

ON-THE-FLY CALIBRATION FOR RAPID RAMAN CHONDRITE CLASSIFICATION. L.C. Welzenbach, Galactic Analytics, 15918 Mesa Verde Dr, Houston TX 77059 (galacticanalyticsmeteorites@gmail.com).

Introduction: Classification of ordinary chondrites is typically done through measurements of the composition of olivine and pyroxenes, via electron microprobe, oil immersion or other methods [1-4]. These methods can be time consuming and costly through lost sample material during thin section preparation. Previously the author described the methods by which Raman microscopy can perform the same measurements [5] but considerably faster and with much less sample preparation. Raman spectroscopy as a classification tool is now being tested and corroborated by other researchers [6] to speed the classification of large amounts of chondrites such as those retrieved from Antarctica.

The concept of using Raman spectroscopy to classify meteorites is scientifically robust as seen in previous uses of this technique for olivine composition analyses [8-13]. It has also been shown that the analysis is insensitive to isotopic variation [14]. However, one difficulty must be overcome before Raman analysis can be used as a standard method for classifying meteorites – the need for robust, high fidelity spectral calibration in order to discern the relatively small peak shifts that must be measured. While this is not a severe technological limitation, it must be addressed.

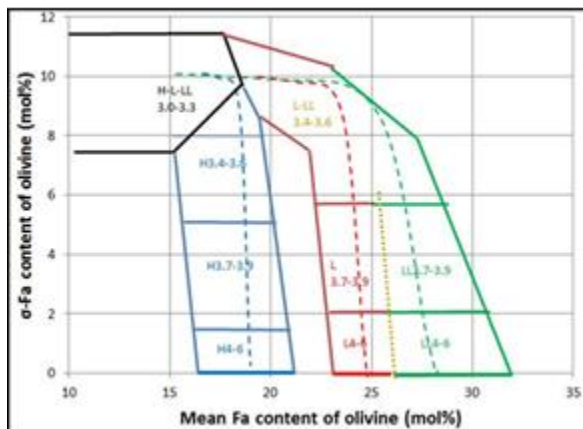


Figure 1: Classification of chondrites by type and petrographic grade, using composition vs. standard deviation of composition values. These graphs are from the Meteoritical Society Database website [7] with a detailed description provided on that site. Ordinary chondrites can be classified using a statistically relevant number of olivine and/or pyroxene

The Challenge: Classification of ordinary chondrites is made by measurement of the chemical composition of olivine and pyroxene (Figure 1)[7,8]. Composition of olivine is a straightforward measurement by

Raman spectroscopy, as described in detail by Kuebler *et al* (2006) (Figure 2)[9]. The composition of pyroxenes has likewise been demonstrated in a semi-quantitative fashion [10,11]. For the purpose of this study, we will focus on olivine. The Raman spectrum of olivine is dominated by two vibrational modes that appear at ~ 820 and ~ 850 cm^{-1} . These peaks shift in accordance with Fo [8-12]. The full range of Raman peak shift over the 0-100 Fo range is ~ 10 cm^{-1} for the ~ 820 cm^{-1} Raman peak, and ~ 19 cm^{-1} for the ~ 850 cm^{-1} peak. The span of Fo numbers exhibited by ordinary chondrites covers ~ 60 to 90 Fo, for a span of about 30 Fo units. Therefore, the range of Raman peak positions of interest run span a range of ~ 3 cm^{-1} for the ~ 820 cm^{-1} peak and 5.7 cm^{-1} for the ~ 850 cm^{-1} peak. This means that single- cm^{-1} spectral resolution is necessary, which is a reasonable constraint for most Raman instruments. More importantly, it means that the spectral calibration must be stable and repeatable with a sub- cm^{-1} accuracy. This is a challenge. The normal vibrational and thermal environment can be sufficient to cause variation in spectral calibration on the order of one or two cm^{-1} in the course of the normal operation of a typical Raman instrument.

