Thermal-Infrared Emission Spectroscopy of Graybody Materials: Sulfide K. M. Hubbard (k.m.h@asu.edu),[1,2] C. W. Haberle[1,3], L. T. Elkins-Tanton[1], and P. R. Christensen.[1] [1]Arizona State University, School of Earth and Space Exploration, Tempe, AZ, [2]Luxembourg Space Agency, Luxembourg, [3]Northern Arizona University, College of the Environment, Forestry, and Natural Sciences Flagstaff, AZ.

Introduction: Thermal-infrared (TIR) emission spectroscopy provides a means for studying geologic materials in the laboratory and in space. The method is based on vibrational spectroscopy, the principle that as an object radiates, vibrational motions occur within a crystal lattice at specific frequencies [1], which are directly related to crystal lattice geometry and the force constants between atoms [2]. Key features observed in TIR emissivity spectra that allow for mineral identification and grain size determination are the position, shape, and depth of absorption features (i.e., Restrahlen bands), the position of Christiansen frequencies (CF) and the appearance of transparency features [3]. While the major rock-forming materials (e.g. silicates, carbonates, sulfates, oxides etc.) exhibit fundamental molecular vibrations that produce spectral features in the infrared [1], some minerals lack a CF in the mid-infrared, which leads to miscalculations of sample temperature and misinterpretations of spectral emissivity. Here we report a new laboratory technique developed to mitigate these issues. The new technique accurately determines the absolute emissivity of materials which lack a CF in the mid-IR (~6–50 μm) and/or violates the assumption of unit emissivity.

The motivation of this work is to determine if TIR emission spectroscopy can be applied as a tool for the identification of resources such as Ni, Co, and the platinum group elements. Because magmatic sulfide deposits contain these elements, the most common constituent of magmatic sulfide–pyrrhotite ($Fe_{(1-x)}S$)– was chosen for investigation. The sample was collected from the Stillwater Complex's J-M Reef and was liberated from its coexisting silicate using Electric Pulse Disaggregation (EPD) [4].

Technique and Results: The new laboratory technique is adopted from the calibration routine reported in [5]. In short, a sample's emissivity is derived using (1):

$$(1)\ \varepsilon_{samp} = (V_{meas}\ /\ IRF) - B_{env} + B_{inst}\ /\ B_{samp} - B_{env}$$

where V_{meas} is the measured voltage, IRF is the instrument's response function, B_{env} is the Planck radiance at the temperature of the sample chamber, B_{inst} is the Planck radiance at the temperature of the instrument, and B_{samp} is the Planck radiance at the temperature of the sample. The desired quantity, sample emissivity (ε_{samp}), must be separated from the calibrated sample radiance (B_{samp}), which varies by wavelength and temperature according to the Planck equation. Traditionally, B_{samp} is derived from the calibrated sample radiance by determining the sample's maximum brightness temperature. This calibration routine assumes that over some portion of the spectrum, the sample exhibits unit emissivity ($\varepsilon = 1.0$, R = 0.0). In most materials, this condition is met at the principal CF. Because >95% of materials have a reflectivity minimum of 2% or less in the mid-IR, this assumption typically does not impart significant errors in calibrated emissivity. In general, for every 1% departure from unity of the CF results in an equal amount of error in sample emissivity [5]. Yet certain minerals, including pyrrhotite, exhibit graybody behavior and do not reach an emissivity near 1.0, making it difficult to accurately determine the sample's true kinetic temperature as well as its emissivity. For these minerals, another method for
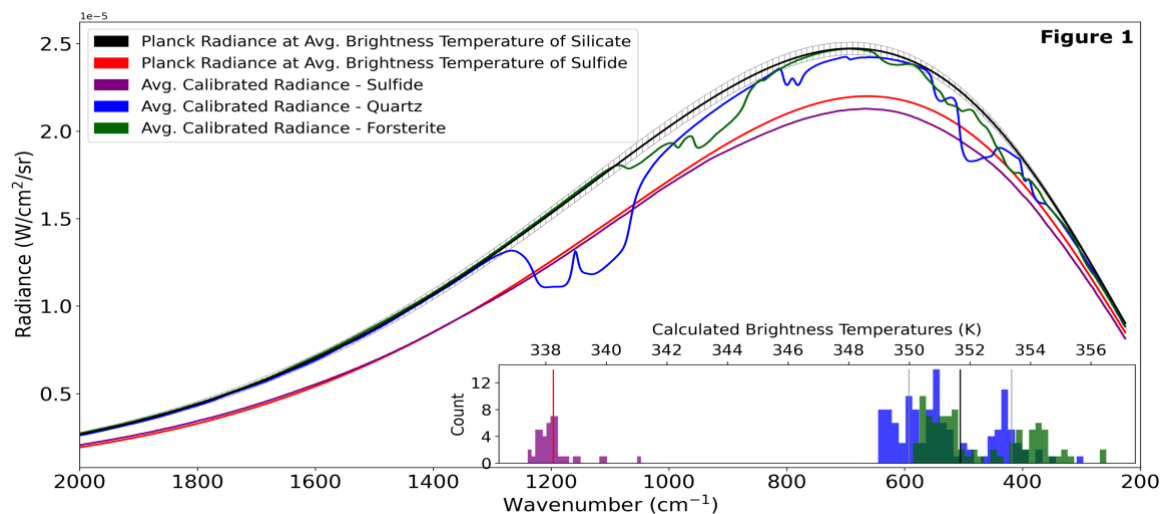
Figure 1

