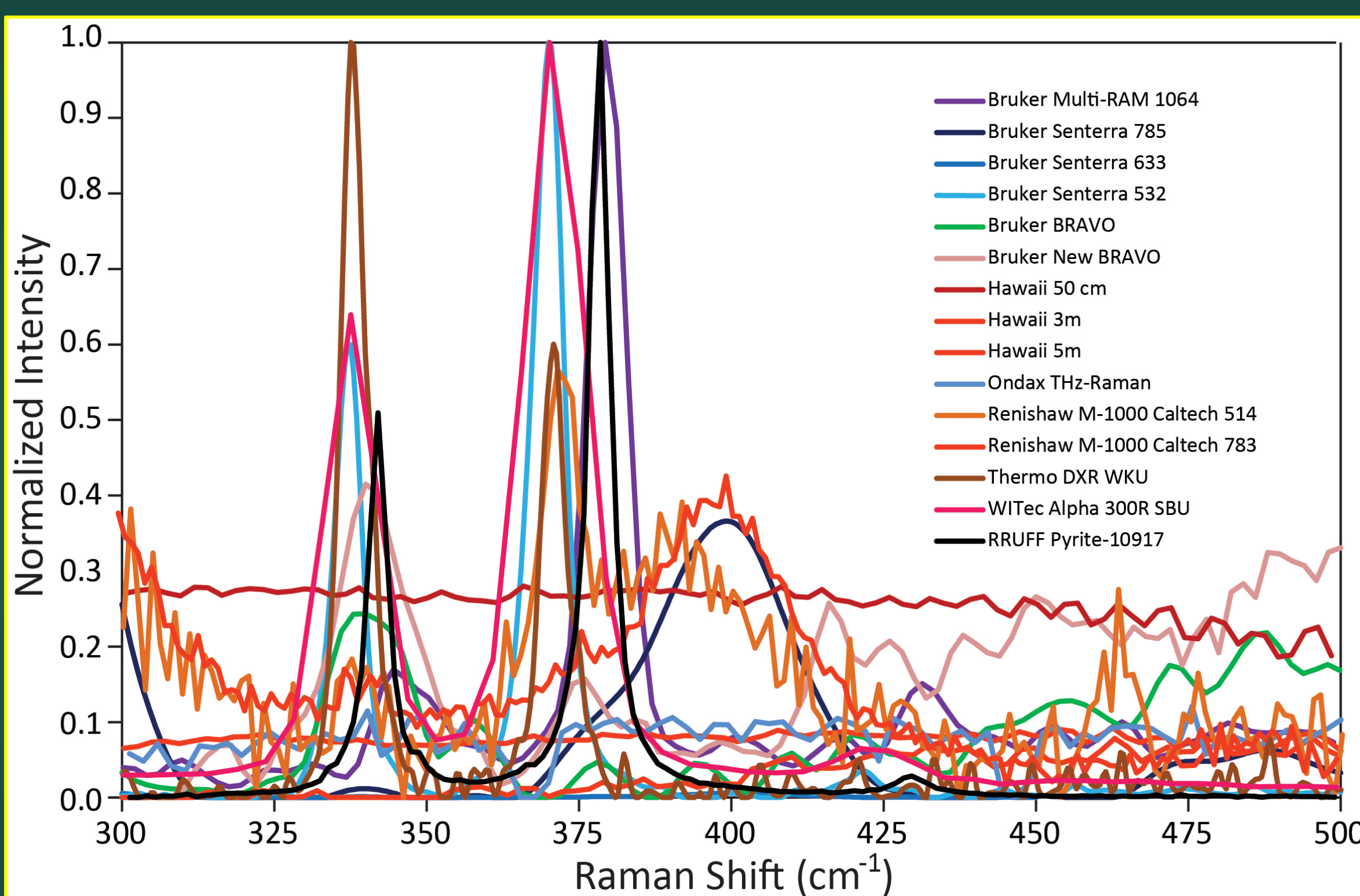
Raman data collected on the exact same forsterite sample on various instruments. Spectra were normalized and baseline-removed. This is Dyar forsterite 194, and RRRUFF forsterite 10108.

