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 Fe$^{3+}$ ions or form a veneer of ferric oxide phases that might obliterate the diagnostic Fe$^{2+}$ crystal field (CF) spectral features used to identify pyroxenes and olivines. Previous measurements of oxidized olivines [1] demonstrated that the appearance of Fe$_2$O$_3$ phases (hematite, maghemite) obscure the characteristic olivine bands at 0.85, 1.05 and 1.20 $\mu$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, Fe$_{59}$Mg$_{70}$Ca$_{1}$; pigeonite, Fe$_{37}$Mg$_{47}$Ca$_{16}$; augite, Fe$_{16}$Mg$_{41}$Ca$_{46}$; a hedenbergite, Fe$_{42.5}$Mg$_{58}$Ca$_{1}$ containing 10% Fe$^{3+}$ [5]; and a Mn hedenbergite, Fe$_{40}$Mn$_{10}$Mg$_{50}$Ca$_{95.5}$. The specimens were selected to encompass different site occupancies of iron cations in the pyroxene crystal structure, particularly the M2 position, since 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 $\mu$m [3,6,7]. In magnesian orthopyroxenes and pigeonites, the Fe$^{2+}$ ions are strongly enriched in the M2 positions with relatively small proportions in the M1 positions [8]. In calcic clinopyroxenes, although the Fe$^{2+}$ ions are more concentrated in the M1 positions, they preferentially fill any Ca$^{2+}$ vacancies in the M2 positions except in competition with Mn$^{2+}$ ions, which have a stronger preference than Fe$^{2+}$ for the pyroxene M2 positions [8]. The Mn hedenbergite, therefore, was expected to contain negligible 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$^\circ$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 maghemitite) were weakly developed indicating the formation of nanophase Fe$_2$O$_3$ phases in and on the surfaces of the pyroxene crystallites. The 4.2K spectra also indicated magnetic ordering of structural Fe$^{2+}$ and 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 Fe$^{2+}$ site occupancies are demonstrated by the spectra of orthopyroxene (Fig.1) and Mn-hedenbergite (Fig.4). In orthopyroxene, M2-site Fe$^{2+}$ ions are responsible for the absorption bands at 0.9 and 1.8 $\mu$m, the band depths of which are considerably reduced by oxidation of Fe$^{2+}$ to Fe$^{3+}$ ions. After heating in air, the increased absorption between 0.4 and 0.9 $\mu$m may be attributed to Fe$^{3+}$ CF transitions (which, for hematite, occur at 0.44, 0.51, 0.65 and 0.88 $\mu$m [10]) and to Fe$^{2+}$→Fe$^{3+}$ intervalence charge transfer transitions (IVCT) occurring in orthopyroxene around 0.7 $\mu$m [6]. The Mn-hedenbergite spectra (Fig.4) originating from CF transitions in M1-site Fe$^{2+}$ at approx. 0.95 and 1.15 $\mu$m are severely modified after oxidation by spectral features attributable to nanophase Fe$_2$O$_3$ and structural Fe$^{3+}$, particularly the Fe$^{2+}$→Fe$^{3+}$ IVCT occurring in calcic clinopyroxenes around 0.8 $\mu$m [5,6]. In the spectrum of the Ca$^{2+}$-deficient hedenbergite (Fig.3), the M2-site Fe$^{2+}$ CF bands at 1.05 and 2.3 $\mu$m are obliterated by oxidation of Fe$^{2+}$ to Fe$^{3+}$, a similar trend also being observed in the spectra of the heated augite (Fig.2).
**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 Fe$^{2+}$ ions in the pyroxene M2 sites after they become oxidized to Fe$^{3+}$ ions; and second, increased absorption by the ferric iron, either as structural Fe$^{3+}$ ions in the pyroxenes, or as nanophase Fe$_2$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 $\mu$m in remote-sensed reflectance spectral profiles of Mars [12,13]: it results from aerial oxidation of structural Fe$^{2+}$ ions in olivines and pyroxenes to highly disseminated Fe$_2$O$_3$ [14].


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