

ANOMALOUS SPECTRA OF HIGH-Ca PYROXENES: FURTHER CORRELATIONS BETWEEN NIR AND MÖSSBAUER PATTERNS. E. J. Hoffman¹, U. Schade², and L. Moroz³. ¹Physics Department, Morgan State University, Baltimore, MD 21251, USA (ehoffman@morgan.edu), ²BESSY, Albert-Einstein-Strasse 15, 12489 Berlin, Germany, ³German Aerospace Center (DLR), Rutherfordstrasse 2, 12489 Berlin, Germany.

Introduction: Near-infrared (NIR) reflectance spectroscopy gives intriguing results for three well-studied angrites, meteorites containing large abundances of high-Ca pyroxenes [1]. Their spectra correspond to the Type A (“normal”) and Type B (“anomalous”) patterns that turn up almost at random in spectra of terrestrial high-Ca pyroxenes (clinopyroxenes) [2, 3]. Fe ions are responsible for the pertinent absorption bands, and an additional Fe-sensitive method, Mössbauer spectroscopy, shows a similar dichotomy of results, with an anomalously-intense ferric-ion signature appearing for most NIR Type B samples [4-7]. In a few samples, detailed microscopic analysis suggests that minute amounts of iron-rich minor phases may be responsible [2, 8].

NIR spectroscopy is a principal tool in the study of igneous rock whether remote or in the laboratory, so planetary science would benefit from knowledge of the origin and probable extent of the anomaly. This report presents Mössbauer data for an additional set of NIR-characterized pyroxenes [3] in the hope of contributing to clarification.

Experimental: The samples [3] were placed in holders at an areal density of 7 mg Fe/cm². ⁵⁷Fe-Mössbauer spectra were taken at room temperature with least-squares curve fitting to Lorentzians using approximate literature values as starting parameters. In this preliminary study seven of 13 available samples [3] were selected to provide a variety of NIR types.

Results: Figure 1 presents Mössbauer results for one each of the three NIR spectral types reported, A, B, and AB [3]. Present to varying degrees in these Mössbauer spectra is an absorption doublet of quadrupole splitting $QS < 1.2$ mm/s centered at 0-1 mm/s (the isomer shift, IS). Such a doublet is typical of ferric ion in a wide variety of silicates, and ϕ , the relative area under this doublet, generally gives a good approximation of Fe-III content (Table 1, footnote). The more widely-spaced doublet, QS of 1.5–3.0 mm/s, IS about 1 mm/s, generally comes from Fe-II in octahedral sites. Comparison with chemical analysis gives a clue to NIR spectral type: Type B correlates well with a Mössbauer pattern showing Fe-III content higher than that indicated by chemical analysis [4-7].

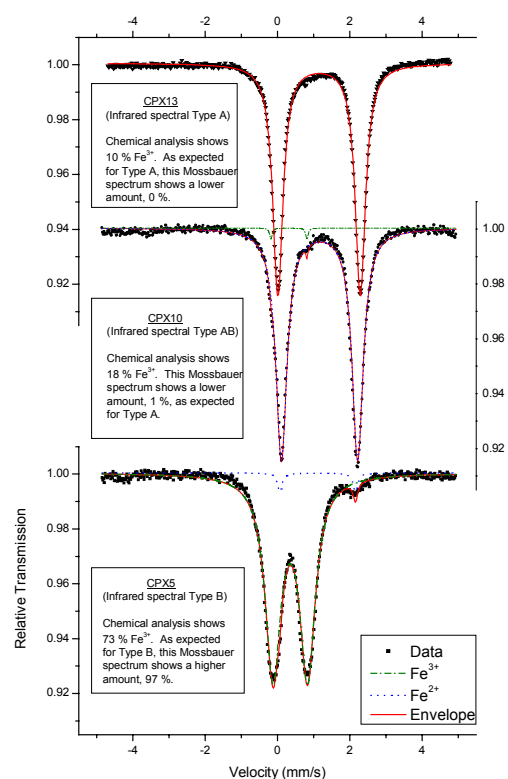


Figure 1. Mössbauer results for one each of the three NIR spectral types reported, A, B, and AB [3].

