

**A RE-EVALUATION OF OLIVINE-PYROXENE SPECTRAL CALIBRATIONS AND IMPLICATIONS FOR APOPHIS.** E. A. Cloutis<sup>1</sup>. <sup>1</sup>Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3C 2C1; e.cloutis@uwinnipeg.ca.

**Introduction:** Asteroid (99942) Apophis has been characterized as a possible LL ordinary chondrite and is in the Sq taxonomic class [1]. The 2029 encounter offers an unprecedented opportunity for its detailed examination. Its reflectance spectrum and LL affinity suggest a surface dominated by olivine, orthopyroxene, clinopyroxene, and minor metal.

Cloutis et al. [2] introduced a scheme for determining end member abundances and compositions of olivine (OLV) and low-calcium pyroxene (LCP, also commonly referred to as orthopyroxene) using 0.3-2.5  $\mu\text{m}$  reflectance spectra. This was subsequently extended [3], in a more qualitative way, to account for the spectrum-altering effects of high-calcium pyroxene (HCP, also commonly referred to as clinopyroxene).

It was found that some key spectral properties could be used to quantify OLV and LCP abundances and their compositions in such two-component mixtures. Spectral properties of most importance included the wavelength position of a band center in the 1  $\mu\text{m}$  region, and ratio of various measures of area enclosed by a reflectance spectrum and straight line continua. Using these two metrics, a very well-constrained relationship was found for an olivine-LCP series containing ~10 mol%  $\text{Fe}^{2+}$ . LCP and spectral type B HCP exhibit absorption bands in the 1 and 2  $\mu\text{m}$  region (termed Band I and Band II, respectively), while OLV only has an absorption feature in the 1  $\mu\text{m}$  region (Band I). It was found that increasing LCP:OLV ratio results in an increasing Band II/Band I area ratio (termed BAR), and a decrease in wavelength position of Band I (because it occurs at shorter wavelengths in LCP than in OLV) (Figure 1).

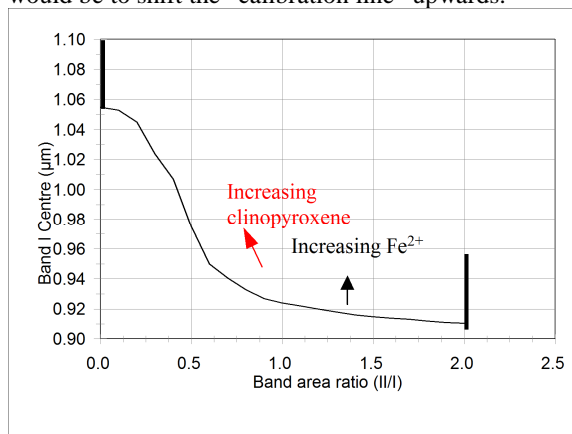
Here we look at how deviations from this series affect the derived spectral metrics.

**1. Presence of  $\text{Fe}^{3+}$ .** Most natural terrestrial pyroxenes contain some amount of  $\text{Fe}^{3+}$ . Its presence results in a 0.75  $\mu\text{m}$  region  $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$  charge transfer band, but more importantly, an increasingly steep red slope. This red slope reduces the depth and area of Band I. To overcome this, [2] included spectral slope in determination of Band I area.

**2. Presence of alteration.** Many natural terrestrial pyroxenes exhibit evidence of alteration, specifically, narrow  $\text{H}_2\text{O}$ -related absorption bands near 1.9  $\mu\text{m}$  and a greater downturn in reflectance beyond this region, due to the short wavelength wing of the 2.7-3  $\mu\text{m}$  region OH/ $\text{H}_2\text{O}$  stretching fundamental. [2] examined

different ways to measure Band II area to overcome these effects.

**3.  $\text{Fe}^{2+}$  content in OLV and LCP.** Increasing  $\text{Fe}^{2+}$  content results in a systematic shift of OLV and LCP band centers to longer wavelengths [3,4,5,6]. The effect on the Band I center vs. BAR plot (Figure 1) would be to shift the “calibration line” upwards.



**Figure 1.** Plot of Band I center vs. BAR for OLV+LCP mixtures (curved line) from [1] for ~10 mol%  $\text{Fe}^{2+}$  (equilibrium mixture). The left and right vertical bars show the range over which the curved line can move up or down (a 100 mol.%  $\text{Fe}^{2+}$  mixture would be at the top of the range – as indicated by the black arrow). The red arrow show direction of movement of a mixture where HCP is replacing LCP.

**4. Addition of HCP.** The addition of HCP at the expense of LCP will result in a reduction in BAR and an increase in Band I center position, as HCP has weaker absorption bands and Band I and Band II centers at longer wavelengths than LCP (for a given  $\text{Fe}^{2+}$  content; Figure 1).

**5. Exsolved pyroxenes vs. pigeonite.** In ordinary chondrites, pyroxenes can exist as pigeonite (with an intermediate (~10 mol%) Ca content, or exsolve to Ca-rich (HCP) and Ca-poor (LCP) end members. Pigeonites are spectrally similar to LCPs and follow the general trend of band positions versus  $\text{Fe}^{2+}$  content [3].