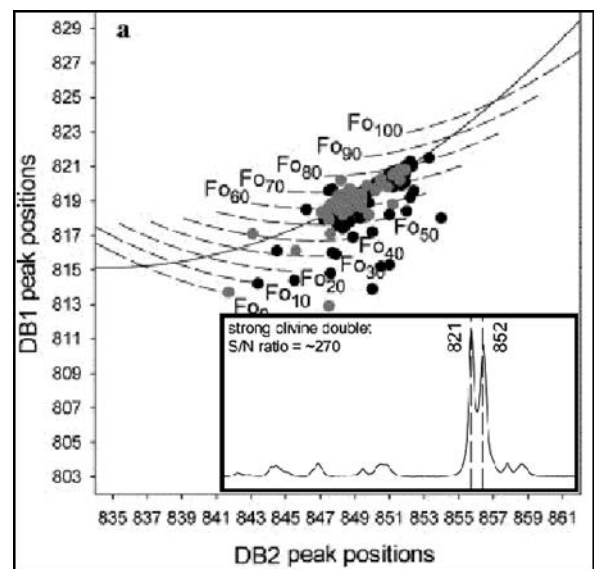


Figure 2: Raman spectrum (inset) of olivine showing two strong Raman peaks around ~ 820 and ~ 850 cm^{-1} ("DB1" and "DB2", respectively). The positions of these peaks are an indicator of olivine Fo number. The graph shows the Fo number calculated from individual spectra collected from EETA79001 as a function of positions of the Raman peaks. Figure adapted from [9].

This small shift can affect calculated Fo values and lead to erroneous classifications.

The Solution: One way to solve this problem is with spectral calibration cycles before and after every spectrum, but this is a time-consuming operation. To solve this problem we devised a second option; real-time spectral calibration. We have modified a Raman instrument to collect Raman spectra and neon emission lamp spectra concurrently. Every spectrum, regardless of the actual physical alignment of the instrument, comes with a reference spectrum of sufficient fidelity to calibrate the spectrum to sub- cm^{-1} accuracy. The reference spectrum comes from the NIST Atomic Spectra Database [15]. This is a standard spectroscopic technique, but consistent measurements of individual wavenumber cm^{-1} -accuracy may also allow us to accurately identify the classes of un-equilibrated chondrites as well.

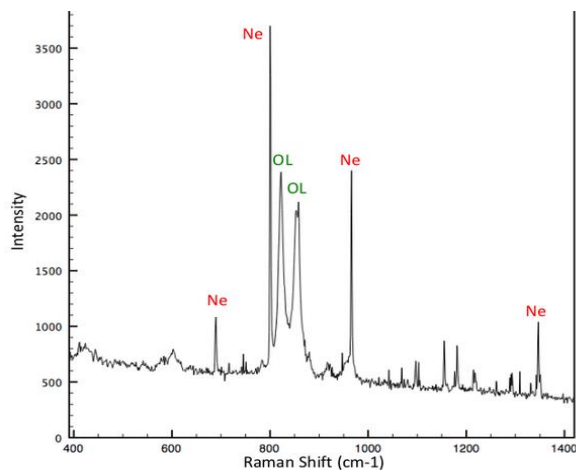


Figure 3: Raman spectrum from the Fukang pallasite showing the typical olivine doublet and Ne spectra that will be used for real-time calibration of every spectra. After spectra has been calibrated, the Ne peaks will be subtracted from the spectra for calculation of Fo values.

References: [1] Van Schmus W. and Wood J. (1967) *GCA* **31** 447-465. [2] Dodd R. *et al* (1967) *GCA* **31** p.921-951 [3] Krot S. *et al* (2004) *Treatise on Geochemistry*, Ch. 1.05 p. 84-128. [4] Lunning N. *et al* 2012 Abstract #1566. [5] Fries M.D. and Welzenbach L. (2014) LPSC Abstract #2519. [6] Pitarello L. *et al* (2014) 77th Meteoritical Society Meeting, Abstract #2087. [7] Meteoritical Society Database website accessed 06 Jan 2014 and references there, [http://www.lpi.usra.edu/meteor/drawplot.php?x=24.9&y=0.4&z=&plot=2&label=Kato1%20\(L6\)&meth](http://www.lpi.usra.edu/meteor/drawplot.php?x=24.9&y=0.4&z=&plot=2&label=Kato1%20(L6)&meth)

[od=linear&slope=0.52](#) [8] Kuebler K. *et al* 36th LPSC (2005) Abstract #2086. [9] Kuebler K. *et al* *Geo. et Cosmo. Acta* **70** (2006) pp. 6201-6222. [10] Foster N.F. *et al* *Geo. Et Cosmo. Acta* **121** (2013) 1-14. [11] Mouri T. and Masaki E. *J. Miner. Petrolog. Sci.* **103** (2008) 100-104. [12] Guyot F. *et al* *Phys. Chem. Minerals* **13**, 2 (1986) 91-95. [13] Kolesov B.A. and Tanskaya J.V. *Mat'ls. Res. Bull.* **31**, 8 (1996) 1035-1044. [14] Kolesov B.A. and Geiger C.A. *Phys. Chem. Minerals* **31**, 3 (2004) 142-154. [15] Kramida A *et al* and NIST ASD Team (2014). *NIST Atomic Spectra Database* (ver. 5.2), <http://physics.nist.gov/asd> National Institute of Standards and Technology.