Raman Spectral Features of Pyroxene —- Application to Martian Meteorites Zagami & EETA 79001

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Raman spectroscopic patterns and peak positions of the pyroxenes in lunar KREEP basalt fragment 15273, 7039 [1] were used previously to distinguish orthopyroxene, clinopyroxene, and pyroxenoid structures. These spectra were calibrated with electron microprobe analyses (EMPA) to correlate major Raman peak positions with the Mg' (Mg/(Mg+Fe)) and Wo content of the pyroxenes. In anticipation of the 2003 and 2005 Mars Surveyor lander missions, we are testing these correlations for their applicability to pyroxene spectra from a more diverse suite of pyroxenes, including those from the Zagami and EETA79001 Martian meteorites using the calibrated lunar pyroxene curve.

The major Raman peaks of pyroxene occur in five spectral regions: (1) near 1000 cm^{-1}; (2) near 670 cm^{-1}; (3) near 530 cm^{-1}; (4) between 300–400 cm^{-1}; and (5) below 300 cm^{-1}. These peaks arise from various vibrational modes in the pyroxene structure, and the correlation can be complicated. We focus on the peaks near 1000 cm^{-1}, 670 cm^{-1}, and 320 cm^{-1} because they are the most commonly observed peaks on unprepared rock surfaces and in spectra where multiple phases are sampled (e.g., pyroxene + olivine, plagioclase, or phosphates). The following table lists the correlation coefficients found between these three peak positions, Mg', and the Wo content for the pyroxenes in the 15273,7039 lunar rock fragment.

	~1000 cm^{-1} peak	~670 cm^{-1} peak	~320 cm^{-1} peak
~ Mg'	0.86	0.88	0.95
~ Wo content	-0.48	-0.61	-0.33

These data show that the peak near ~320 cm^{-1} has the most direct correlation (R^2=0.95) with Mg'. That peak probably originates from a lattice vibrational mode involving the translational motion of the cation in the M1 site in the pyroxene structure. All three peaks generally correlate better with Mg' (R^2>0.86) than with Wo content (max. R^2 ~0.61).

In order to use these correlations to characterize the pyroxenes from other rocks, especially the Shergottite meteorites, we plotted the ~670 cm^{-1} versus the ~320 cm^{-1} peak positions, using the regions delimited by Mg' from the lunar calibration (Figs. 1 & 2). The lunar data points from 15273,7039 (open symbols) form a wide band along the central regression line, which is caused mainly by experimental uncertainty resulting from different depths of penetration of the electron beam in EMPA and the laser in the Raman measurements [1]. This source of uncertainty exceeds errors related to locating the same spots for analysis, especially when compositional zoning occurs over a short distance relative to the separation of analytical spots. Other compositional parameters could also affect the correlation curves, however, we have attempted to minimize such affects by considering only pyroxenes that have limited non-quadrilateral components.

Over seven hundred Raman spectra were obtained from five linear traverses on sawn surfaces of Zagami and four traverses on irregular rock surfaces of EETA79001,476 (lithology A). The point counting method of [2] was used in these measurements to simulate the degraded measurement conditions we anticipate in future surface exploration on Mars. Thus, most data points were acquired outside of the focal plane of the excitation laser beam, yielding Raman spectra with a less than ideal signal-to-noise ratio. A total of 243 spectra that have pyroxene peaks were obtained from Zagami, and 481 spectra for EETA79001. The positions of the ~670 cm^{-1} and ~320 cm^{-1} peaks from these spectra are plotted against those of the lunar pyroxene (Fig. 1 for Zagami and Fig. 2 for EETA-79001). In addition, a histogram of the ~320 cm^{-1} peak is included with each of these figures.

The data points for the Zagami pyroxenes shown in Figure 1 suggest a distribution of Mg' between 0.4 and 0.75, and are in general agreement with the microprobe data of [3,4,5], but apparently overestimating the upper Mg' limit by about 0.10. The histogram provides a measure of the relative abundance of Zagami pyroxenes that have different Mg' values. It is consistent with the observation that small magnesian cores (Mg' ~0.65) are overgrown by fairly extensive zones of intermediate Mg' (in both pigeonite and augite), and that these tail off to thin rims of low Mg' [3]. This kind of zoning is indicative of rapid cooling associated with volcanism, but from the pattern of zoning as deduced from multiple Raman analyses along a traverse, we can estimate the grain size and the scale of zoning [6] and thus have some idea of the basaltic texture and of the nature of the volcanic environment where the rock formed.

The Mg′ values of the pyroxene grains in EETA-79001 (lithology A) are shown in Fig. 2. They mainly span a range from 0.5 to 0.75, which overlaps the regions defined by two petrographic studies [7,8] on lithology A of EETA79001. The histogram based on ~320 cm^{-1} peak suggests that the most abundant pyroxene in lithology A has Mg' values ranging from 0.5 to 0.65. However, we did not encounter grains whose spectra indicate Mg′ as high as 0.8–0.85 as found by [7] in orthopyroxene-olivine xenocrysts. The few Opx grains encountered in our automated Raman measurements appear to have Mg' below 0.8, and they are not associated with olivine grains. Furthermore, among the spectra showing both olivine and pyroxene Raman peaks, ~80% of them appear to be Cpx, not Opx, meaning that our traverses did not intersect any olivine-Opx xenocrysts. A few of the analyzed pyroxene grains appear to have rather low Mg', one of them, below 0.4 (Fig. 2), as found in some grains in lithology B, but not A [7].

