

Oxidation (or not) of Hot Rocks in a Laboratory Vacuum

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Abstract

To assess the effects of high temperature on ultraviolet through infrared reflectance spectra, we heat-treated olivines and pyroxenes in mid to high vacuum using temperatures analogous to Mercury surface conditions. Samples darkened and changed absorption band properties with increasing temperature. Some samples returned to pre-heated reflectance values when cooled back to standard temperatures. Others, when heated beyond 500-525 K developed darkening that remained after cooling. Whether this darkening is the result of oxidation, surface flaw annealing, or some other process is still under investigation.

1. Introduction

Reflectance properties of silicate minerals change with temperature and pressure as predicted by theory [1] and experiments [2,3]. Positions and intensities of crystal field bands in the visible region are affected, and reflectance spectra show changes in band shape resulting from thermal population of vibrational levels within crystal field states [1,2]. These effects have been demonstrated for near-Earth objects [3, 4], and may be most pronounced at the hottest surface temperatures of the inner solar system planets. In addition to band shifts and shape changes, increased temperature generally results in broadening and/or shallowing of the 1 μm Fe absorption band in olivines and pyroxenes (Figure 1). The change of reflectance with temperature is referred to as a thermospectrum [5].

The day-side surface of Mercury can achieve temperatures as high as 700K. Rocks and regolith are exposed at these temperatures in vacuum, so creating a proper analog environment in the laboratory requires a high vacuum as well as high temperature. The Applied Physics Laboratory Optical Lab chamber can achieve vacuums as high as 10^{-9} torr at cryogenic to room temperatures, and 10^{-6} to 10^{-7} torr at temperatures up to 650-675K. For this project, we heated olivines and pyroxenes to a range of temperatures up to >600K; “permanent” darkening

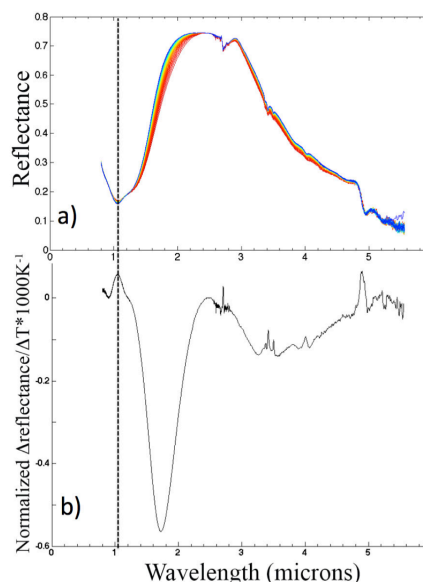


Figure 1: a) Temperature series of Globe Olivine reflectance spectra heated from 333K (blue) to 550K (red). b) Derived thermospectrum.

appeared that did not disappear upon cooling, similar to results of other TEM [6] and spectral studies [7, 8].

2. Assessing Causes of Darkening

Permanent darkening of samples may have several causes, including breakdown into other phases, annealing of crystalline flaws, destruction of color centers [9], and oxidation. The latter possibility would inhibit the ability of laboratory analog observations to properly address the properties of materials in the vacuum of space and was further investigated.

Mössbauer analyses of heated and unheated olivine and pyroxene samples from our experiments were undertaken to determine if the darkening could be due to oxidation, even at a vacuum $\sim 10^{-7}$ torr. Figure 2 shows an example of San Carlos olivine before and

after heating to 630K and 647K. In both cases, the sample underwent permanent darkening, and in both cases an Fe^{3+} component (2 and 3% of Fe in the sample, respectively) was present only post-heating. This demonstrates slight but conspicuous oxidation in the sample. The Mössbauer parameters of the newly-formed doublet in the heat-treated olivine are characteristic of 4-coordinated Fe^{3+} . Because olivine contains only 6-fold sites, this suggests that olivine is breaking down to another phase as seen in [6]. In contrast, a second olivine sample from Globe AZ heated to similar temperatures under the same vacuum conditions yielded no oxidation product. The two olivines have the same composition (Fo_{91}) so the difference in oxidation may result from varying H contents [10] or different defect populations relating to eruptive history. Finally, heating also induced oxidation in a diopside sample similarly heated (from 18 to 20% Fe^{3+}). Because the unannealed diopside already contained Fe^{3+} , Fe^{2+} oxidation likely occurred *in situ* within the pyroxene structure and would not require formation of a second phase as was the case for olivine. These results show that the reaction of mineral structures to high temperatures is difficult to generalize given the diversity of possible causes.

