IMPLICATIONS OF OLIVINE STABILITY FOR LABORATORY SPECTROSCOPY STUDIES. M.J. Jones[1,2] (mattjones3414@gmail.com), N.R. Izenberg[1], C.A. Hibbitts[1], K.D. Burgess[3], and K.R. Stockstill-Cahill[1] [1]Johns Hopkins University Applied Physics Laboratory, MD, U.S.A., [2]State University of New York at New Paltz, NY, U.S.A., [3]U.S. Naval Research Laboratory, Washington, DC, U.S.A.

Introduction: Remote-sensing reflectance spectroscopy is commonly used to interpret surface composition of planetary bodies. Because planetary surface temperatures can vary drastically, and because mineral spectra change with temperature, quantifying thermal effects on reflectance spectra is vital to making correct mineralogic interpretations [1-3]. Temperature-dependent spectral changes, which can be described by a "thermospectrum" (graphically, $\Delta R / \Delta T$ vs. wavelength where R is sample reflectance and T is temperature [1, 2]), generally consist of changes in overall reflectance, wavelength-specific reflectance, and/or shape and position of crystal field absorption bands [1, 2]. Specific changes differ for varying materials and within solid solutions [1, 2]. The changes that define a material's thermospectrum are typically not permanent, i.e. changes will revert when the sample is returned to a lower or higher temperature.

To produce a thermospectrum, spectrometers can be used to measure reflectance across desired wavelength ranges as a sample is cooled and heated [1, 2]. This data can be processed to determine such relationships as ΔR vs. ΔT at individual wavelengths or an overall $\Delta R / \Delta T$ vs. wavelength relationship (i.e. the thermospectrum).

While compiling a library of thermospectra for rock-forming minerals, two samples of Fe-poor olivine (San Carlos and Globe, both ~Fo_{90}) were previously thermospectrally characterized in the Laboratory for Spectroscopy in Planetary Environmental Conditions (LabSPEC) at the Johns Hopkins University Applied Physics Laboratory (JHU-APL). After heating beyond approximately 500 K, permanent overall spectral darkening and reddening developed between 0.8 and 1.5 μm [4]. These permanent changes indicated some unexpected process presumed not to be related to typical thermospectral changes. Mössbauer spectroscopic analysis revealed oxidation (a possible cause of permanent darkening and reddening [5]) of 2-3% of Fe^{2+} to 4-fold Fe^{3+} in San Carlos olivine, indicating breakdown to another phase, but Globe olivine showed no evidence of oxidation [4]. To reconcile the apparent lack of oxidation in Globe olivine we considered thermally-activated crystal annealing as a contributor to the permanent changes as suggested by work at another laboratory [5], but other literature [6-12] contradicts this hypothesis.

Laboratory Setup: For spectral measurements conducted in this study, samples of <125 nm powder were loaded in a copper sample holder which was mounted on a base cryostat in the LabSPEC vacuum spectroscopy chamber. A visible-range spectrometer with multiple detectors was used, with a functioning range from ~0.5-1.8 μm. The sample holder was heated using a connected electrical power supply. From back to front (relative to the spectrometer) the sample holder consisted of: the copper body of the sample holder with attached Au and $MgFl_2$ reflectance measurement standards; an aluminum disk with a ~1.5" diameter depression for holding the sample, fixed with sample-embedded thermocouples; ~50 mg of sample powder; a transparent $MgFl_2$ disk to secure the powder; an anodized aluminum ring to minimize reflectance from the sample holder; and an enclosing copper ring attached to the sample holder body.

Characterization of Effects: For this study, we heated unprocessed San Carlos olivine to test for and characterize the previously observed changes. The sample was heated to 620 K (the maximum temperature achievable) and held at ~600 K for 3 hours. The level of vacuum during this experiment was ~10^{-10} atm, corresponding to an oxygen fugacity (fO_2) of approximately 2×10^{-11} atm based on atmospheric partial pressure of oxygen. Reflectance spectra were taken at room temperature before and after heating to check for permanent changes. Some reflectance measurements were also taken at higher temperatures, including three while the sample was held at ~600 K. The resultant data confirm permanent overall reddening after heating, but darkening only in visible wavelengths, with no permanent change in the 1 μm absorption band characteristic of olivine [Figure 1]. The spectral changes developed within 3 hours between 405 and 599 K [Figure 2], and no further change occurred despite holding the sample at 600 K [Figure 3].

Interpretation of Processes: At a maximum temperature of 620 K and minimum fO_2 of ~10^{-11} atm, our experiments were well outside the stability field of olivine [6]. This would have allowed for heterogeneous oxidation and precipitation of magnetite (among other phases) [6, 7], a phase which has significant effects on the olivine reflectance spectrum even at low concentrations [8]. Depending on the similarity of the spectral effects of magnetite to nanophase metallic iron ($npFe^0$), noticeable effects could result from as low as ~0.01 wt.

% [9]. Also, thermally-induced precipitation of magnetite nanoparticles can be used to produce low concentrations of npFe^0, and such a low concentration of magnetite nanoparticles may be detectable only by methods such as TEM or magnetic susceptibility/hysteresis measurements [9].