determining B_{samp} is required. Here, we use a custom-built sample heater to maintain B_{samp} at a consistent and repeatable range of known temperatures.

Figure 1 displays the average calibrated radiance of 110 measurements of granular quartz (blue curve) and 90 measurements of forsterite (green curve) measurements. The silicate samples were measured to test the repeatability the new sample heater. The brightness temperature of the individual measurements determined from their CF features are displayed in the subplot. The average temperature of the quartz (351.22 K, ±1.56 K) is within ~1.07 K of the forsterite (352.29 K, ±1.68 K), confirming the heater's capacity to maintain a consistent temperature regardless of composition. Together, the average temperature sustained by the heater is 351.68 K (± 1.7K).

To illustrate, the red curve in Figure 1 is a Planck curve at the average brightness temperature of 45 measurements of granular pyrrhotite (purple curve). Because a CF was not known *a priori* for pyrrhotite, a brightness temperature was calculated for all wavelengths of the radiance spectrum, and the highest value was used [5]. The brightness temperatures of the individual sulfide measurements are displayed in the subplot. Assuming unit emissivity, the average brightness temperature of the pyrrhotite was 338.25K (±0.67 K), 13.43K colder than the silicate. A Planck curve at the average brightness temperature of the silicate measurements (black curve) determined from their CF features is also shown in Figure 1 (gray curves correspond to the standard deviation) to compare with the inaccurate Planck radiance curve fit to the pyrrhotite measurements. The results from the silicate measurements allow for confident replacement of (B_{samp}) into equation (1) with an appropriate Planck radiance curve at a temperature determined from the reference sample method.

Figure 2 displays 45 TIR emissivity spectra of pyrrhotite ($Fe_{(1-x)}S$) from 2000–250 wavenumbers (~6–50 μm) using both calibration methods. The red spectra exhibit a severe negative slope from high to low wavenumbers, which are 'non-physical' ($\varepsilon > 1.0$) in nature at high wavenumbers. This slope is a result of the apparent brightness temperature of the pyrrhotite determined by the conventional calibration routine being ~13K cooler than its kinetic temperature. When using the reference temperature during calibration, pyrrhotite's spectra remains spectrally featureless, with a maximum absolute emissivity of ~0.7, and the negative slope from high to low wavenumbers shallows significantly.

Unlike most geologic materials, which exhibit graybody behavior in discrete regions of the electromagnetic spectrum, pyrrhotite exhibits broadband graybody behavior in the mid-IR. The percent difference in emissivity between the two methods is shown in the subplot of Figure 2, ranging from ~24–36% from low to high wavenumbers (long to short wavelengths). The stark difference between the two spectra highlights the importance of the CF in temperature determination and on a sample's spectral emissivity.

References: [1] Christensen P.R. et. al. (2000) *JGR, 105,* 9735–9739. [2] Nash D.B. et al. (1993) *JGR, 32,* 23,535–23,552. [3] Skuleti, A. et. al. (2020) *Plan. and Sp. Sci.,* 1–14. [4] Cabri, L.J. et. al. (2008) *40th Ann. Meeting of Canadian Mineral Processors.* 1–25. [5] Ruff, S. W. et. al. (1997) *JGR, 102,* 14,889–14,913.

Figure 2. Emissivty of J-M Reef Magmatic Sulfide: Comparing Calibration Procedures