

INVESTIGATING THE ORIENTATION OF MINERALS USING FTIR MICROSPECTROSCOPY. D. J. P. Martin¹, A. Leiva¹, S. K. Bell¹, J. F. Pernet-Fisher¹, K. H. Joy¹, A. Morlok², R. A. Wogelius¹, H. Hiesinger². ¹School of Earth and Environmental Sciences, University of Manchester, Oxford Road, Manchester, M13 9PL, UK. dayl.martin@manchester.ac.uk; ²Institut für Planetologie, Wilhelm-Klemm Strasse 10, 48149 Münster, Germany.

Introduction: Mid-infrared (mid-IR; 3-15 μm) spectroscopy of planetary samples and analogues has increased in recent years due to the improved capabilities of FTIR spectrometers, and due to some planetary missions analyzing the surfaces of airless bodies in infrared wavelengths (such as the Diviner Lunar Radiometer and the Mercury Thermal Infrared Spectrometer: MERTIS). FTIR analyses of geologic samples are sensitive to variations in crystal lattices (such as chemical or structural influences) [1]. As many common rock forming minerals do not have symmetric lattices, their orientations alter the positions and intensities of the Reststrahlen Bands (\sim 7-15 μm), a region of the EM spectrum sensitive to silicate minerals [2]. RAMAN spectroscopy (a complementary technique to FTIR) is sensitive to crystallographic orientation in both terrestrial and lunar minerals [3]. FTIR studies at Caltech have identified orientation variations in some silicate minerals, though not those commonly found in planetary samples. Therefore, we have investigated the variations in FTIR spectra due to crystallographic orientation within minerals commonly found in extraterrestrial materials.

Samples: Three common rock forming minerals were studied: olivine, enstatite, and plagioclase. Single well-defined olivine and enstatite crystals, loaned from the Manchester Museum (ID: N19335 and 1166 respectively), were cut and polished perpendicular to their 3 crystallographic axes. An anorthite crystal from Miyake Jima, Japan was also prepared in the same way [4]. Miyake Jima (MJ) anorthite may be similar to lunar anorthite [5] so may be a suitable lunar analogue. Samples were also loaned from the International Space Analogue Rockstore (ISAR [6]) and include olivine and enstatite for spectral comparison with minerals of unknown orientation. An anorthosite from Shawmere, Ontario, was prepared as a polished thin section for spectral comparison of randomly aligned anorthite with the Miyake Jima anorthite.

FTIR Techniques: A PerkinElmer Spotlight-400 spectrometer with attached mapping unit has been used to obtain mid-infrared (3-15 μm) spectra of the polished surfaces of the mineral samples, using a spot size of 25 μm and resolution of 4 cm^{-1} . For the Shawmere anorthosite thin section, an FTIR image was collected using the same spot size and resolution as the individual spectra (for consistency). A principle component analysis routine (PCA – a multivariate statistical procedure used for phase identification) was applied to the FTIR image to create a color projection that distinguishes between spectral differences (and,

hence, minerals or mineral orientation). See [7] for more details related to FTIR imaging.

Olivine N19335: The spectra of crystal faces cut perpendicular to the b- and c-axes are similar, with bands located at \sim 1025 (shoulder), 974, 942, 890 (shoulder) and 834 cm^{-1} (low %R i.e. <20 %R) (Fig. 1a). The difference between these spectra and those of the a-axis is the %Reflectance (%R) value of the 974 peak, with the a-axis having a reduced value (45 %R compared to 75 %R). A-axis spectra show a different profile, with peaks at \sim 1080 (low %R), 974 (low %R), and 890 cm^{-1} . Also, CF positions vary between the b- and c-axes (\sim 1122 cm^{-1}) and a-axis (1107 cm^{-1}) spectra. Faces 110 and 120 were analyzed, with spectra resembling mixing between those of a- and b-axes.

Enstatite: Spectra of a- and b-axes show similar reflectance band positions but varying %Reflectance values for those peaks (with b-axis spectra being 20-30 %R lower than those of the a-axis). C-axis spectra have band positions that are shifted to higher wavenumbers (shorter wavelengths) and possess a highly reflective (>80 %R) peak at 1100 cm^{-1} .

Miyake Jima Anorthite: Each axis displays spectra with some similar RB trends; for example, the dominant reflectance peak is situated at 940 cm^{-1} . However, a-axis spectra have a single peak at 1156 cm^{-1} , whereas b- and c- axis spectra have 2 peaks at 1140 cm^{-1} (shoulder) and \sim 1108 cm^{-1} . An absorption feature varies in position with orientation: 1087, 1069, and 1050 cm^{-1} for the a-, b-, and c-axes respectively.

Shawmere anorthosite: Following PCA analysis, the spectral image of the Shawmere anorthosite thin section distinguishes the anorthite crystals in different crystallographic orientations. Both simple and multiple twinning can be observed in some of the grains.

Comparison to ISAR Mineral Standards: The ISAR minerals are chemically well characterized, but their mounting orientations are unknown. We compare their FTIR spectra with those of the Manchester Museum minerals to estimate mounting orientation.

Olivine: The ISAR olivine standard (12PK03-1) displays spectra with similar peak positions as the a- and c-axes of N19335. This suggests that 12PK03-1 was mounted at an orientation angled between the a- and c-axes (such as face 101 or similar). The CF position of the 12PK03-1 is 1141 cm^{-1} , which does not match the range of N19335. This is likely due to chemical differences between the minerals and indicates that N19335 is more fayalitic than 12PK03-1.

Enstatite: FTIR spectra of the ISAR enstatite standard (12TZ01-1) matches those of c-axis spectra of

1166. The CF positions also match (at 1206 cm^{-1}), indicating they are also chemically similar. Again, chemical characterization of this sample is required.

