**SPECTROSCOPY OF SYNTHETIC PIGEONITE STANDARDS.** T. D. Glotch[1], C. Ye[1], J. M. Young[1], D. H. Lindsley[1], H. Nekvasil[1], M. D. Dyar[2,3], E. C. Sklute[2], [1]Stony Brook University, Stony Brook NY 11794-2100 (timothy.glotch@stonybrook.edu), [2]Planetary Science Institute, 1700 E. Fort Lowell Rd. Ste. 106, Tucson, AZ. 85719, [3]Department of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA. 01075.

**Introduction:** Pigeonite is a low-Ca clinoproxene, typically containing 5-20% Wo, where Wo (atomic %) = $100Ca/(Ca+Mg+Fe^{2+})$). It is found in igneous and high-temperature metamorphic rocks and can be a major phase in extraterrestrial fine-grained, rapidly cooled igneous rocks [1]. Because of its minimum thermal stability temperature, upon cooling, pigeonite inverts to a combination of augite lamellae in an orthopyroxene host. This exsolution makes natural pigeonite unsuitable for spectroscopic studies, even though such studies are critical for enabling quantitative remote compositional analysis of extraterrestrial bodies. We have synthesized a range of synthetic pigeonites in gram quantities for use by the Earth and planetary science spectroscopic communities [2]. Samples can be requested by sending an email to the lead author. Here, we summarize initial infrared reflectance and emission, Raman, and Mössbauer studies of these synthetic samples. Samples can be requested by sending an email to the lead author.

**Methods:** Pigeonite samples were synthesized in the Experimental Petrology laboratory at Stony Brook University. Briefly, all samples described here were made from initial starting mixes of stoichiometric quantities of dried $CaSiO_3$, MgO, $SiO_2$ (quartz), $Fe_2O_3$, and $Fe^0$ sponge. Ground mixtures were pre-reacted at 900-920 °C, yielding a composition consisting of augite, olivine and quartz. Pre-reacted materials were then packed into iron capsules, loaded in vacuum sealed silica tubes with an oxygen "getter," partially melted at ~20-25 °C above the pigeonite solidus, and then held at a fixed temperature below the solidus to directly synthesize pigeonite. Additional experimental details can be found in [2]. All samples were characterized by optical microscopy, powder X-ray diffraction (XRD), and electron microprobe analysis (EMPA). Samples are primarily pigeonite with 0.5-2 wt.% unreacted silica, rare olivine inclusions, and up to 0.9 wt.% Fe metal.

Thermal infrared (TIR) emission spectra were collected at Stony Brook's Center for Planetary Exploration (CPEx) on a Nicolet 6700 FTIR modified for emissivity measurements. Samples were run as compact pellets to minimize multiple scattering effects.

Visible/near-IR (VNIR) reflectance spectra were acquired at CPEX on an ASD FieldMax 3 spectroradiometer and calibrated to absolute reflectance using a calibrated Labsphere Spectralon target. Bidirectional VNIR spectra were also acquired at RELAB.

Raman spectra were acquired at CPEX using a WITEc alpha300R confocal Raman system equipped with a 532 nm Nd:YAG laser and a 50X objective. Mössbauer data were acquired at MHC on a SEE Co. spectrometer at 295K, and referenced to α-Fe foil.

**VNIR Reflectance:** VNIR spectra (Figure 1) display characteristic pyroxene electronic absorption bands at ~ 1 and 2 μm. Both bands shift position with X number ($X=100Fe^{2+}/(Fe^{2+}+Mg)$ molar), with higher X samples having band centers at longer wavelengths. In addition, each sample displays three narrow spin-forbidden bands centered at ~430, 508, and 550 nm.