Methods

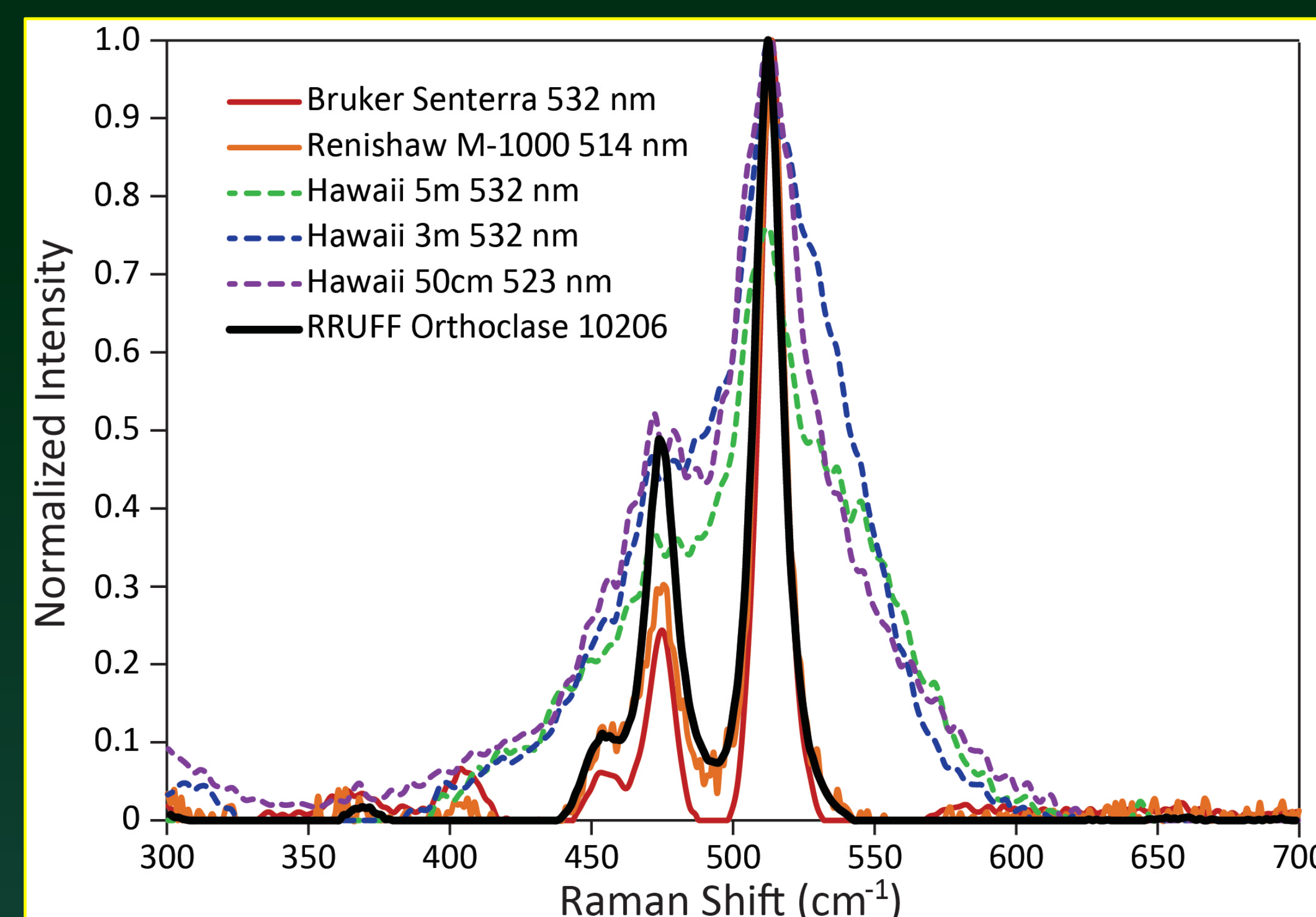
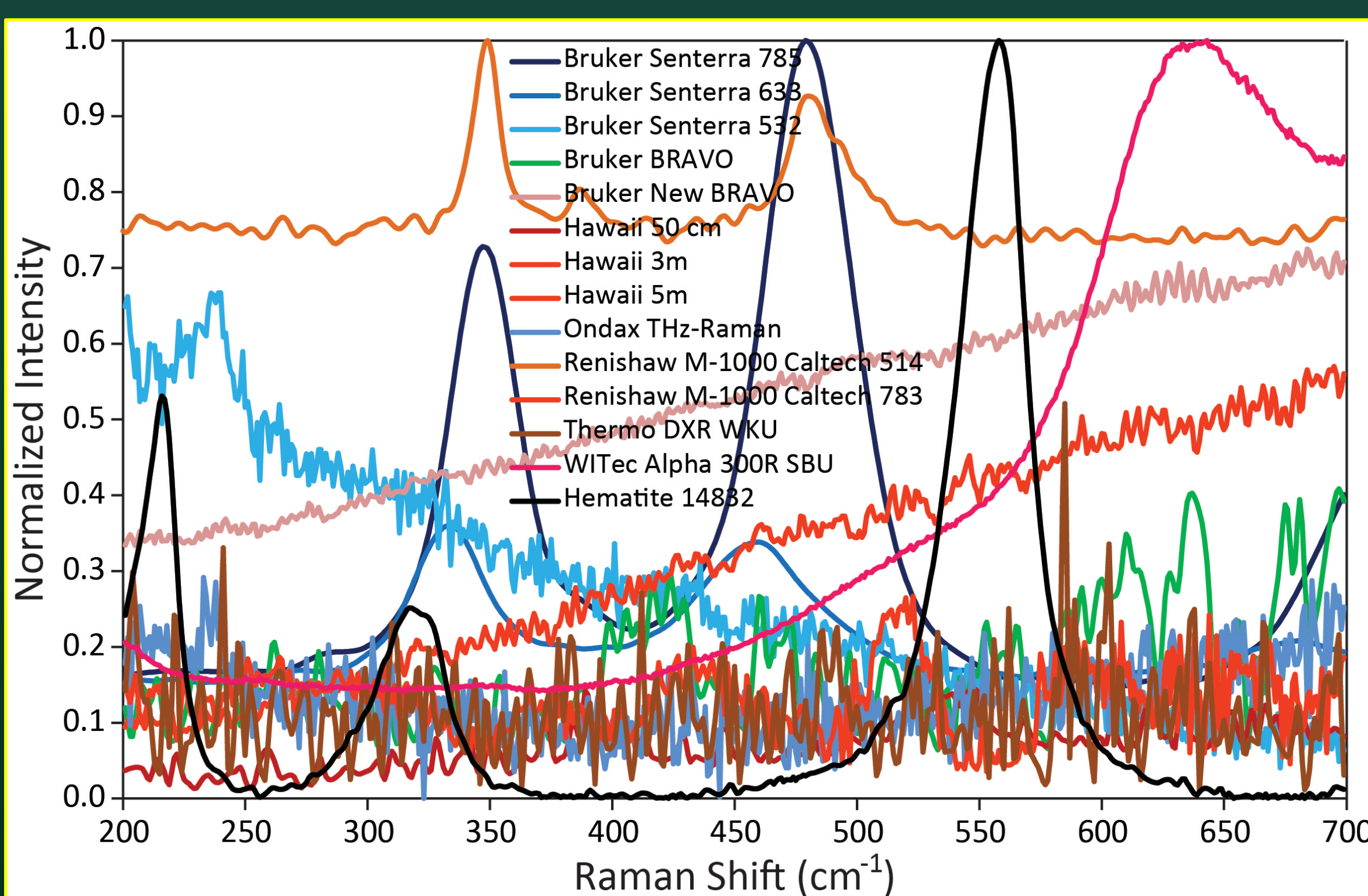
To date, we have collected 15 complete datasets on the 96-sample suite; additional measurements are in process at other labs:

- B&W Tek i-Raman (532 nm laser)
- B&W Tek NanoRam (785 nm)
- Bruker Senterra (532, 633, and 785 nm lasers)
- Bruker MultiRAM 1064
- BRAVO (758 and 852 nm lasers simultaneously)
- An in-house system using a HoloPlex grating, custom-gated thermo-electrically cooled mini-ICCD detector, and 2.5" Meade ETX-125 telescope at the University of Hawaii (532 nm laser) with samples studied at 0.5, 3, and 5 cm standoff distances
- WITec alpha 300R Micro-Imaging spectrometer (532 nm laser) at Stony Brook University
- Thermo DXR dispersive microscope at Western Kentucky University (780 nm laser)
- Ondax THz-Raman system (785 nm laser)
- Caltech Renishaw M-1000 microRaman system (514 and 783 nm lasers)

Data were processed using standard protocols at each institution. These typically include noise, white light, CCD dark-field, substrate and fluorescence corrections and subtraction of cosmic ray events. Spectra were not baseline corrected so as to allow us to manipulate the algorithm used for data from each instrument.



Normalized Raman spectra of the exact same pyrite #79 (above) and hematite #108 (below) samples collected at participating labs. In each plot, a single-crystal spectrum of the same mineral species from the RRUFF database is included in black. These spectra highlight the difficulties in determining mineralogy from Raman spectra of powders, as in planetary exploration when Raman beam size < mineral size.



Comparison of orthoclase data acquired with a 532 nm laser showing differences between powders (dashed lines) and single-crystals (solid lines). RRUFF data are from sample #10206 and all other data are from our orthoclase. Although all spectra here show the pronounced orthoclase doublet, differences in resolution and sensitivity among varying instruments will make it difficult to match these peaks, especially in mixtures.

Issues with Use of the RRUFF Database

Although the RRUFF database is the *de facto* standard for Raman data interpretation, there remain significant difficulties in using those data. These include:

1. RRUFF data are acquired at different laser wavelengths (514 nm, 532 nm, 780 nm, and 785 nm) and from oriented and un-oriented single crystal samples that are not always appropriate when matching against powdered samples.
2. 35.9% of RRUFF samples are without confirmed identifications by independent techniques, making those data useless.
3. By design, RRUFF focuses on representing a broad range of the ~4,000 known mineral species rather than on complete coverage of common rock-forming species.
4. Important mineral groups such as the pyroxene quadrilateral and the olivine solid solution are not well-represented in RRUFF.
5. Many RRUFF spectra are contaminated by mild to strong fluorescence features resulting from minor elements that give rise to fluorescence centers; these are not characteristics of the individual minerals, and have the potential to confuse matching algorithms.
6. RRUFF contains no data on mineral mixtures because it uses single crystals. Depending on the beam sizes used in planetary exploration, it is likely that mineral mixtures will be encountered on planetary surfaces.
7. The RRUFF database is no longer growing.

Although several mission concepts are currently being developed that will use Raman spectroscopy, much work remains to be done to provide appropriate and sufficient mineral and mineral mixture databases for calibration. A theoretical framework and improved software for mineral identification and un-mixing are also badly needed.

<http://nemo.cs.umass.edu:54321/>

Acknowledgments: Work supported by NASA SSERVI grant NNA14AB04A (RIS⁴E) and the Massachusetts Space Grant Consortium.