The likelihood that crystal annealing was an agent of the observed changes is lessened by the fact that dislocation density does not vary significantly in olivine regardless of heating duration and temperature [10]. Furthermore, extrapolating from high-temperature (~1300-1900 K) studies [10-12], we calculated generous diffusion length-scales for dislocations, oxygen, and Fe-Mg interdiffusion, for a period of 3 hours at 600 K. All determined length-scales are insignificant for the temperatures of our experiments (~10^{-16} nm for dislocations; ~10^{-7} nm for O and Fe-Mg), so we conclude that diffusion likely played little to no part in the observed changes or even in oxidation. Therefore, oxidation may have occurred only on the surface of the olivine grains in contact with limited gaseous O_2. This seems to be supported by stronger spectral changes for finer sample grain sizes [5], as greater total surface area in finer grain sizes would enable more oxidation.

Implications for Study of Olivine: In comparison to our experimental conditions, the stability field of iron-poor olivine requires a maximum fO_2 of $<10^{-16}$ atm at 600 K, or a minimum temperature of ~1100 K at fO_2 of 10^{-11} atm [6]. Our laboratory setup was not able to achieve these conditions, and other recent studies in which similar spectral changes were observed have also been performed outside this range of conditions [5]. Based on our previous experiments and the information that we have collected, we cannot conclude that crystal annealing plays a part in the spectral changes we observed. Instead, we propose that the changes may be a result of nm-scale iron-oxides precipitated due to heterogeneous surface oxidation, and that much more robust fO_2 control would be needed to perform proper thermospectral characterization and related study of olivine at temperatures above ~500K. However, further investigation is needed to empirically prove this conclusion. TEM observation of the predicted precipitates in samples that did not test positive for oxidation, as well as quantification of the low-concentration effects of heterogeneous oxidation products (i.e. magnetite, pyroxene, and silica), would likely provide the most useful tests of this hypothesis.

References: [1] Hinrichs J.L. and Lucey P.G. (2001) *Icarus, 155*, 169-180 [2] Lucey P.G. et al. (2002) *Icarus, 155*, 181-188 [3] Singer R.B. and Roush T.L. (1985) *JGR, 90*, 12,434-12,444 [4] Izenberg N.R. et al. (2015) *EPSC 2015*, Abstract 127 [5] Maturilli A. et al. (2014) *Earth Planet. Sci. Letters, 398*, 58-65 [6] Nitsan U. (1974) *JGR, 79*, 706-711 [7] Kohlstedt D.L. and Vander Sande J.B. (1975) *Contrib. Mineral. Petrol., 53*, 13-24 [8] Singer R.B. (1981) *JGR, 86 no. B9*, 7967-7982 [9] Kohout T. et al. (2014) *Icarus, 273*, 75-83 [10] Goetze C. and Kohlstedt D.L. (1973) *JGR, 78*, 5961-5971 [11] Gerard O. and Jaoul O. (1989) *JGR, 94*, 4119-4128 [12] Chakraborty S. (1997) *JGR, 102*, 12,317-12,331
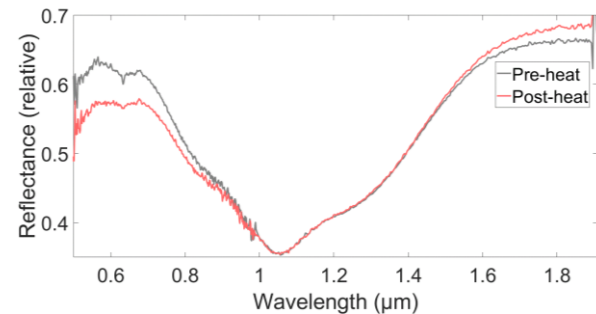
Figure 1: Room temperature visible-wavelength reflectance spectrum of San Carlos olivine before and after heating to 620 K. Permanent spectral change visible as subtle increase in slope (reddening) shortward of ~0.65 μm, darkening shortward of ~0.9 μm, and reddening/brightening longward of ~1.5 μm.
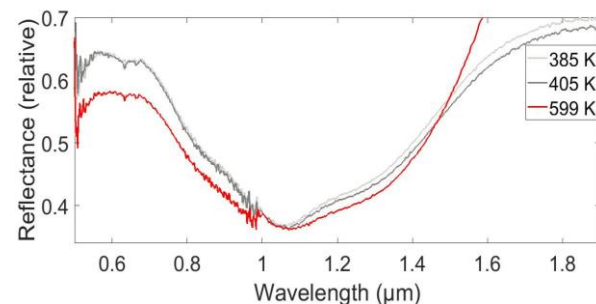
Figure 2: Visible-wavelength reflectance spectra of San Carlos olivine during heating from room temperature to 620 K. Permanent spectral change occurs between 405 and 599 K.
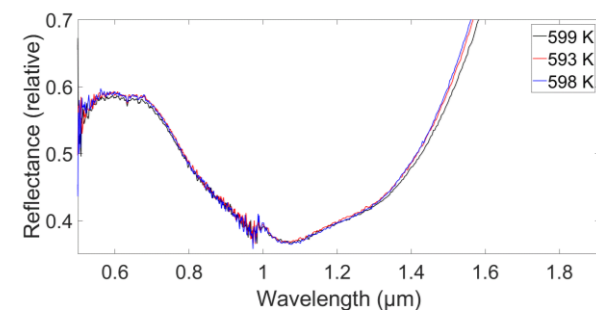
Figure 3: Visible-wavelength reflectance spectra of San Carlos olivine taken while the sample was held at ~600 K for three hours. No change occurred. Difference in band shape from Figure 1 is due to thermospectral character of olivine. Steep red slope above ~1.5 μm is due to high-temperature infrared "glow".