

## OXIDIZED PYROXENES AND DEGRADATION OF THEIR VISIBLE - NEAR INFRARED SPECTRA: IMPLICATIONS TO REMOTE-SENSING OF MARS

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**INTRODUCTION.** Pyroxenes and olivines in basaltic magma extruding onto surfaces of terrestrial planets such as Mars, Earth and Venus are vulnerable to atmospheric oxidation during cooling of the igneous rocks. Ferrous iron in these ferromagnesian silicates may be oxidized to structural  $\text{Fe}^{3+}$  ions or form a veneer of ferric oxide phases that might obliterate the diagnostic  $\text{Fe}^{2+}$  crystal field (CF) spectral features used to identify pyroxenes and olivines. Previous measurements of oxidized olivines [1] demonstrated that the appearance of  $\text{Fe}_2\text{O}_3$  phases (hematite, maghemite) obscure the characteristic olivine bands at 0.85, 1.05 and 1.20  $\mu\text{m}$ . The 1 micron and 2 micron regions used to identify pyroxene structure-types and compositions in telescopic spectral measurements [2,3] may be similarly compromised. We report here measurements made on heated pyroxenes to assess the effects of aerial oxidation on their visible-near infrared spectra.

**PYROXENE SPECIMENS.** A suite of well-characterized pyroxenes [4] representative of different structure-types and compositions was chosen for the spectroscopic measurements and consisted of orthopyroxene,  $\text{Fe}_{29}\text{Mg}_{70}\text{Ca}_1$ ; pigeonite,  $\text{Fe}_{37}\text{Mg}_{47}\text{Ca}_{16}$ ; augite,  $\text{Fe}_{10}\text{Mg}_{41}\text{Ca}_{46}$ ; a hedenbergite,  $\text{Fe}_{42.5}\text{Mg}_{10}\text{Ca}_{47.5}$  containing 10%  $\text{Fe}^{3+}$  [5]; and a Mn hedenbergite,  $\text{Fe}_{40}\text{Mn}_{10}\text{Mg}_{0.5}\text{Ca}_{49.5}$ . The specimens were selected to encompass different site occupancies of iron cations in the pyroxene crystal structure, particularly the M2 position, since  $\text{Fe}^{2+}$  ions in this highly distorted non-centrosymmetric site are responsible for the positions and intensities of the diagnostic pyroxene "1 micron" and "2 micron" absorption bands [3]. Ferrous ions located in less distorted pyroxene M1 sites contribute relatively weak absorption bands centered near 0.9 and 1.15  $\mu\text{m}$  [3,6,7]. In magnesian orthopyroxenes and pigeonites, the  $\text{Fe}^{2+}$  ions are strongly enriched in the M2 positions with relatively small proportions in the M1 positions [8]. In calcic clinopyroxenes, although the  $\text{Fe}^{2+}$  ions are more concentrated in the M1 positions, they preferentially fill any  $\text{Ca}^{2+}$  vacancies in the M2 positions except in competition with  $\text{Mn}^{2+}$  ions, which have a stronger preference than  $\text{Fe}^{2+}$  for the pyroxene M2 positions [8]. The Mn hedenbergite, therefore, was expected to contain negligible  $\text{Fe}^{2+}$  ions in its M2-sites.