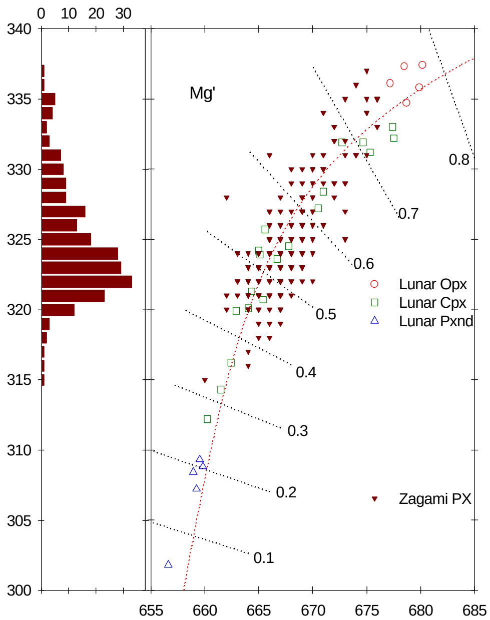

Figure 1. Data from 243 Raman spectra of pyroxenes in Zagami overlain onto a calibrated Mg′ grid.

Additional Raman measurements and electron microprobe analyses were made on the same spots of a sample of EETA79001 (lithology B). The preliminary results suggest that the lunar calibration is accurate to within about 0.03 Mg′ units of the EETA79001 data. Thus, using the calibration for Mg' according to the lunar KREEP basalt, the correct distribution of Mg' for basaltic pyroxene in these two Martian meteorites can be obtained within the reasonable limits. The discrepancy between the Mg' range of EETA79001 (lithology A) pyroxene found by this Raman study and those by previous petrographic studies are probably caused by having analyzed different parts of this somewhat heterogeneous lithology.

Pyroxenes in basaltic rocks cool relatively rapidly and thus are not well equilibrated. Brearley [4] found exsolution lamellae in low-Ca pyroxene cores in Zagami, suggesting slow cooling, perhaps in a holding chamber prior to eruption, but these lamellae are very thin and the pyroxene overgrowths on these cores are zoned strongly to Fe-rich compositions. Compared to their plutonic counterparts, these pyroxenes have disordered cation distributions among M1 and M2 sites.

Additional Raman measurements made on four sets of well equilibrated pyroxenes in lunar and terrestrial rocks indicate that the calibration for Mg′ can not be applied directly to equilibrated pyroxenes. Equilibrated (and presumably well ordered) Opx trends toward higher peak positions, whereas equilibrated Cpx trends toward lower peak positions. This may explain why our Raman spectra for magnesian Opx cores in Zagami, which may have cooled more slowly than the rest of the rock, indicate Mg′ values higher than EMPA. Thus, it appears that different correlation curves need to be developed for pyroxene having different ranges of Wo contents.

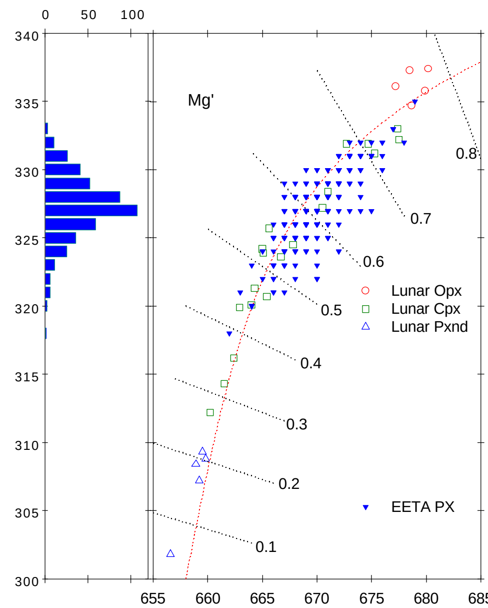

Figure 2. Data from 481 Raman spectra of pyroxenes in EETA79001 Martian meteorite (lithology A).

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References: [1] Wang et al. (1997) Raman spectroscopic characterization of different types of pyroxene. *Lunar Planet. Sci. XXVIII*, 1491–1492; [2] Haskin et al. (1997) Raman spectroscopy for mineral identification and quantification for in–situ planetary surface analysis: A point-count method. *J. Geophys. Res.* **102**, 19,293–19,306; [3] Stolper and McSween (1979) *Geochim. Cosmochim. Acta* **43**, 1475–1498; [4] Brearley (1991) Subsolidus microstructures and cooling history of pyroxenes in the Zagami shergottite. *Lunar Planet. Sci.* ***XXII***, 135–136. [5] McCoy et al. (1992) Zagami: Product of a two-stage magmatic history. *Geochim. Cosmochim. Acta* **56**, 3571–3582; [6] Wang et al. (1999) Raman Spectroscopic Characterization of a Martian SNC Meteorite – Zagami, submitted; [7] McSween and Jarosewich (1983) *Geochim. Cosmochim. Acta* **47**, 1501–1513; [8] McSween (1994) *Meteoritics* **29**, 757–779.