Implications of Olivine Stability for Laboratory Spectroscopy Studies

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Introduction

Heating of powdered samples of Globe and San Carlos olivines in vacuum resulted in permanent spectral changes in both varieties above a threshold of ~500-550 K. Mössbauer spectroscopic analysis indicated oxidation in San Carlos olivine but not in Globe olivine, seemingly suggesting a process additional to oxidation that contributes to permanent spectral changes in heated olivine. Thermally-activated crystal annealing was initially considered a candidate process, but does not appear feasible under our experimental conditions.

Background

Understanding the spectral behavior of rock-forming minerals is essential to the use of remote sensing data for interpretation of planetary surface mineralogy. Minerals including olivine and pyroxene display significant temperature-based variance in overall reflectance and absorption band shape or position, among other characteristics, although these effects have not yet been thoroughly quantified for all rock-forming minerals.

These so-called “thermospectral” behaviors are separate from the permanent changes to olivine observed here. However, the nature of these permanent changes could have important implications for the viability of laboratory characterization of olivine, or otherwise for consideration in mineralogic interpretations.

Olivine under Laboratory Conditions

The ~600 K maximum temperature achieved in our experiments is not enough to allow significant crystal annealing through diffusion or dislocation climb. Calculated diffusion lengthscales for 3 hours at 600 K are ~10⁻¹⁵ nm for O and Fe-Mg and ~10⁻¹⁶ nm for dislocations. In addition, dislocation density in olivine does not vary significantly after thermal processing, even at high temperatures.

Furthermore, the stability field of olivine lies at high temperatures and extremely low fO₂. The conditions necessary to keep olivine stable are far beyond the capabilities of our lab; outside of these conditions, olivine can undergo heterogeneous oxidation, precipitating other silicate phases in dislocations including magnetite, pyroxene, and silica.

Spectral Effects of Magnetite

Magnetite has a strong effect on overall reflectance when mixed with olivine. Depending on the similarity of its low-concentration effects to those of nanophase iron (associated with space weathering), noticeable effects may result from as little as 0.01% wt. magnetite.

Conclusions

Because internal diffusion occurs at a negligible rate in olivine at the temperatures of our experiments, crystal annealing cannot be considered an agent of the permanent spectral changes we observed.

Instead, because we heated olivine outside of its stability field, the small amount of oxygen in the vacuum chamber may have reacted with grain surfaces, leading to precipitation of small concentrations of magnetite and noticeable changes in reflectance properties. Reactions being limited to grain surfaces is supported by stronger spectral changes for smaller grain sizes (more surface area) as seen in other studies.

This conclusion requires empirical proof, such as direct TEM observation of nm-scale precipitates in our samples as well as quantification of the low-concentration spectral effects of magnetite, but this study generally implicates that much more robust temperature and fO₂ control are required to properly conduct spectral studies on olivine at temperatures above ~500 K.

References


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 changes occurred within 3 hours 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”.

Figure 4: Stability field of olivine based on Fe content from Nisita 1974.

Figure 5: Mixed spectra of olivine and magnetite from Singer 1981.

Figure 6: Stability field of olivine based on Fe content.