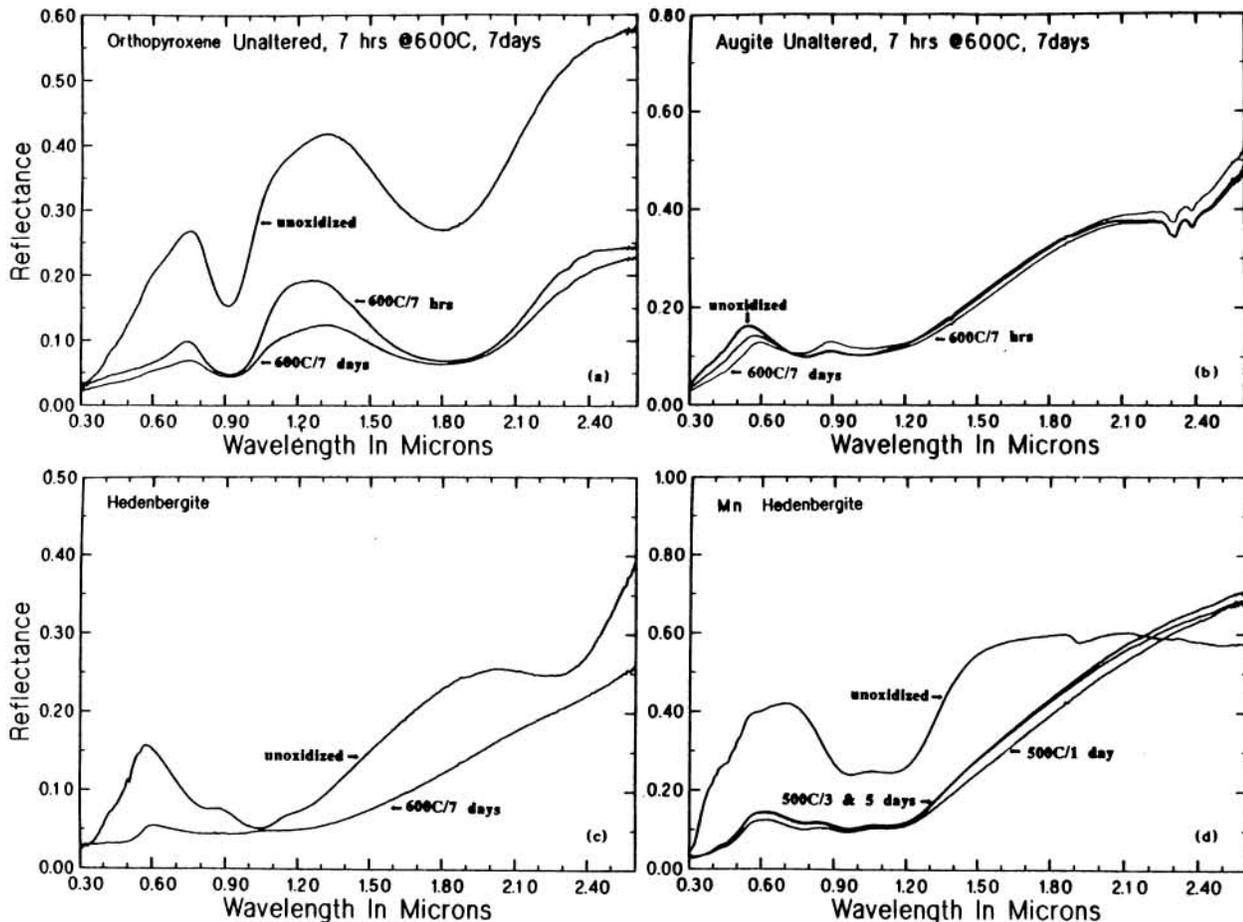
**EXPERIMENTAL DETAILS.** Powdered pyroxenes (particle sizes <45 microns) were heated in air in the temperature range 400-800°C for different time periods. Mossbauer spectra at ambient temperatures and at 4.2K were used to identify the appearance of ferric iron in the oxidized pyroxenes. For most specimens, only ferric doublets (in addition to ferrous doublets) were present in the 295K Mossbauer spectra, but at 4.2K sextets attributable to ferric oxides (hematite, maghemite or magnesioferrite) were weakly developed indicating the formation of nanophase  $\text{Fe}_2\text{O}_3$  phases in and on the surfaces of the pyroxene crystallites. The 4.2K spectra also indicated magnetic ordering of structural  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the two hedenbergites. Visible - near infrared reflectance spectra of selected samples were measured by Steve Pratt at Brown University using the RELAB facility there [9].

