

The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals

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The RRUFF project is an integrated study of the physical properties of minerals with freely accessible data that can be obtained from the Internet at RRUFF.geo.arizona.edu. The goal is to obtain representative samples of all known minerals from which X-ray diffraction patterns and chemical composition are obtained. These two sets of data are used to identify and characterize the samples. The samples are then oriented along crystallographic and optic directions, mounted and polished on pins. Polarized Raman and infrared spectra are then obtained in a number of orientations. The data is presented in a searchable format through a web interface. Algorithms and software are being developed to permit searching and identifying unknown samples from chemistry, diffraction profiles or vibrational spectra. A database of Raman spectra is being developed for use in remote sensing, such as on the Mars Rover, and for the new generation of compact, hand-held Raman instruments that are coming to the commercial market.

P03-01

Resonant ultrasound spectroscopy of natural polycrystalline samples

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The elastic properties of minerals have been determined largely using ultrasonic techniques on single crystals. Bulk moduli have also been obtained by fitting equations of state to single crystal diffraction data for unit cell volume as a function of pressure. These are then converted to bulk and shear moduli for polycrystalline samples using the Voigt/Reuss/Hill or Hashin-Shtrikman averaging schemes. We have started to use resonant ultrasound spectroscopy (RUS) to measure the bulk and shear moduli directly for natural monomineralic polycrystalline samples. Data from natural anorthosite samples show close agreement with known single crystal values for shear moduli, within the limits of the Voigt and Reuss averages. For pure anorthite, good agreement has also been obtained with known values for its bulk modulus. We have also used RUS to follow the evolution of the bulk and shear moduli and the quality factor (Q) through the high temperature phase transitions in quartz. These experiments show the same softening of the bulk and shear moduli on approaching the α - β phase transition at 573°C as determined from single crystal experiments. There is a slight discrepancy between the two data sets close to the transition; however this inaccuracy may be due to the significant decrease in Q in the vicinity of the transition, the evolution of which can be followed easily using this method. This approach will also allow the systematic variation of elastic properties as functions of composition and temperature across a solid solution series to be determined quickly and accurately using natural samples or synthetic polycrystalline pellets.

P03-02

XAS and structure refinement allied to understand site preference and local environment of major and trace elements in garnets

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Notwithstanding the many published studies undertaken with a plethora of experimental and theoretical approaches, some important details of the crystal chemistry and thermodynamics of garnets are still to be fully understood. XAS analysis is useful to clarify two important issues: (i) site preference and local environment of trace elements, to obtain a better interpretation of experimental partition coefficients; (ii) changes in the local coordination and possible clustering effects in non-ideal solid solutions (e.g. pyrope-grossular, prp-grs).

XAS measurements at different elemental absorption edges were done on natural and synthetic garnets of various composition, previously characterised by electron and ion microprobe and single-crystal structure refinement.

Combining all the available information, we obtained the following conclusions:

1. REE enter the X site. In the loose structure of melanites, their local environment (in terms of X-O distances) varies linearly with their ionic radii; however, site distortion, expressed as $\Delta X-O = X-O_{\text{long}} - X-O_{\text{short}}$, tends to decrease as a function of the ionic radius.

2. The local coordination of REE and Ca changes in distinct garnet compositions (e.g., melanites, pyrope, grossular). Moreover, the trends obtained for Ca and REE have different slopes in different garnet compositions, suggesting a failure of the ionic model at least in the prp-grs join.

3. Measurements done at the Ca K-edge along the prp-grs join show that Ca local environment depends on the overall composition of the sample, and that $\Delta X-O$ tends to decrease passing from grossular to pyrope. At prp60grs40, the two distances are indistinguishable by EXAFS analysis, whose resolution is however limited by the presence of oxygen as back-scatterer species.

4. Measurements done at the Sc K-edge show that Sc may enter all the available structural sites depending on the overall composition and the relative dimension of the sites. In the very compact structure of pyrope, Sc enters the X site, and local charge balance is achieved by Mg at the adjacent T site.

5. Sc is generally considered an octahedral cation in garnets. We found that Sc at Y does not exceed 0.20 apfu when the dominant cation is Al, whereas the Sc vs. Fe³⁺ exchange is almost ideal.

Given the complexity of the problem, the intrinsic limits of each technique, and the implications of these results, we are presently comparing our data with those obtained with other spectroscopic techniques, such as NMR, and with potential-based computations done by other groups.

P03-03

Chemical state of Fe in igneous rocks using high resolution X-ray fluorescence, HRXRF

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The Moessbauer spectroscopy is only method for practical use, when someone wishes to analyze the chemical state of Fe without destruction of the sample. However, the method is not so high sensitivity, and possible utilizing place has been limited due to the necessity of radioisotope.

On the contrary, X-ray fluorescence spectroscopy (XRF) is so wide use method for qualitative and quantitative analysis as well known. And, it was already reported on several fields that the spectrum profile of characteristic X-ray obtained by high resolution measurement shows the change in proportion to the chemical state. Using this phenomenon, the chemical state of any element can be decided.

In this report, the application result of this high-resolution X-ray fluorescence spectroscopy (HRXRF) for the chemical state analysis of Fe in the typical volcanic rock samples was presented. The method is not necessary of ultra vacuum around the sample. And it is available for insulators, solutions, materials containing water. HRXRF is only method for correct chemical state information for bulk. The HRXRF spectra were measured by the double crystal type spectrometer whose crystals are the ++ alignment. The standard samples for assignment of chemical state were Fe₂O₃ for Fe(III) and FeTiO₄ for Fe(II). In the following report, we would like to mainly discuss the result of the volcanic rocks of Asama Volcano.

From the comparison between the of Fe K α 1 spectra of two standard samples, the peak position of FeTiO₄ (Fe(II)) was 0.10eV higher than that of Fe₂O₃ (Fe(III)). On the other hand, the peak position Fe K α 1 of the lava sample obtained from Onioshidashi lava in Asama volcano appeared between the positions of these two standards, 0.07eV higher than Fe₂O₃, and the width of the peak was also broader than Fe₂O₃. Then, the peak separation technique with measured spectra for components spectra were adopted to this spectrum, and it was found that Fe(II) : Fe(III) was 64:36 with the sufficient precision of the calculation. In addition, two pyroclastic fall samples obtained at Asama B' were also analyzed with same process, and it was also found that the amount of Fe(III) existed further than Fe(II). Additionally we could discuss the results about the other igneous rocks. Finally, we would like to suggest this method. HRXRF could be contributed for the progress of mineralogy, petrology and volcanology.