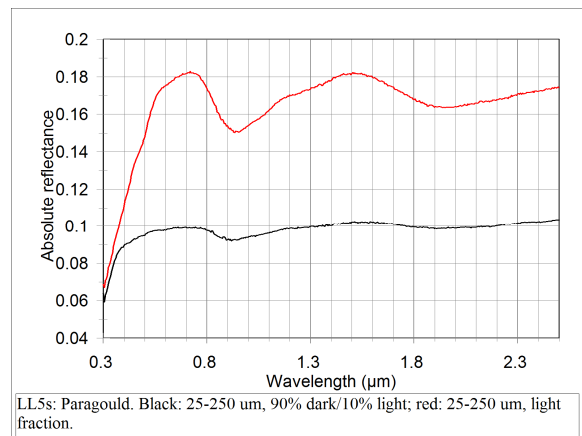
**6. Grain size effects.** The effect of increasing grain size is to reduce overall reflectance and increase band depths up to optical saturation. For pyroxene and olivine, optical saturation occurs in the range of two to a few hundreds of microns [7]. Beyond this range, absorption band depths will begin to decrease (as their reflectance cannot decrease further) and widen (as the

wings of the bands also reach saturation). Overall slopes can also change, and the change will depend on the relative amount of optical saturation of different absorption bands. For spectra of solid unpowdered samples, they appear to be invariably blue-sloped compared to powders.

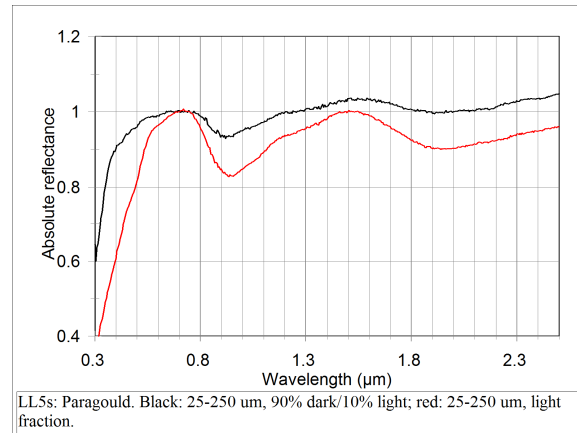
**Laboratory spectral studies and Apophis.** Our re-examination of mafic mineral mixture spectra is a necessary first step for robust analysis of Apophis. It will be accompanied by a wide-ranging analysis of ordinary chondrite (LL) spectra, and synthesis of laboratory studies of shock and space weathering. We are exploring different continuum-removal procedures, and assessing existing ones. We are also examining the effects of other phases, such as nanophase iron, metal, and sulfides, including the results of laboratory experiments on various types of space weathering. The goal is to develop easy-to-apply and robust spectral metrics for unraveling and characterizing the physical state and composition of Apophis and other LL chondrite parent bodies.

**Apophis: 1. Space weathering.** The spectrum of Apophis from [1] is more red-sloped than LL ordinary chondrites, likely due to space weathering, which reddens and darkens its spectrum. It does not appear to affect band depths [8], although they appear shallower due to the decrease in reflectance. Laboratory space weathering experiments also indicate that ion irradiation does not affect band centers [8].

**Apophis: 2. Shock effects.** The effect of impact shock on ordinary chondrites is to comminute and darken them, largely due to melt and dispersal of opaque components such as metal and sulfides [9]. Comparison of a shocked-darkened and unshocked spectrum of the LL5 chondrite Paragould, (Figures 2 and 3) indicates that impact shock darkens it and does reduce band depths, but does not appear to affect absorption band centers.



**Figure 2.** Reflectance spectra of the Paragould LL5 chondrite, showing a 90% shock-darkened+10% unshocked mixture (red spectrum) and an unshocked fraction; grain sizes are the same for both [from RELAB archive].



**Figure 3.** Same as Figure 2, normalized at 0.75 μm.

**Implications for Apophis, Didymos (and Itokawa).** Apophis and Didymos have been classified as probable LL chondrite parent bodies [1,10] and Itokawa is known to be one [11]. The results of our reanalysis of LL chondrite-relevant minerals, mixtures, laboratory experiments, and meteorites will enable us to better unravel the spectrum-altering effects of variations in physical properties versus composition. This, in turn, should allow for new insights into the history and evolution of these (and other) LL chondrite parent bodies.

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**References:** [1] Binzel R.P. et al. (2009) *Icarus*, 200, 480. [2] Cloutis E.A. et al. (1986) *JGR*, 91, 11641. [3] Cloutis E.A. and Gaffey M.J. (1991) *Earth, Moon, and Planets*, 53, 11. [4] King T.V.V. and Ridley I.W. (1987) *JGR*, 92, 11457. [5] Sanchez J.A. et al. (2014) *Icarus*, 228, 288. [6] Adams J.B. (1974) *JGR*, 79, 4829. [7] Craig M.A. et al. (2007) *LPSC XXXVIII*, Abstract #1356. [8] Brunetto R. et al. (2006) *Icarus*, 184, 327. [9] Rubin A.E. (2004) *GCA*, 68, 673. [10] Dunn T.L. et al. (2013) *Icarus*, 222, 273. [11] Nakamura T. et al. (2011) *Science*, 333, 1113.