

Changing the Science of Mineralogy: The Use of Raman Spectroscopy in Mineral Identification and the RRUFF Project

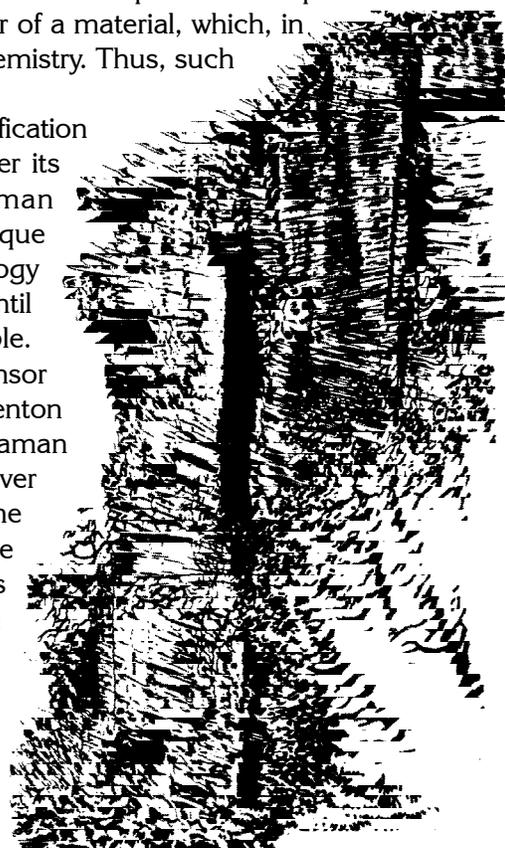
By Charlene F. Estrada, University of Arizona Geosciences Department

Raman spectroscopy is a technique that is revolutionizing the daunting task of identifying minerals. When encountering minerals, it can be difficult to know the identity of a specimen with certainty. In the past, destructive and time-consuming methods such as X-ray diffraction were required to confirm a mineral's identity. However, with Raman spectroscopy, it may take only seconds to complete the same task for a wide variety of minerals.

The Raman effect was first discovered in 1928 by C. V. Raman. When a material is exposed to an incident laser beam, its atoms are excited into various vibrational states. While the atoms oscillate, the incident light is scattered and captured by a spectrometer. Depending on the specific vibrational modes of the material, some of the incident photons may experience a change in energy, which is recorded in the spectrum as a peak. The Raman spectra reflect the vibrational behavior of a material, which, in turn, is dictated by its underlying structure and chemistry. Thus, such spectra act as fingerprints of particular materials.

The potential of Raman spectroscopy for identification purposes was recognized almost immediately after its discovery, but the cost and difficulty of Raman spectrometers limited the availability of the technique to most mineralogists. Laser and CCD technology improved Raman spectroscopy, but it was not until recently that the method became readily accessible. In 2003, NASA funded Hamilton Sundstrand Sensor Systems and Drs. Robert Downs and M. Bonner Denton of the University of Arizona to miniaturize the Raman spectrometer to less than 200 cm³ for a future rover mission to Mars. The machine, once occupying the space of a large table, has been condensed into the size of a book, which is convenient for mineralogists who may encounter a specimen in the field. When the United States government considered the use of Raman spectroscopy to identify unknown materials for homeland security, the device continued to decrease in size and cost. Currently

(Continued on page 6) ►



In This Issue...

Features

- 14 AAPG House of Delegates Passes Graduated Dues Structure
- 20 Foundation Gifts Exceed \$70,000 in 2006
- 21 2007 Coalbed Methane Symposium
- 33 Extensional Tectonic Systems in Exploration and Production Sponsors
- 36 AAPG Spring Courses

Association News

- 10 13th Annual 3-D Seismic Symposium
- 16 RMAG Golf Tournament
- 16 RMAG Fall Symposium
- 28 RMAG Membership Application Form
- 35 GEOLANDSKI 2007

Departments

- 2 Welcome to New Members
- 3 President's Column
- 4 Friday Luncheon Programs
- 15 In Memoriam
- 15 RMAG Auxiliary
- 18 In the Pipeline
- 24 Revisions, Moves and Gyration
- 27 March RMAG Board Highlights
- 37 On the Rocks Field Trips
- 37 This Month's Advertisers
- 40 Geo-Calendar

Changing the Science of Mineralogy

(Continued from page 1) ▼

there are models available for under ten thousand dollars, and the price is expected to further decrease.

Following the NASA project, Downs and his colleagues predicted how the demand for Raman technology would rise in the coming years and proposed a project to construct a database of Raman spectra for every known mineral on Earth to support the new handheld Raman devices. While NASA regarded this proposal as too ambitious, Mike Scott, a gem enthusiast, Caltech graduate of physics, and founding president of Apple Computers, provided Downs with the means to create the database on the condition that it be made available to the public. From this agreement, the RRUFF Project – named after Scott's cat – was born.

