

THE OPTICAL CONSTANTS OF MANGANESE-BEARING OLIVINE: THE SYNTHESIS. D. Trang¹, J. J. Gillis-Davis¹, J. E. Hammer², and J. T. S. Cahill³, ¹University of Hawai'i at Mānoa, Hawai'i Institute of Geophysics and Planetology, Honolulu, HI (dtrang@higp.hawaii.edu), ²University of Hawai'i at Mānoa, Department of Geology and Geophysics, Honolulu, HI, ³Applied Physics Laboratory, Johns Hopkins University, Laurel MD.

Introduction: Near-infrared spectroscopy is a common method of detecting olivine on planetary surfaces. Iron-bearing olivines exhibit three absorptions in the near infrared located at 0.9, 1.1, and 1.3 μm . [e.g., 1–2]. From these three absorptions, it is possible to determine [e.g., 3–4] the abundance and mineral chemistry of olivine through the use of the radiative transfer techniques [i.e., 5]. However, the radiative transfer techniques only permit determination of Fo content because the optical property models of olivine incorporate only Fe^{2+} to Mg^{2+} cations [6–7]. In their study of the near-infrared absorption strengths of naturally-occurring Fe-rich olivines, *Trang et al.* [7] suggest that small proportions of Mn^{2+} affect the relative strengths of the absorptions. Characterization of near-infrared absorptions of olivine with respect to Mg^{2+} , Fe^{2+} , and Mn^{2+} , could result in a tool for the future determination of Mn^{2+} proportions on planetary surfaces.

The effects of Fe^{2+} in olivine on near-infrared spectra are understood [1]. The presence of Fe in the M2 crystallographic sites result in the 1.1 μm absorption, whereas Fe in the M1 crystallographic sites causes the 0.9 and 1.3 μm absorptions. Regardless of Fo content, Fe^{2+} occurs in nearly equal proportions in M1 and M2 sites [1] and the absorption strengths should increase with decreasing Fo content. However, *Trang et al.* [7] observe that the 1.1- μm absorption strength in naturally-occurring olivine do not consistently increase with decreasing Fo content. Instead they observe that the 1.1- μm absorption strength in $\text{Fo}_{<80}$ begins to level off in olivines with low Fo content (Fig. 1). This observation is interpreted to be a result of an increase proportion of Mn^{2+} in the olivine structure (Fig. 1) because the addition is Mn^{2+} relative to other cations is the most consistent with this observation.

The proposed effects of Mn^{2+} on the near-infrared spectra of olivine are indirect. Because Mn^{2+} cations are portioned preferentially into larger M2 crystallographic sites [1], Fe^{2+} is displaced into the smaller M1 sites. As a result, the 1.1- μm absorption is relatively weak compared with the 0.9- and 1.3- μm absorptions [1,8]. If the M2 sites only contain Mn^{2+} and all the Fe^{2+} is in the M1 sites, then the spectrum would only show the 0.9- and 1.3- μm absorptions.

The goals of this study are to first synthesize olivines at various Mn^{2+} , Fe^{2+} , and Mg^{2+} proportions. The second goal is to model the optical constants of Mn-bearing olivine as a function of Fe^{2+} and Mn^{2+} content.

Optical constants are physical parameters that describe the refraction (n) and absorption of light (k) through a medium [5]. Our overarching objective is to produce a model that accurately describes the changes in absorption strengths with respect to Mn^{2+} content. This would permit future radiative transfer models to determine the presence and Mn^{2+} proportion of Mn-bearing olivines. Future findings pertaining to Mn-bearing olivines are important to petrological models of planetary mantles [e.g., 9–10]. Also, these models could assist in determining which previous optical constant models [e.g., 6–7] are most appropriate for radiative transfer modeling. In this presentation, we focus on the first goal, the synthesis of Mn-bearing olivines, beginning with stoichiometric Fe-Mg olivines.

Olivine Synthesis: We attempted two different synthesis techniques to produce pure Fo_{50} . In both methods, we produced batches of Mg_2SiO_4 , Fe_2SiO_4 , and Mn_2SiO_4 from metallic (Fe^0 sponge characterized in-house following Lindsley pers. comm.), oxide (MgO , Fe_2O_3), and carbonate (MgCO_3) reagents. In the first method, the hydrothermal experiment, we used cold-seal pressure vessels in which the pressurizing medium was a mixture of Ar and CH_4 gas in proportions intended to maintain $f\text{O}_2$ between the IW and FMQ buffers. Total pressure was maintained at 70 MPa at a temperature of 925°C for 24 hours. The second method involves holding the reagents in Ag foil with an accompanying Fe^0 oxygen getter sealed within an evacuated silica glass tube for three to four weeks at 930°C at 1 atm.