Comparison of MJ Anorthite with Shawmere Anorthosite: As crystals in the Shawmere anorthosite are randomly oriented, comparison of their spectra with those of MJ anorthite allows for orientation to be estimated. The spectra of Plag 1 (black in Fig. 1c) match those of the c-axis spectra of MJ anorthite. The lightest color (Plag 2) matches those of the a-axis. Plag 3, an intermediate blue, spectrally matches the b-axis spectra of MJ anorthite. However, Plag 4 (dark blue) represents a mixed orientation, likely between a- and c-axes (as the absorption feature is situated at 1060 cm^{-1} , and a double peak at 1156 and 1108 cm^{-1}). It is unclear whether any b-axis component is present, though spectral unmixing routines may further aid this investigation. These comparisons show that approximate orientations of anorthite can be determined from FTIR spectroscopy and applied to rock sections to determine the presence (or absence in the case of the Shawmere anorthosite) of a fabric.

Discussion: The comparison of ISAR and Manchester Museum samples indicate that FTIR spectroscopy of olivine and enstatite can be used to infer their orientation in polished samples. A well-defined mineral face or a plane through the mineral (e.g. observed in polished sections) will result in a spectrum that represents a mixture of 2 or more of the axes. As the CF positions vary between different orientations of the same crystal, the apparent chemical composition may also differ, i.e., orientation may skew the measured chemistry due to the proportions of each atom at the sample surface being different when the lattice is viewed from different angles.

Anorthite results: Within unconsolidated (i.e., soil)

samples where crystal orientation is random, a bulk sample spectrum represents an average mixture of all orientations present. However, in polished sections, individual minerals, or coarse-powders, orientation effects of the minerals present should be accounted for. This is important when applying band ratios to such spectra, as variations in band ratio values could be due to mineral orientation. The spectral variations due to orientation as a result of this study were applied to [8] to develop 2 band ratios for identifying randomly oriented plagioclase crystals within Apollo soils.

Conclusions: For upcoming missions, such as BepiColombo that will analyse Mercury's surface using the MERTIS instrument, understanding the physical and chemical properties that alter the mid-IR spectra of minerals is essential for investigating the chemistry and mineralogy of planetary surfaces. As such, these data will be included in the IRIS spectral database, being developed at the Institut für Planetologie, Münster [9].

Future Work: Chemical analyses of the minerals used in this study need to be performed to understand the spectral variations due to chemistry. Further investigations into the spectral properties of lunar and martian analogues will take place as part of ESA's Sample Analogue Curation Facility [10-12] in order to develop analogues with similar spectral properties to lunar and martian samples.

References: [1] Smith B. C. (1996) *Fundamentals of Fourier Transform Infrared Spectroscopy*. [2] Farmer V. C. (1974) *Min. Soc. London*. 539pp. [3] Haskin L. A. et al. (1997) *JGR: Planets*, 102, 19293-19306. [4] Pernet-Fisher et al. (2017) *Scientific Reports*, 7, 5888. [5] Brydges T. F. V. et al. (2015) *LPSC XLVI*, Abstract #1251. [6] Westall, F. et al., (2013) *LPSC XLIV*, Abstract #1397 [7] Martin D. J. P. et al. (2017) *MaPS*, 52, 1103-1124. [8] Martin D. J. P. et al. (2018) *LPSC XLIX* Abstract #2123. [9] – Weber I. et al. (2018) *LPSC XLIX* Abstract #1430 [10] Sample Analogue Curation Facility website - <http://www.nhm.ac.uk/our-science/our-work/origins-evolution-and-futures/esa-exploration-sample-analogue-collection-curation-facility.html> [11] Smith C. L. et al. (2018) *LPSC XLIX* Abstract #1623. [12] Manick K. et al. (2018) *LPSC XLIX* Abstract #1411.

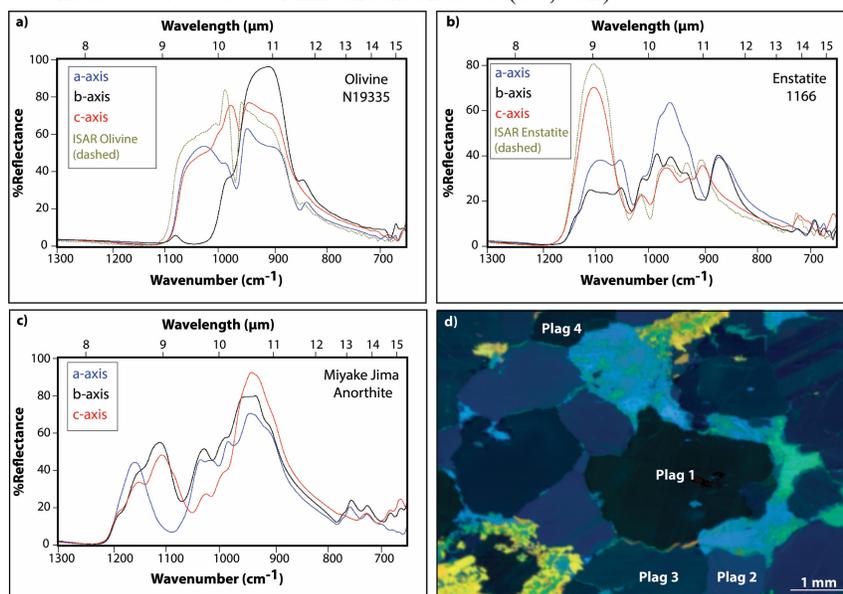


Figure 1 – FTIR spectra of a) olivine and b) enstatite from Manchester Museum and ISAR. c) Miyake Jima anorthite showing the spectral variations due to orientation. d) an FTIR image following PCA analysis to visualize the orientation variations of anorthite in a Shawmere anorthosite.