The University of Arizona, partnering with Caltech's mineral spectroscopy expert, Dr. George Rossman, has since become home to the RRUFF Project. Now entering its third year, the database has integrated 1300 mineral species and 2500 samples with emphasis on common gems and rock-forming minerals. Accompanying each sample is a thorough process of identification that ensures that every mineral is fully characterized in the database. The sample is first examined with Thermo's Almega XR, which is equipped with 532nm and 785nm lasers. The laser beams, about 1-2 microns in diameter, will excite an area of the mineral that has been targeted using a microscope. The depth at which the laser penetrates the sample will vary. A Raman spectrum is collected under each laser for the unoriented sample.



The Reporte[®] system, an eleven ounce Raman spectrometer developed by DeltaNu. When released, it will be the first pocket-sized Raman system. As Raman technology continues to develop, it is anticipated that Raman spectrometers will become more portable for practical use by the public. Photo courtesy of DeltaNu, Inc.

Another property of the Raman spectrometer is its ability to record non-Raman related peaks, such as fluorescence peaks related to trace element chemistry. It is anticipated that these additional peaks may be locality specific, but as of yet they remain poorly understood.

Four Raman spectra are collected for a single unoriented sample. In their unedited form the spectra frequently contain cosmic rays that confound the interpretation of the sample. The software that was available at the inception of the RRUFF Project was insufficient to evaluate Raman and X-ray diffraction spectra, and therefore new software was required. The RRUFF Project developed software called CrystalSleuth, which was designed specifically to analyze X-ray diffraction profiles and Raman spectra. The software, now popular in labs across the nation, easily removes cosmic rays, corrects background and evaluates the spectra so that they can be studied and identified online.

While collecting Raman spectra of mineral samples is undeniably the heart of the RRUFF Project, the database contains information that reaches beyond this technique to illustrate the properties of the mineral. After the sample is examined under the Almega XR, it is photographed at both the macro and micro scale. For the latter of these, the photographers use a Leica microscope and Olympus CCD camera to capture the mineral at scales ranging from centimeters to micrometers. In many cases, these photographs may represent the first quality pictures of a particular mineral.

The parent rock is then broken and crystals are extracted. They are mounted, polished, and analyzed with

