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

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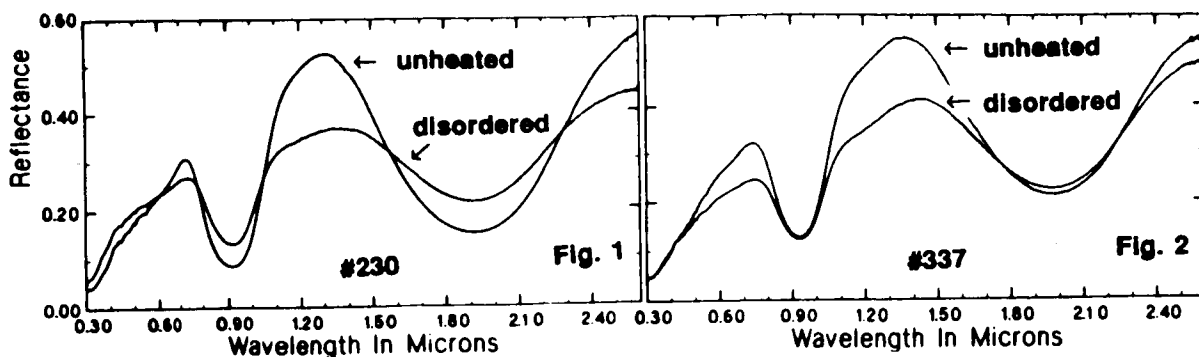
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Introduction. Pyroxenes are identified in telescopic and laboratory reflectance spectra by the broad, intense bands centered at 0.90-1.05 μm and 1.80-2.30 μm [1]. These spectral features originate from crystal field (CF) transitions in Fe^{2+} ions located in the very distorted, non-centrosymmetric M2 sites of the pyroxene crystal structure. In pigeonites and orthopyroxenes, strong enrichments of 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 Fe^{2+} ions situated in the less distorted M1 octahedral sites that are occupied mainly by Mg^{2+} ions [2]. Numerous experimental studies [e.g., 3-6] have shown that temperature-induced disordering of Fe^{2+} (M2 site) and 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 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 comprised 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]; 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 ($\text{Fs}_{38}\text{En}_{48}\text{Wo}_2\text{Mn}_{12}$); specimens #4645 ($\text{Fs}_{26}\text{En}_{74}$) and KC ($\text{Fs}_{61}\text{En}_{38}\text{Mn}_1$); and a synthetic ferrosilite (Fs_{85}). Specimens heated to 700 $^{\circ}\text{C}$ were equilibrated for several hours in CO_2/H_2 atmospheres providing oxygen fugacities close to or less than the iron-wüstite buffer. Different samples of specimen TZ were equilibrated under these conditions for time periods ranging from a few minutes to several hours. Orthopyroxene specimens heated to 500 $^{\circ}\text{C}$ were equilibrated at this temperature for three months in evacuated quartz tubes containing metallic Fe. The 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 77 K [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 Fe^{2+} - 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 μm and 1.95 μm , especially in specimen #230 (Fig. 1), and the increased absorption around 1.20 μm . Both of these effects are indicative of the removal of 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 Mn^{2+} ions for the M2 sites which cause higher concentrations of 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. For example, 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% Fe^{3+} and 3.1% Fe^{3+} to $\sim 4.3\%$ Fe^{3+} in both #230 and #337, respectively), which produce increased absorption around 0.66 μm in the reflectance spectra (Figs 1 and 2).

Similar trends occur in specimen TZ following Fe^{2+} - Mg^{2+} disordering at 700 $^{\circ}\text{C}$. The development of the 1.20 μm spectral feature with increasing duration of heating is illustrated in Figure 3, with equilibrium disordering being achieved in about 1 hour. In Figure 4, the reflectance spectra of unheated (Fig. 4A) and equilibrated (Fig. 4B) samples have been



Figures 1 and 2 (above). Reflectance spectra of orthopyroxenes unheated and disordered at 500 °C.

