

**A NEW INTERPRETATION OF ANOMALOUS “TYPE B” NEAR-INFRARED SPECTRA OF Ca-RICH CLINOPYROXENES: IMPLICATIONS FOR REMOTE SENSING OF INNER SOLAR SYSTEM BODIES.**

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Pyroxene is an important rock-forming mineral found in the Earth's upper mantle and on the surfaces of inner solar system planets, the moon and asteroids. The existence of pyroxene on the surfaces of these solar system bodies has been mainly inferred by remote reflectance spectroscopy (mainly in the near-infrared (NIR) region), thus making the laboratory studies of pyroxenes so crucial for their remote spectral characterization. The NIR spectra of low-Ca pyroxenes are generally simple, whereas the spectra of Ca-rich clinopyroxenes (with  $C2/c$  symmetry) are more complicated and their interpretation is more difficult [1]. Some terrestrial and extraterrestrial Ca-rich clinopyroxenes show anomalous “type B” NIR spectra with an absorption band at  $\sim 2 \mu\text{m}$ , indicative of the presence of  $\text{Fe}^{2+}$  at the M2 crystallographic site, even when M2 is almost completely occupied by the larger Ca cation [1-3]. Different interpretations of the anomaly have been proposed, e.g. presence of higher than calculated  $\text{Fe}^{3+}$  contents [4], presence of minor phases [5]. This anomaly is similar to that observed in Mössbauer spectra of some Ca-rich clinopyroxenes where the Mössbauer relative area of  $\text{Fe}^{2+}$  at M2 is anomalously larger than that expected from stoichiometry [6,7]. X-ray crystal-structure analysis of Ca-rich clinopyroxenes (with  $\text{Ca} < 1$  at M2) has also been problematic, and the average structure refinement of these pyroxenes shows a residual electron density peak in the difference-Fourier synthesis, located at  $\sim 0.6\text{-}0.7 \text{ \AA}$  from the M2 site; the split M2' site [8].

X-ray structure refinement of synthetic  $C2/c$  clinopyroxenes on the hedenbergite ( $\text{CaFeSi}_2\text{O}_6$ )-ferrosilite ( $\text{Fe}_2\text{Si}_2\text{O}_6$ ) join, using a split-atom model, shows the existence of two different local configurations in the M2 cavity, a hedenbergite-like arrangement and a  $C2/c$  clinoferrosilite-like arrangement that are centered by Ca and  $\text{Fe}^{2+}$ , respectively [9]. This means that in these clinopyroxenes Ca at M2 assumes a local coordination similar to that of Ca in hedenbergite (8-coordinated) and  $\text{Fe}^{2+}$  at M2' assumes a local coordination similar to that of  $\text{Fe}^{2+}$  at M2 in  $C2/c$  clinoferrosilite (6-coordinated). The Mössbauer spectroscopic results on the same samples are consistent with the structure refinement data, and indicate the presence of  $\text{Fe}^{2+}$  in three local environments that are similar to those of  $\text{Fe}^{2+}$  at the M1 site in hedenbergite, and  $\text{Fe}^{2+}$  at the M1 and M2 sites in  $C2/c$  clinoferrosilite [9]. In natural (Ca, Fe, Mg) $_2\text{Si}_2\text{O}_6$  clinopyroxenes with a split M2-M2' site, the 6-coordinated  $\text{Fe}^{2+}$  is expected to be in a local environment similar to that of  $\text{Fe}^{2+}$  in high pigeonite (i.e. pigeonite with  $C2/c$  symmetry). Based on these results, and since NIR spectroscopy is also sensitive to the local environment, we may assign the absorption band at  $\sim 2 \mu\text{m}$  in “type B” NIR spectra to  $\text{Fe}^{2+}$  in high pigeonite. This assignment can be verified by comparing NIR and Mössbauer spectra of Ca-rich clinopyroxenes for which X-ray structure refinement data are available. I will present results on three natural clinopyroxene samples and on druse clinopyroxene from the D'Orbigny meteorite. The average structure refinement of the studied samples showed a residual electron density peak in the difference-Fourier synthesis, corresponding to the split M2' site, and their NIR and Mössbauer spectra (when interpreted using the above approach) are in accord with the structure refinement data. The results would enable us to obtain more reliable spectroscopic data on pyroxenes, e.g. accurate  $\text{Fe}^{2+}$  occupancies at the M1 and M2 sites [9], and will have important implications for NIR-remote sensing and mineralogical investigation of terrestrial planets and asteroids.

**References:** [1] Cloutis E. A. and Gaffey M. J (1991) *Journal of Geophysical Research* 96:22809–22826. [2] Schade U. et al. (2004) *Icarus* 168:80-92. [3] Burbine T. H. et al. (2006) *Meteoritics & Planetary Science* 41:1139-1145. [4] Hoffman E. J. et al. (2005) *LPS XXXVI*, Abstract #2096. [5] Hoffman E. J. et al. (2006) *LPS XXXVII*, Abstract #1215. [6] Williams P. G. L. et al. (1971) *Nature Physical Science* 230:149-151. [7] Dowty E. and Lindsley D.H. (1973) *American Mineralogist* 58: 850–868. [8] Rossi G. et al. (1987) *Physics and Chemistry of Minerals* 14:514-520. [9] Abdu Y. A. and Hawthorne F. C. (2013) *American Mineralogist* 98:1227–1234.