**RESULTS.** Examples of reflectance spectra of different pyroxenes oxidized in air are illustrated in Figures 1 to 4. Two extreme situations reflecting different  $\text{Fe}^{2+}$  site occupancies are demonstrated by the spectra of orthopyroxene (Fig.1) and Mn-hedenbergite (Fig.4). In orthopyroxene, M2-site  $\text{Fe}^{2+}$  ions are responsible for the absorption bands at 0.9 and 1.8  $\mu\text{m}$ , the band depths of which are considerably reduced by oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ions. After heating in air, the increased absorption between 0.4 and 0.9  $\mu\text{m}$  may be attributed to  $\text{Fe}^{3+}$  CF transitions (which, for hematite, occur at 0.44, 0.51, 0.65 and 0.88  $\mu\text{m}$  [10]) and to  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  intervalence charge transfer transitions (IVCT) occurring in orthopyroxene around 0.7  $\mu\text{m}$  [6]. The Mn-hedenbergite spectra (Fig.4) originating from CF transitions in M1-site  $\text{Fe}^{2+}$  at approx. 0.95 and 1.15  $\mu\text{m}$  are severely modified after oxidation by spectral features attributable to nanophase  $\text{Fe}_2\text{O}_3$  and structural  $\text{Fe}^{3+}$ , particularly the  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  IVCT occurring in calcic clinopyroxenes around 0.8  $\mu\text{m}$  [5,6]. In the spectrum of the  $\text{Ca}^{2+}$ -deficient hedenbergite (Fig. 3), the M2-site  $\text{Fe}^{2+}$  CF bands at 1.05 and 2.3  $\mu\text{m}$  are obliterated by oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , a similar trend also being observed in the spectra of the heated augite (Fig. 2).

**PYROXENE REFLECTANCE SPECTRA: Straub, D.W. and Burns, R.G.**

**DISCUSSION.** The reduced band depths of the pyroxene 1 micron and 2 micron spectral features may be attributed to two related causes: first, loss of  $\text{Fe}^{2+}$  ions in the pyroxene M2 sites after they become oxidized to  $\text{Fe}^{3+}$  ions; and second, increased absorption by the ferric iron, either as structural  $\text{Fe}^{3+}$  ions in the pyroxenes, or as nanophase  $\text{Fe}_2\text{O}_3$  formed in and on the surfaces of the pyroxene grains. Similar contrasts of band depths may be seen between dark-region and bright-region spectra of Mars [11]. These and earlier results [1] suggest a mechanism for producing the nanophase hematite popularly considered to be responsible for the features observed around 0.65 and 0.87  $\mu\text{m}$  in remote-sensed reflectance spectral profiles of Mars [12,13]: it results from aerial oxidation of structural  $\text{Fe}^{2+}$  ions in olivines and pyroxenes to highly disseminated  $\text{Fe}_2\text{O}_3$  [14].

**REFERENCES.** [1] K.S.Bartels & R.G.Burns, *Lunar Planet. Sci.*, **XX**, 44 (1989); [2] J.B.Adams, *JGR*, **79**, 4829 (1974); [3] R.G.Burns, *Min. Mag.*, **53**, 135 (1989); [4] M.D.Osborne *et al.*, *Proc. 9th LPSC*, 2949 (1978); [5] R.G.Burns & F.E.Huggins, *Am. Min.*, **58**, 955 (1973); [6] G.R.Rossmann, *Rev. Min.*, **7**, 93 (1980); [7] G.Steffen *et al.*, *Phys. Chem. Min.*, **16**, 120 (1988); [8] M.Cameron & J.J.Papike, *Rev. Min.*, **7**, 5 (1980); [9] C.Pieters, *JGR*, **90**, 12393 (1985); [10] D.M.Sherman & T.D.Waite, *Am. Min.*, **70**, 1262 (1985); [11] R.B.Singer, *Adv. Space Sci.*, **5**, 59 (1985); [12] R.V.Morris *et al.*, *JGR*, **94**, 2760 (1960); [13] J.P.Bell *et al.*, *JGR*, in press; [14] Research supported by NASA grants NGR 7604 and NAGW 1078. We thank Steve Pratt for the reflectance spectral measurements.



**FIGURE 1.** Reflectance spectra of pyroxenes before and after aerial oxidation. (a) orthopyroxene; (b) augite; (c) hedenbergite; and (d) Mn hedenbergite.