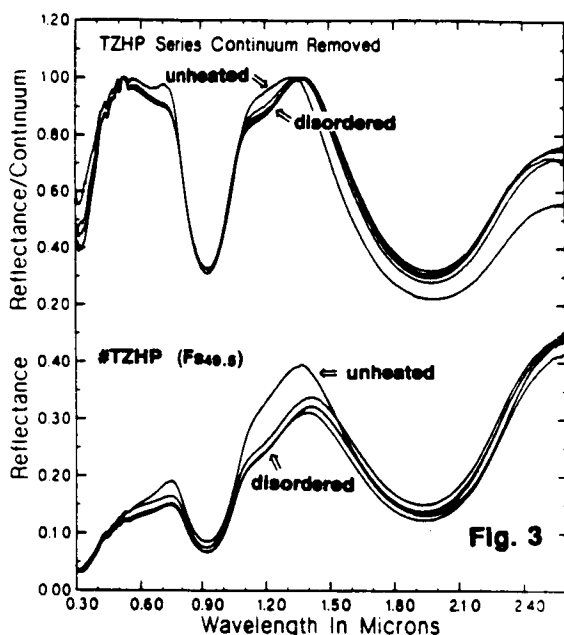
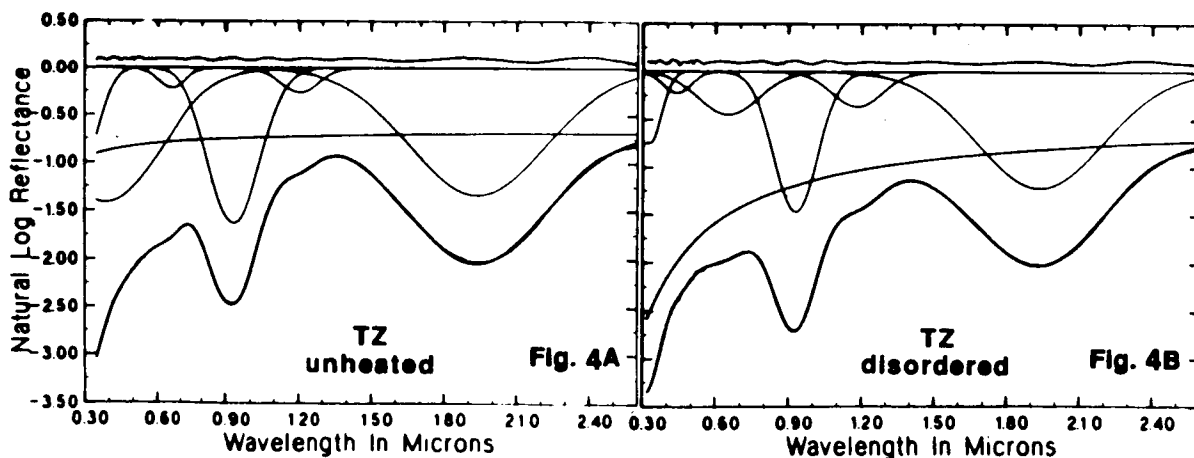


Figure 3 (left). Reflectance spectra of orthopyroxene specimen TZ before and after Mg^{2+} - Fe^{2+} disordering at 700 °C for time periods ranging from 6 minutes to 20 hours. Note the intensification of the Fe^{2+} /M1 site crystal field spectral feature at 1.20 μm .

Figure 4 (below). Deconvoluted reflectance spectra of specimen TZ before (Fig. 4A) and after (Fig. 4B) equilibrium cation disordering at 700 °C. Note the intensification of the Fe^{2+} /M1 site crystal field band at 1.20 μm and the $Fe^{2+} \rightarrow Fe^{3+}$ intervalence charge transfer band at 0.66 μm .



deconvoluted into component gaussian bands. The increased relative intensity of the band at 1.20 μm in Figure 4B correlates with the change of M1 site $Fe^{2+}/(Fe^{2+}+Mg^{2+})$ ratio from 0.15 (unheated) to 0.28 (re-equilibrated). The band at 0.66 μm in the reflectance spectra may be assigned to an intervalence charge transfer (IVCT) transition between Fe^{2+} and Fe^{3+} ions in M1 sites separated by only 3.15 Å. The higher intensity of this $Fe^{2+} \rightarrow Fe^{3+}$ IVCT band in the re-equilibrated sample (Fig. 4B) again results from increased M1 site occupancy of Fe^{2+} ions.

