

## OXIDIZED OLIVINES ON MARS: SPECTROSCOPIC INVESTIGATIONS OF HEAT-INDUCED AERIAL OXIDATION PRODUCTS

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**Introduction.** Olivines in komatiitic lavas that erupted onto the surface of Mars were vulnerable to low-temperature aerial oxidation as the magma cooled, by analogy with the occurrence of ferrifayalite (intergrowths of fayalite,  $\text{Fe}_2\text{SiO}_4$ , and laihunite,  $\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{0.8}\text{SiO}_4$ ) in terrestrial near-surface and extrusive igneous rocks {1,2}. Similar ferric-bearing Mg-Fe olivines on Mars, contributing to remote-sensed reflectance spectral profiles of the martian surface, could interfere with diagnostic  $\text{Fe}^{2+}$  crystal field bands used to identify ferromagnesian silicates occurring there, particularly in the visible-near infrared spectra of "dark" regions on Mars {3}. We report here measurements made on heated olivines that were aimed at characterising spectral features originating from products of aerial oxidation.

**Experimental Details.** Several olivines [synthetic ( $\text{Fa}_{100}$ ) and Rockport ( $\text{Fa}_{96}$ ) fayalites, hortonolite ( $\text{Fa}_{49}$ ), peridot ( $\text{Fa}_{15}$ ), and knebelite ( $\text{Fa}_{51}\text{Te}_{47}$ )] were heated in air in the temperature range 300-900°C. Mossbauer spectra measured at ambient (295°K) and liquid He (4.2°K) temperatures aided in the identification of structural (olivine) and superparamagnetic (hematite)  $\text{Fe}^{3+}$  ions. Reflectance spectra were obtained for selected specimens using the RELAB facility at Brown University {4}.

**Results: Mossbauer Spectra.** The presence of structural paramagnetic  $\text{Fe}^{3+}$  ions in fayalites heated in air between 300 and 600°C is suggested by Mossbauer spectra of reaction products measured at ambient temperatures. However, an additional sextet originating from magnetic hyperfine splitting of hematite appears in heat-treated fayalites, the intensity of which increases with prolonged heating. Analogous heat-oxidation experiments on hortonolite, peridot and knebelite also produced ferric-bearing assemblages, the 295°K Mossbauer spectra of which yielded  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  doublets but negligible magnetic sextet peaks. The ferric doublet could originate from structural  $\text{Fe}^{3+}$  ions in the ferri-olivines and/or interstitial nanocrystalline Fe(III) oxides {5} resulting from oxidation of  $\text{Fe}^{2+}$  in, and diffusion of  $\text{Fe}^{3+}$  from, the olivine structure {2}. The 4.2°K spectra, however, reveal a magnetic sextet originating from ferrifayalite alone, in fayalites heated to 300°C and 400°C. By 600°C, hematite sextets are also present and, after 10 days' heating at this temperature, a maghemite sextet joins that of hematite. These two  $\text{Fe}_2\text{O}_3$  phases persist in fayalites heated to higher temperatures, but the proportion of ferrifayalite decreases. In 4.2°K spectra of Mg-Fe and Mn-Fe olivines heated to 600°C, sextets comparable to that of ferrifayalite appear (c.f. Fig. 1c in the accompanying abstract {6}) but no hematite is present. Prolonged heating at 600°C and higher temperatures produced maghemite-like sextets (which could also be assigned to spinel  $\text{MgFe}_2\text{O}_4$  or  $\text{MnFe}_2\text{O}_4$  phases) in the 4.2°K spectra of each olivine.

**Results: Reflectance Spectra.** Characteristic spectral features of olivine in the visible-near infrared region, which enable this Mg-Fe silicate to be identified in telescopic reflectance spectral measurements of terrestrial planets {7}, are highlighted in Figure 1 and include: the  $\text{Fe}^{2+}$  (M2 site) band centered at 1.05  $\mu\text{m}$ ; the  $\text{Fe}^{2+}$  (M1 site) bands occurring at  $\sim 0.85$  and  $\sim 1.20$   $\mu\text{m}$ ; and, sometimes, the  $\text{Fe}^{2+}$  (spin-forbidden) peak at 0.63  $\mu\text{m}$  (Fig. 1a). However, with increasing oxidation of structural  $\text{Fe}^{2+}$  ions in olivine to  $\text{Fe}^{3+}$ , a red-shift of the ultraviolet absorption edge into the visible region occurs which obliterates the 0.63  $\mu\text{m}$  peak and masks the 0.85  $\mu\text{m}$  band (Figs 1b & c). The appearance of  $\text{Fe}_2\text{O}_3$  phases further obscures the diagnostic olivine- $\text{Fe}^{2+}$  bands at 1.05 and 1.20  $\mu\text{m}$  (Fig. 1d). The reflectance spectra illustrated in

Figure 1 indicate that absorption due to  $Fe^{3+}$  ions in  $(Mg,Fe^{2+})_xFe^{3+}_ySiO_4$  ferri-olivines, as well as maghemite or hematite, contribute significantly to the 0.40-0.90 micron region, in which  $Fe^{3+}$  crystal field and  $Fe^{2+}-Fe^{3+}$  intervalence transitions are located {8}.

**Applications to Mars.** Petrological studies {9,10} suggest that Fe-rich basaltic melts, formed by partial melting of the martian mantle, may have erupted as highly turbulent komatiitic lava flows {11} which, on account of their very low viscosities, covered vast areas of the planet and underwent rapid cooling as they thermally eroded the surface {12}. Hortonolite crystallizing from the lava flows was vulnerable to aerial oxidation and might have produced ferric-bearing olivine and nanocrystalline  $Fe_2O_3$  phases. These surface oxidation products on basaltic lava flows may contribute to the 0.8-1.2  $\mu m$  region of "dark" areas on Mars {3}. The olivines would also be susceptible to chemical weathering by acidic hydrosphere if sub-aqueous extrusion of the komatiitic lavas occurred {13}.

**References.** {1} M.W.Schaefer, *Am. Mineral.*, **70**, 729 (1985); {2} S. Kondoh *et al.*, *Am. Mineral.*, **70**, 737 (1985); {3} R.B.Singer, *Adv. Space Sci.*, **5**, 59 (1985); {4} C.Pieters, *JGR*, **88**, 9534 (1983); {5} R.W.Morris *et al.*, *Lunar Planet. Sci.*, XVIII, 668 (1987); *JGR*, in press.; {6} R.G.Burns, this vol.; {7} C. Pieters *et al.*, *JGR*, **90**, 12393 (1985); {8} R.G.Burns, *Ann. Rev. Earth Planet. Sci.*, **9**, 345 (1981); {9} G.Bussod & T.R.McGetchin, *Lunar Planet. Sci.*, X, 172 (1979); {10} C.M.Bertka & J.R.Holloway, *Proc. 18th LPSC*, 723 (1988); {11} H.E.Huppert *et al.*, *Nature*, **309**, 19 (1984); {12} A.K.Baird & B.C.Clark, *Nature*, **311**, 18 (1984); {13} D.S.Fisher & R.G.Burns, this vol.; {14} Research supported by NASA grants NSG-7604 and NAGW-1078. We thank Steve Pratt for the reflectance spectral measurements.

**Figure 1.** Reflectance spectra of olivine (Fa<sub>15</sub>) before and after aerial oxidation. Positions are highlighted of the characteristic  $Fe^{2+}$  crystal field transitions in olivine. Note the loss of resolution of these spectral features in oxidized olivines.

