

# REFLECTANCE SPECTRA OF $\text{Fe}^{2+}$ - $\text{Mg}^{2+}$ DISORDERED PYROXENES: IMPLICATIONS TO REMOTE-SENSED SPECTRA OF PLANETARY SURFACES

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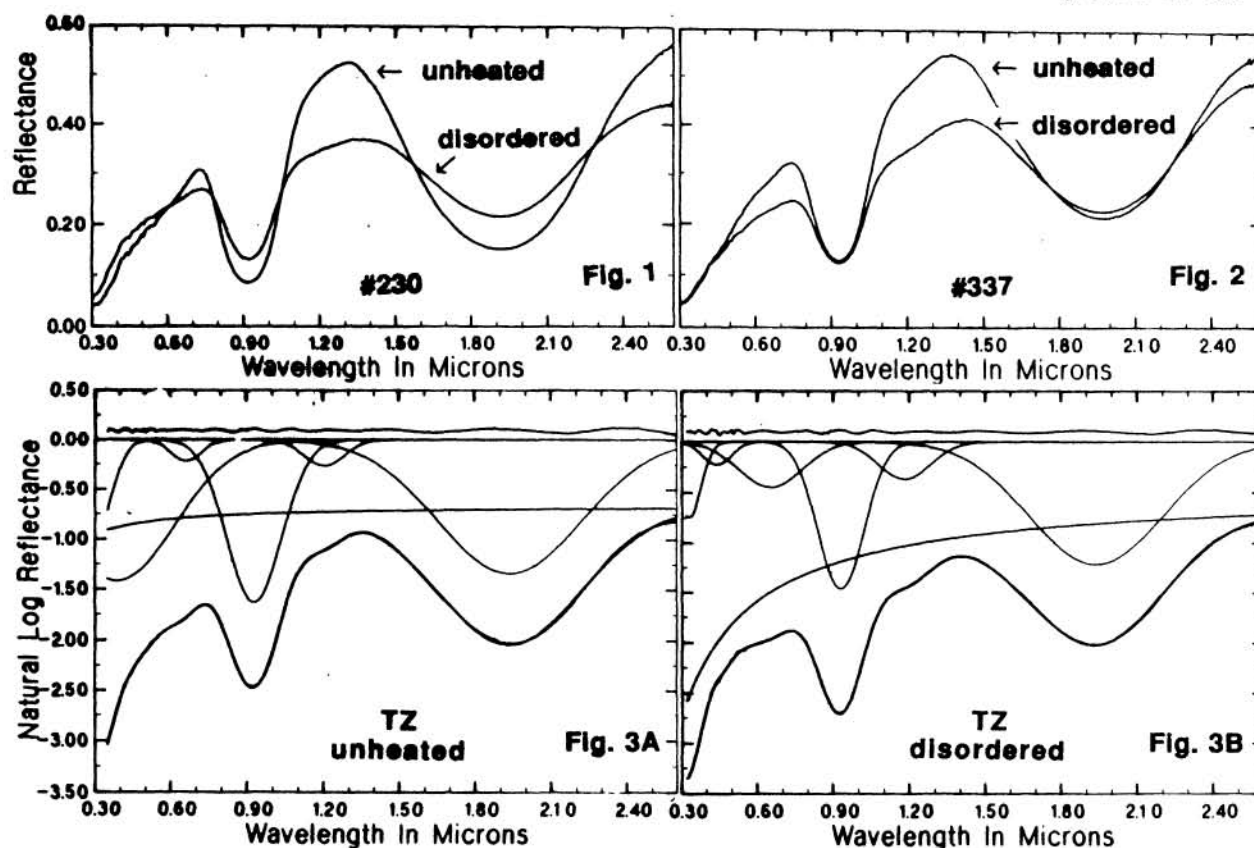
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**Introduction.** Pyroxenes are identified in telescopic and laboratory reflectance spectra by the broad, intense bands centered at 0.90-1.05  $\mu\text{m}$  and 1.80-2.30  $\mu\text{m}$  [1]. These spectral features originate from crystal field (CF) transitions in  $\text{Fe}^{2+}$  ions located in the very distorted, non-centrosymmetric M2 sites of the pyroxene crystal structure. In pigeonites and orthopyroxenes, strong enrichments of  $\text{Fe}^{2+}$  ions in the M2 sites obscure weaker CF bands at  $\sim 0.9 \mu\text{m}$  and  $\sim 1.20 \mu\text{m}$  produced by electronic transitions in minority proportions of  $\text{Fe}^{2+}$  ions situated in the less distorted M1 octahedral sites that are occupied mainly by  $\text{Mg}^{2+}$  ions [2]. Numerous experimental studies [e.g., 3-6] have shown that temperature-induced disordering of  $\text{Fe}^{2+}$  (M2 site) and  $\text{Mg}^{2+}$  (M1 site) cations in orthopyroxenes takes place relatively rapidly even at temperatures as low as 450-500  $^{\circ}\text{C}$  [6]. Since re-equilibration of  $\text{Fe}^{2+}$  ions between the M2 and M1 sites is expected to affect near infrared spectra [7,8], we undertook reflectance spectral measurements of a variety of orthopyroxenes after they had been heated under controlled oxygen fugacities.