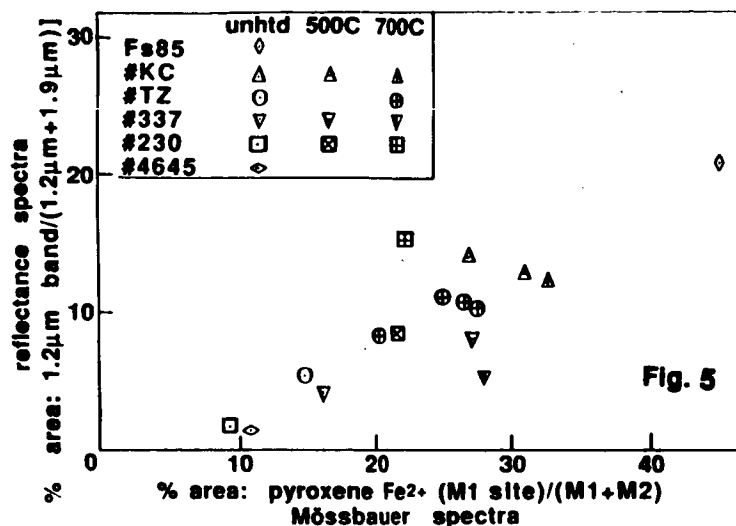


Figure 5. Correlations between peak area data obtained from deconvoluted reflection spectra and fitted Mössbauer spectra of unheated and disordered orthopyroxenes.

Correlations between the $\text{Fe}^{2+}/\text{M1}$ site occupancies determined from computed peak areas in the reflectance spectra and the Mössbauer spectra are illustrated in Figure 5 for the suite of orthopyroxenes studied. There is clearly a linear trend between Fe^{2+} (M1 site)/(M1+M2) ratios estimated from the deconvoluted reflectance spectra and the two-ferrous doublet fits of the Mössbauer spectra of the orthopyroxenes.

Applications. The reflectance spectra of Fe^{2+} - Mg^{2+} disordered orthopyroxenes illustrated in Figures 1-4 are relevant to surfaces of terrestrial planets onto which basaltic magma has been extruded. If cooling rates of basalt lava flows were fast, equilibrium iron intersite partitioning may not have been achieved so that abnormal enrichments of Fe^{2+} ions in M1 sites would occur. The two intense pyroxene $\text{Fe}^{2+}/\text{M2}$ site CF bands in the "1 micron" and "2 micron" regions would continue to dominate the reflectance spectra so that the pyroxene composition and structure-type would be readily identified in telescopic spectral profiles. However, abnormal intensification of the $\text{Fe}^{2+}/\text{M1}$ site CF band at $1.20 \mu\text{m}$ could lead to the false identification of olivine in remote-sensed spectra because in pyroxene-olivine mixtures the inflection around $1.20 \mu\text{m}$ is the only spectral feature for detecting the presence of olivine [12]. The identification of iron-bearing plagioclase feldspars, too, would be obscured by the pyroxene $\text{Fe}^{2+}/\text{M1}$ site CF band at $1.20 \mu\text{m}$. Such interference at $1.20 \mu\text{m}$ from pyroxene $\text{Fe}^{2+}/\text{M1}$ site cations would be a major problem if *in situ* reflectance spectra could be measured on the surface of Venus where ambient temperatures are as high as $475 \text{ }^\circ\text{C}$. Disordering of Fe^{2+} and 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 $\text{Fe}^{2+}/\text{M1}$ site spectral features need to be carefully assessed in remote-sensed spectra before deductions are made about the presence of olivine on planetary surfaces.

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