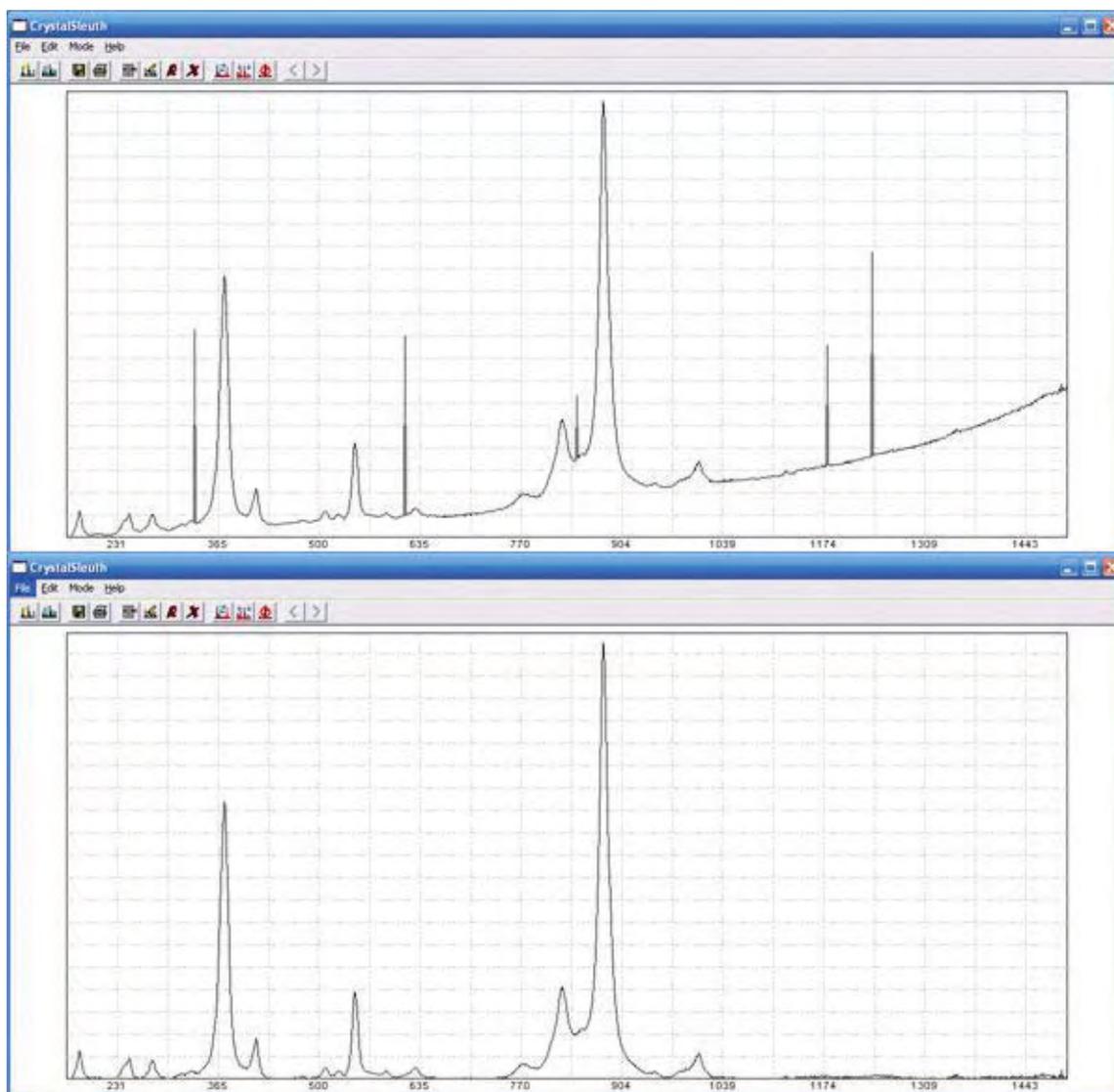


A student collecting Raman spectra on the Almega XR at the RRUFF Lab of the University of Arizona. Undergraduate students regularly screen mineral samples in the RRUFF Project.

(Continued on next page) ►

Changing the Science of Mineralogy

(Continued from page 6) ▼



(Top) A Raman spectrum of grossular recorded by the spectrometer with cosmic ray interference, illustrated by the sharp peaks. (Bottom) The same spectrum analyzed with the software, CrystalSleuth, which removes cosmic rays and corrects background. CrystalSleuth is available to download for free at the RRUFF project website.

X-ray diffraction to confirm the Raman identification by mapping the crystal's underlying structure. The sample crystal is next oriented under a 514 nm laser in order to collect more Raman spectra. The spectra are obtained for every possible orientation determined from X-ray diffraction analysis. This records any variation within a mineral that is dependent on crystal orientation and includes all Raman peaks that a single sample might emit. The single crystal sample also undergoes Electron Microprobe Analysis to confirm the chemistry of the mineral and complement the X-ray diffraction data. All three techniques are essential to

capture the information necessary to make the RRUFF Project database a reliable and accurate resource in crystallography.

Approximately one hundred samples undergo this process each month. Additionally, the RRUFF Project is adding encyclopedic references and associated journals to the database to enhance the amount of data available for any given mineral. With funding from the National Science Foundation and in collaboration with the IMA, the RRUFF Project is compiling the first list of all known

(Continued on page 8) ►

Changing the Science of Mineralogy

(Continued from page 7) ▲

minerals and their crystal structure data. A goal of the RRUFF Project is to permit estimates within 1-2% of major element chemistry and temperature-dependent order-disorder states of minerals. It will not only be the leading resource on Raman spectroscopy of minerals, but it will redefine the fields of mineralogy and its corollaries.

The RRUFF Project's mission is pioneering and considerable, and as such, it has been supported by researchers around the nation. Partnered with Caltech University, it has become an intercollegiate effort. The mineralogical societies of America, Canada, Great Britain and Japan have also provided invaluable information to the project by making their journals available online. Furthermore, the lab receives rare sample donations from museums, collectors and dealers along with those in Scott's collection to push the database closer to completion.

The amount of support and research from collaborating mineralogists and collectors has aided the RRUFF Project in establishing itself as one of the most groundbreaking efforts in geosciences. What furthermore places the RRUFF Project apart from other endeavors is that it is largely student-operated. Approximately 30 students participate

in compiling the database, the majority of whom are undergraduates with a wide variety of majors. These students perform tasks requiring graduate-level skills, from collecting Raman spectra to conducting X-ray diffraction experiments. These students have emerged from the RRUFF Project with valuable experience that employers such as Phelps Dodge have pursued.

Raman spectroscopy is steadily changing the science of mineralogy. In the near future, field scientists will be able to identify a material in situ using a handheld Raman device. This will save hours in laboratories and decrease the need for X-ray diffraction and microprobe methods. The RRUFF Project has already anticipated this change, and it is leading the movement toward this future. For the present, it is producing the largest known archive of spectroscopic data on the world's minerals. When the practical implementation of Raman spectroscopy becomes an option, the RRUFF Project database will have met the evolving needs of the scientific community.

The RRUFF Project database is available online at <http://rruff.info>. ◀

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