**TIR Emission:** TIR emission spectra display diagnostic features (Figure 2) found in other synthetic pyroxenes [3]. All spectra have a Christiansen feature (CF) emissivity maximum at ~1196 $cm^{-1}$ that does not appear to vary systematically with composition over the range of compositions studied here. Fundamental Reststrahlen bands are present for each sample at ~1090, 950, 880, 555, 515, 395, and 330 $cm^{-1}$. For both the Wo8 and Wo10 samples, differences between the X=20 and X=30 samples are minor. For the X=40 and X=55 samples, major Reststrahlen bands tend to occur at slightly lower frequencies (longer wavelengths) than the other samples, Although the samples were pressed into pellets, some effects of multiple scattering are still clearly present including a systematic drop in emissivity at frequencies higher than the CF, and a weak transparency feature centered at ~780 $cm^{-1}$.
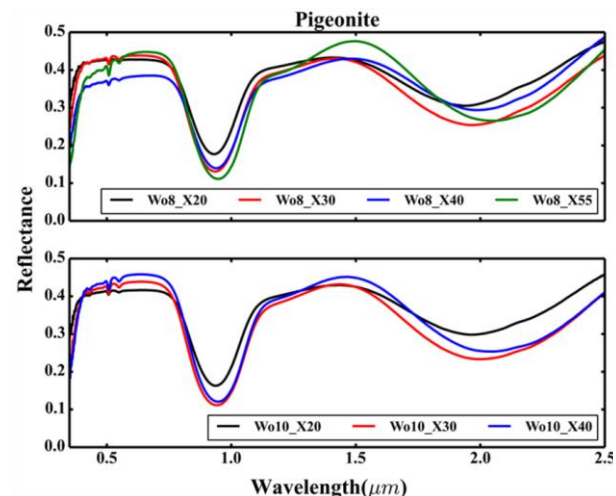
**Raman:** Raman spectra display numerous diagnos-



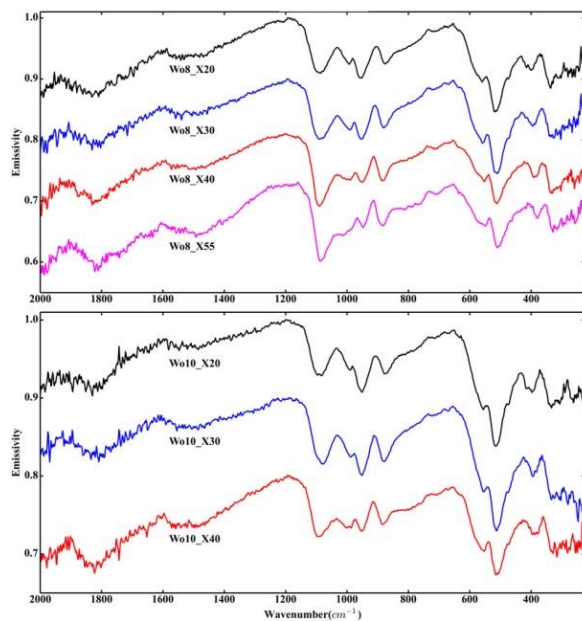**Figure 1**. VNIR reflectance spectra of pigeonites acquired at Stony Brook.

**Figure 2**. Thermal emission spectra of synthetic pigeonites.



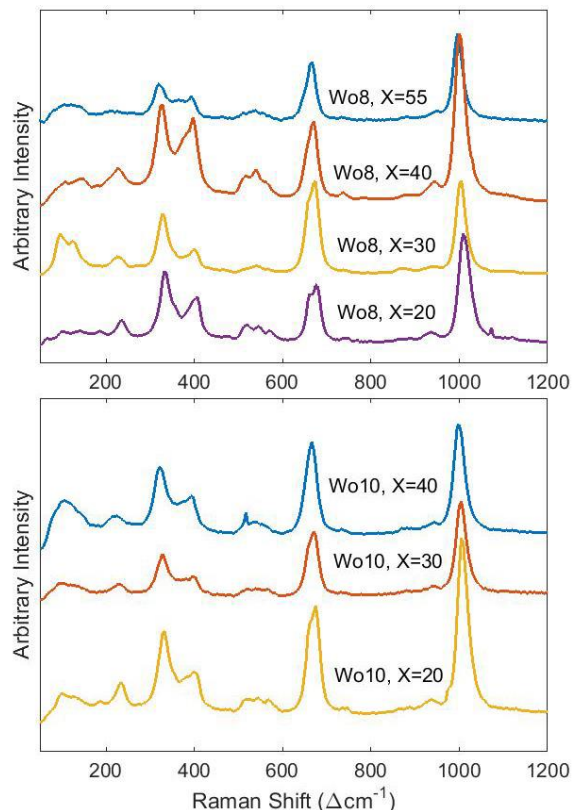**Figure 3**. Raman spectra of synthetic pigeonites