Aliquots of a single Fo_{50} mixture were prepared for synthesis using each method. Analysis by X-ray diffraction (XRD) revealed that the 1 atm method produced fayalite, but the MgO did not react with the other reagents (Fig. 2). A second attempt suffered catastrophic oxidation at some point in the four-week run.

Ultraviolet to near-infrared spectra of two hydrothermal samples, differing in (a) amount of time reagents were crushed in agate mortar and (b) run temperature (with one same sample 10's of °C cooler), were obtained to determine the post-run mineralogy. We used the Analytical Spectral Devices Inc. (ASD) FieldSpec FR spectrometer at the University of Hawai'i at Mānoa. The spectrum ranges from 0.35–2.5 μm at a spectral resolution of 0.001 μm . We set up the observational geometry so that the incidence angle is 0° with an emission angle of 40°. The reflectance was

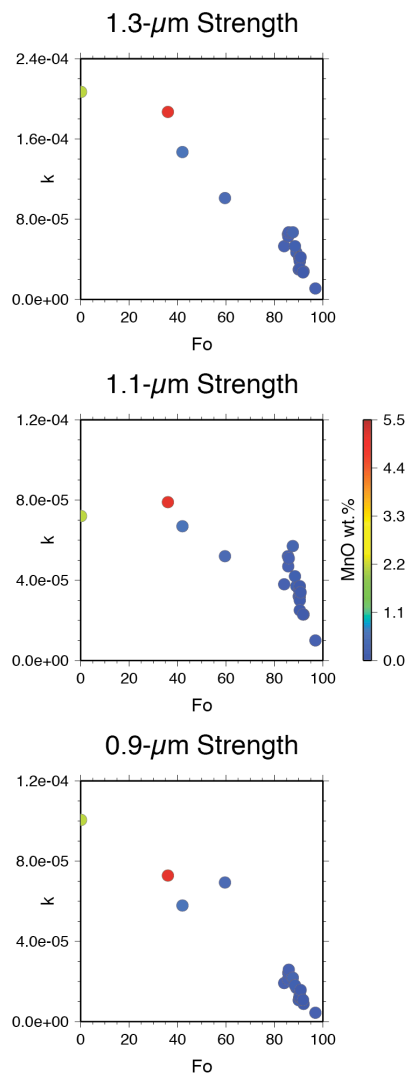


Fig. 1: The 0.9- and 1.3- μm absorptions are nearly constant with decreasing Fo content, but the 1.1- μm absorption appears to level off at $\text{Fo}_{<80}$. [7] suggested, this behavior in the 1.1- μm absorption is due to the presence of Mn^{2+} .

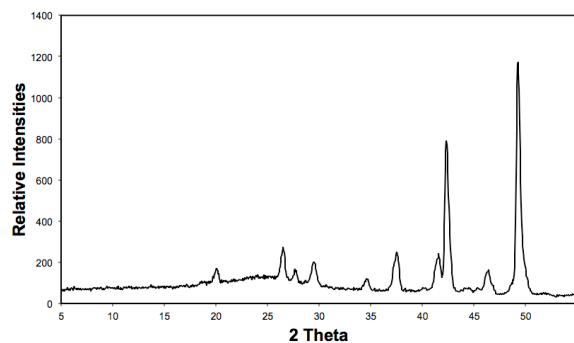


Fig 2: XRD results of the 1 atm experiment. The Fo_{50} sample exhibited the presence of olivine and periclase.

measured relative to the 99% spectralon standard. The reflectance spectra of both of our hydrothermal samples exhibit olivine peaks (Fig. 3), but one of our samples include an additional 2.0 μm absorption, which indicates the presence of pyroxene.

Future Work: We plan to use X-ray diffraction to verify that our synthetic hydrothermal samples consist only of olivine. If our samples exhibit other mineral phases, then we will work to refine our method. Afterwards, we will produce 16 olivine batches at various forsterite and tephroite content, with the highest Mn^{2+} proportion relative to Fe^{2+} , Mg^{2+} , and Mn^{2+} at 2.5 mol.%. Next we will proceed to our second goal, modeling the optical constants of Mn-bearing olivines.

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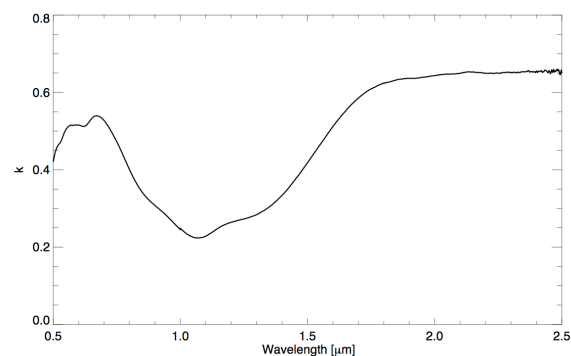


Fig 3: A visible to near-infrared spectra of one of the Fo_{50} samples, which were synthesized by the hydrothermal experiment. This Fo_{50} sample appears to contain only olivine.