3. Conclusions and Next Steps

Our results suggest that laboratory conditions, even with high vacuum, cannot prevent oxidation of samples, either from monolayers of oxygen in the system, or possibly from breakdown of samples themselves due to heating. We can at present neither confirm nor rule out non-oxidation causes for permanent sample darkening at high temperatures.

We are currently conducting a systematic set of experiments heating samples incrementally, at three vacuum levels, and obtaining Mossbauer spectra for each stage and will present the results.

Acknowledgements

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References

- [1] Burns R.G.: *Mineralogical Applications of Crystal Field Theory*, Cambridge Univ. Press, 1995.
 [2] Singer R.B. and Roush T.L.: Effects of temperature on remotely sensed mineral absorption features. *JGR Solid Earth*, 10.1029/JB090iB14p12434, 1985.

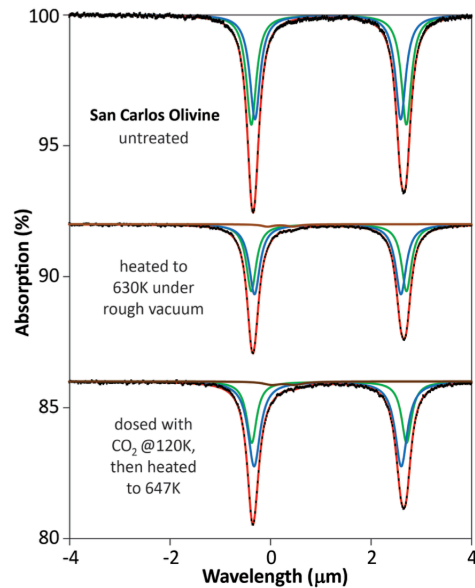


Figure 2: Mössbauer spectra of unheated and heated San Carlos olivine.

- [3] Hinrichs, J. L. and Lucey P.G.: Temperature-dependent near-infrared spectral properties of minerals, meteorites, and lunar soil. *Icarus* 155, 169–180, 2002.
 [4] Lucey, P. G. et al.: Detection of temperature-dependent spectral variation on the Asteroid Eros and new Evidence for the presence of an Olivine-rich silicate assemblage. *Icarus*, 155, 181-188, 2002.
 [5] Fisher et al.: Temperature Dependent Spectral Variation on the Surface of Mercury. *46th Lunar Planet. Sci. Conf.* #1849, 2015.
 [6] Kohnstedt D.L. and Vander Sande J.B.: An electron microscopy study of naturally occurring oxidation produced precipitates in iron-bearing olivines. *Contrib. Mineral. Petrol.*, 53, 13-24, 1975.
 [7] Domingue, D. L. et al.: Mercury's Weather-Beaten Surface: Understanding Mercury in the Context of Lunar and Asteroidal Space Weathering Studies. *Space Sci. Rev.* 181, 121–214, 2014.
 [8] Helbert, J. et al.: Visible and near-infrared reflectance spectra of thermally processed synthetic sulfides as a potential analog for the hollow forming materials on Mercury. *Earth Sci. Planet. Lett.* 369-370, 233-238, 2013.
 [9] Maturilli, A. et al.: Komatiites as Mercury surface analogues: Spectral measurements at PEL. *Earth Sci. Planet. Lett.*, 398, 58-65.
 [10] Kurosawa M. et al.: Patterns in the hydrogen and trace element compositions of mantle olivine. *Phys. Chem. Minerals.*, 24, 385-395, 1997.