tic pyroxene peaks between ~100 and 1200 $\Delta cm^{-1}$ (Figure 3). Major features occur at ~234, 328, 397, 540, 675, 935, and 1004 $\Delta cm^{-1}$. For both the Wo8 and Wo10 samples, major peaks exhibit decreasing Raman shifts as X increases.
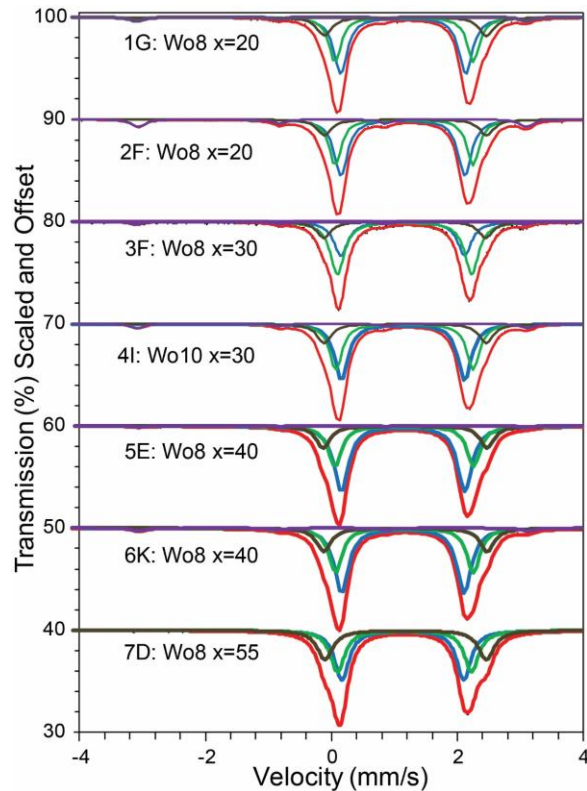


**Figure 4**. Fits to Mössbauer data, with envelopes given in red, M1 peaks in black, M2a peaks in green, and M2b peaks in blue.

**Mössbauer:** Fits to Mössbauer spectra indicate that all samples are completely reduced and contain only $Fe^{2+}$ distributed over the M1 and M2 sites. The M2 site is further split into two component peaks, M2a and M2b, believed to result from slight distortion of the M2 site as a function of the addition of Ca [4]. The distribution of $Fe^{2+}$ among the sites is identical within errors (Figure 4), indicating that site ordering is consistent at the pressures and temperatures at which these samples were synthesized and quenched.

**Summary:** We have spectroscopically characterized seven synthetic pigeonite samples. These analyses indicate that the samples are nearly phase pure. Spectra acquired of these samples will aid in analysis of planetary remote sensing data and extraterrestrial samples.

**References:**[1] Basaltic Volcanism Study Project (1981) *Basaltic Volcanism on the Terrestrial Planets*, Pergamon Press, New York, NY, 1286 pp. [2] Lindsley D. H. et al. (2019), *Amer. Mineral*., in press. [3] Lane M. D. et al. (2018) *LPS XLIX*, Abstract #2722. [4] Dyar M. D. et al. (2013) *Amer. Mineral.*, *98*, 1172-1186.