**Experimental Details.** Orthopyroxenes used in this study included several specimens from granulite facies rocks, including a Tanzanian specimen, TZ ( $\text{Fs}_{50}\text{En}_{47}\text{Wo}_1\text{Mn}_2$ ), used in previous cooling rate experiments [6] and two specimens from Western Australia [9] with similar bulk Fe but different Mn contents, #230 ( $\text{Fs}_{36}\text{En}_{61}\text{Wo}_2\text{Mn}_1$ ) and #337 ( $\text{Fs}_{38}\text{En}_{48}\text{Wo}_2\text{Mn}_{12}$ ), as well as a synthetic ferrosilite ( $\text{Fs}_{85}$ ). Samples of specimen TZ were equilibrated for several hours at 700  $^{\circ}\text{C}$  in  $\text{CO}_2/\text{H}_2$  atmospheres providing oxygen fugacities close to or less than the iron-wüstite buffer, while specimens #230, #337 and  $\text{Fs}_{85}$  were heated for three months at 500  $^{\circ}\text{C}$  in evacuated quartz tubes containing metallic Fe. The  $\text{Fe}^{2+}$  occupancies of the pyroxene M1 and M2 sites before and after heating, as well as the percentage of ferric iron in each orthopyroxene, were determined from computed peak areas in Mössbauer spectra measured at 77K [6]. Visible - near infrared spectra were measured using the RELAB facility [10], and deconvoluted into component bands using a modified Gaussian model [11].

**Results.** Spectra of specimens #230 and #337 before and after  $\text{Fe}^{2+}$ - $\text{Mg}^{2+}$  disordering are illustrated in Figures 1 and 2. Particularly conspicuous in these spectra are the reduction of the band depths at 0.90  $\mu\text{m}$  and 1.95  $\mu\text{m}$ , especially in specimen #230 (Fig. 1), and the increased absorption around 1.20  $\mu\text{m}$ . Both of these effects are indicative of the removal of  $\text{Fe}^{2+}$  ions from the M2 sites into the M1 sites; they are less severe in the spectra of the manganiferous specimen #337 (Fig. 2) due to the stronger preference of  $\text{Mn}^{2+}$  ions for the M2 sites which cause higher concentrations of  $\text{Fe}^{2+}$  ions to occur initially in the M1 sites prior to re-equilibration. These trends are supported by the site occupancies determined from the Mössbauer spectra. Thus, after heating the orthopyroxenes at 500  $^{\circ}\text{C}$  for 3 months, the  $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg}^{2+})$  ratios of the M1 sites increase from 0.09 to 0.22 (specimen #230) and from 0.16 to 0.27 (specimen #337). There are also small increases of ferric iron in the two specimens (from 2.5%  $\text{Fe}^{3+}$  and 3.1%  $\text{Fe}^{3+}$  to  $\sim 4.3\%$   $\text{Fe}^{3+}$  in both #230 and #337, respectively), which produce increased absorption around 0.66  $\mu\text{m}$  in the reflectance spectra (Figs 1 and 2).