Table 1. NIR spectral type predictions based on apparent Fe-III content by Mössbauer spectroscopy: agreement with observed NIR spectral results for seven terrestrial high-Ca pyroxenes [3].

	<u>CPX5</u>	<u>CPX6</u>	<u>CPX9</u>	<u>CPX10</u>	<u>CPX11</u>	<u>CPX12</u>	<u>CPX13</u>
ϕ (Möss) ¹	97%	35%	2%	1%	0%	5%	1%
ϕ (Chem) ²	73%	31%	11%	18%	8%	16%	9%
NIR Type (Möss. Prediction)	B	B	A	A	A	A	A
NIR Type (Observed [3])	B	B	AB	AB	A	A	A
Agreement?	Yes	Yes			Yes	Yes	Yes

Composition [3]

Fs	11.93	16.17	29.86	31.24	44.68	46.36	46.50
En	36.03	39.45	22.14	21.06	6.32	1.50	3.71
Wo	52.05	44.38	48.00	47.70	49.01	52.14	49.80
Fe₂O₃ (wt%)	4.9	2.7	2.0	3.3	1.9	4.0	2.0
FeO (wt%)	1.61	5.46	13.9	13.9	20.6	18.5	17.7
MgO (wt%)	10.20	10.80	6.53	6.38	1.77	< 0.449	0.872
CaO (wt%)	20.50	16.90	19.70	20.10	19.10	19.4	16.3
SiO₂ (wt%)	45.30	43.30	49.00	45.80	48.50	45.5	40.3
Al₂O₃ (wt%)	10.40	11.90	2.30	2.86	1.30	2.52	3.90
Na₂O (wt%)	< 2.40	< 2.40	< 3.00	< 3.00	< 3.50	< 3.50	3.50
P₂O₅ (ppm)	1220	<216	<280	<292	<303	<321	<389
SO₃ (ppm)	<121	<122	<153	<160	<168	4670	32400
K₂O (ppm)	6300	444	<121	<121	134	176	1180
TiO₂ (ppm)	3310	17100	<167	<167	199	33.1	88.2
Cr (ppm)	303	634	14.3	<6.4	<5.1	<7.7	<8.2
Mn (ppm)	1860	1050	12600	13300	5840	21700	25000

¹ Ratio of the area under the “ferric” (narrower) doublet to the total area under the curve (see Fig. 1).

² Molar ratio Fe-III/(Fe-II + FeIII) [3]

Table 1 summarizes these approximations for the seven samples now studied. These lead to the conclusion that for these samples also NIR observation of Type B spectral behavior seems correlated with anomalously-high Fe-III as estimated by Mössbauer spectroscopy.

Discussion: In pyroxenes Fe²⁺ ion in the M2 octahedral sites produces an NIR absorption feature at 2 μ m. These sites are the only ones large enough to accommodate Ca²⁺ ions, however, so in high-Ca pyroxenes Fe²⁺ cannot be in M2 and spectra should be flat at 2 μ m. Type B spectra, with the 2- μ m dip, are thus clearly anomalous [9].

Mössbauer spectra of the Type B samples in this study also show an anomaly, indication of more Fe³⁺ than shown by chemical analysis. Further study by microscopic and other methods may show that the anomalies stem from minor non-pyroxene phases as observed [8] in some other Type B high-Ca pyroxenes.

References: [1] Burbine, T. H. et al. (2001) *LPS XXXII*, Abstract #1857. [2] Cloutis E. A. and Gaffey M. J. (1999) *JGR*, 96, 22809. [3] Schade, U. et al. (2004) *Icarus* 168, 80-92. [4] Hoffman E. J. (2002) *LPS XXXIII*, Abstract #1973. [5] Hoffman E. J. (2003) *MAPS* 38, A152. [6] Hoffman E. J. et al. (2004) *LPS XXXV*, Abstract #1128. [7] (2004) *MAPS* 39, Abstract. [8] Housley, R. M., personal communication. [9] Adams, J. B. (1975) In: Karr, C., Ed., *Infrared and Raman Spectroscopy of Lunar and Terrestrial Minerals*, New York, Academic Press, 91-116.