Similar trends occur in specimen TZ following  $\text{Fe}^{2+}$ - $\text{Mg}^{2+}$  disordering at 700  $^{\circ}\text{C}$ . In Figure 3, the reflectance spectra of unheated (Fig. 3A) and re-equilibrated (Fig. 3B) samples have been deconvoluted into component gaussian bands. The increased relative intensity of the band at 1.20  $\mu\text{m}$  in Figure 3B correlates with the change of M1 site  $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg}^{2+})$  ratio from 0.15 (unheated) to 0.28 (re-equilibrated). The band at 0.66  $\mu\text{m}$  in the reflectance spectra may be assigned to an intervalence charge transfer (IVCT) transition between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in M1 sites separated by only 3.15 Å. The higher intensity of this  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  IVCT band in the re-equilibrated sample (Fig. 3B) again results from increased M1 site occupancy of  $\text{Fe}^{2+}$  ions.

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Figures 1, 2 & 3. Reflectance spectra of unheated and disordered orthopyroxenes.

**Applications.** The reflectance spectra of the  $\text{Fe}^{2+}$ - $\text{Mg}^{2+}$  disordered orthopyroxenes illustrated in Figures 1-3 are relevant to surfaces of terrestrial planets onto which basaltic magma has been extruded. If cooling rates of basalt lavas flowing onto the Moon, Mars and Venus were fast, equilibrium iron intersite partitioning may not have been achieved so that abnormal enrichments of  $\text{Fe}^{2+}$  ions in M1 sites would occur in lunar, martian and venusian orthopyroxenes and pigeonites. The two intense pyroxene  $\text{Fe}^{2+}$  CF/M2 site bands in the "1 micron" and "2 microns" regions would continue to dominate the reflectance spectra so that pyroxene compositions and structure-type would be readily identified in telescopic spectral profiles. However, abnormal intensification of the  $\text{Fe}^{2+}$  CF/M1 site band at 1.20  $\mu\text{m}$  could lead to the false identification of olivine in remote-sensed spectra because in low-Ca pyroxene-augite-olivine mixtures the inflection around 1.20  $\mu\text{m}$  is the only spectral feature for detecting the presence of olivine [12]. In particular, interference at 1.20  $\mu\text{m}$  from pyroxene  $\text{Fe}^{2+}$ /M1 site cations could be a major problem if *in situ* reflectance spectra could be measured on the surface of Venus where ambient temperatures are as high as 475  $^{\circ}\text{C}$ . Equilibrium disordering of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  ions comparable to that in the orthopyroxenes used in this spectral chemical study might be expected in low-Ca pyroxenes occurring on the venusian surface.

We conclude that pyroxene  $\text{Fe}^{2+}$ /M1 site spectral features need to be carefully assessed in remote-sensed spectra before deductions are made about the presence of olivine on planetary surfaces.

**References.** [1] R.G.Burns, *Min. Mag.*, **53**, 135 (1989); [2] S.Ghose, *Z. Krist.*, **122**, 81 (1965); [3] D.Virgo & S.S.Hafner, *Min. Soc. Amer. Spec. Pap.*, **2**, 67 (1969) & *Am. Min.*, **55**, 201 (1970); [4] S.K.Saxena & S.Ghose, *Am. Min.*, **56**, 532 (1971); [5] K.K.Khrstodorov *et al.*, *Dokl. Acad. Nauk. SSSR*, **214**, 909 (1974); [6] J.R.Besancon, *Am. Min.*, **66**, 965 (1981); [7] D.S.Goldman & G.R.Rossman, *Phys. Chem. Min.*, **4**, 43 (1979); [8] G.Steffen *et al.*, *Phys. Chem. Min.*, **16**, 120 (1988); [9] L.R.Davidson, *Contrib. Min. Pet.*, **19**, 239 (1968); L.R.Davidson & C.I.Mathison, *Neues Jahrb. Min., Mh.*, **2**, 47 (1973) [10] C.Pieters, *JGR*, **90**, 12393 (1985); [11] J.M.Sunshine *et al.*, *JGR*, **95**, 6955 (1990); [12] R.B.Singer, *JGR*, **86**, 7967 (1981); [13] Research supported by NASA grants NAGW-2037 (MIT) and NAGW-748 (Brown University).