



# Real-Time Calibration for Rapid Raman Ordinary Chondrite Classification

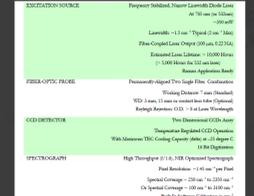
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## Introduction

Classification of ordinary chondrites is typically done through measurements of olivine and pyroxene composition, 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 [8] but considerably faster and with much less sample preparation. Raman spectroscopy as a classification tool has been tested and corroborated by other researchers [7,16] to speed the classification of large amounts of chondrites such as those retrieved from Antarctica and Northwest Africa. 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 are measured. Here we present a robust co-registered spectral calibration from a portable Raman spectrometer to classify ordinary chondrites.

## Raman Instruments and Methods

	Kuebler et al 2006	Pittarello et al 2016	This Work
Instrument	HoloLab 5000	LabRAM HR Evolution (confocal Raman)/ SENTERRA DRM	Enwave EZ Raman-N A-2
Laser	532 nm	532 nm	785 nm
Spectral resolution	<1 cm <sup>-1</sup>	<1 cm <sup>-1</sup>	3 cm <sup>-1</sup>
Olivine standards	Mineral standards co-registered with EMPA data	RRUFF Raman spectra	Antarctic samples with published Fa values
Spectral calibration	Typical periodic 520.7 cm <sup>-1</sup> Si wafer	Typical periodic/continuous automatic calibration (0.1 cm <sup>-1</sup> theoretical accuracy)	Ne lamp with every scan
Scan time	30s	20-30s	60s
Sample type	Polished thin sections/polished sections	Polished thin sections/polished sections	Cut surface



Meteorite Name	Weight g	Class	Fa	Fs	Prep	# spots	Peak A	Peak B	σ A	σ B
WSG 95300	3.189	H3.3	1-21	2-17	PS	6	825.0436	857.2207	0.701	1.064
ALHA 81024	1.505	H3.6	3-28	2-24	cut					
ALHA 77259	1.55	H3.7	11-21	15-20	cut					
GTA 90301	1.157	H3.8	1-46	none	chip					
ALHA 77294	2.695	H6	17	15	chip					
ALHA 77258	2.039	H6	19	16	chip					
MBRA 76001	3.442	H6	18	16	cut	7	825.0436	856.9404	1.361	0.774
LEW 86018	3.771	L3.1	7-32	2-9	PS					
GRO 95505	2.968	L3.4	11-26	15-24	PS	8	825.7156	857.7483	0.617	0.908
ALHA 77215	1.28	L3.8	22-26	9-21	chip					
ALH 85033	0.354	L4	22	9-24	chip					
QUE 94570	0.652	L4 (AN)	10-13	2-17	chip					
ALHA 77002	1.469	L5	25	22	cut	8	824.4477	856.5349	1.195	0.829
WIS 91602	1.252	L5	26	21	cut					
ALHA 77270	1.014	L6	24	21	cut					
ALHA 77272	2.554	L6	24	20	cut					
ALHA 81251	3.458	L3.3	1-29	2-29	PS					
ALH 79128	1.687	L3.5	0-39	none	chip					
ALH 77278	1.448	L3.7	11-29	9-21	chip					
QUE 93050	0.705	L4	29	21-25	chip					
EET 87771	0.614	LL5	27	22	cut	5	820.9551	853.4738	0.659	0.763
MIL 99301	1.317	LL6	28	23	cut	10	824.0427	855.5969	0.693	0.501

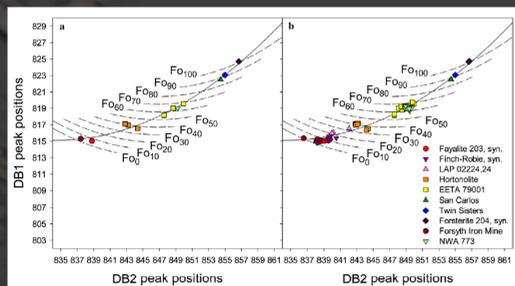


Fig. 1 Two-peak olivine composition curves (best fit parabola) made by projection of positions of a calibration data set. Raman analyses co-registered with EMPA data. Kuebler *et al* (2006)

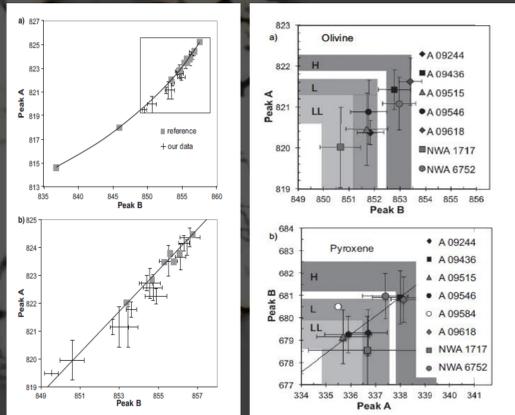


Fig. 2a Two-peak olivine composition curves made from RRUFF standards for olivine over a range of Fa-Fo. Pittarello *et al* (2016)  
Fig. 2b. Calculated range of Raman shift corresponding to H, L, and LL groups. Each point represents 30-50 analyses.

Previous Work: Kuebler *et al* [7] were the first to rigorously demonstrate that olivine compositions (Fa-Fo) could be derived from Raman spectral peak positions (Fig. 1). Pittarello *et al* [16] have shown that ordinary chondrites can be classified by Raman spectroscopy using a similar two-peak approach (Fig. 2a), to include identification of corresponding fields for H, L and LL chondrite classes (Fig. 2b). Data from our effort do not exactly correspond to the olivine compositional curves of either publication, indicating that *individual instrument calibration* of olivine peak position is necessary, along with a standardized instrument calibration technique.



Six Antarctic meteorites of known Fa and Fs were scanned to test the calibration function and to look for trends in wavenumber as a function of class and Fa from previously published Microprobe data. Samples were chosen based on cut surfaces, and represent two examples from each ordinary chondrite class.

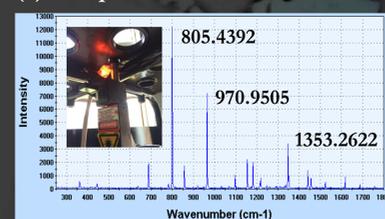
## Real-Time Calibration

Sub-wave number resolution of peak position is necessary. To achieve this, we chose to employ rigid standards of emission line spectra for each spectrum collected. We use three standard neon lines (a) in every spectrum to discern both linear and non-linear spectral shift, as opposed to using a single line from silicon or diamond. We call this **I<sup>3</sup>C- Individual Instrument Instant Calibration**

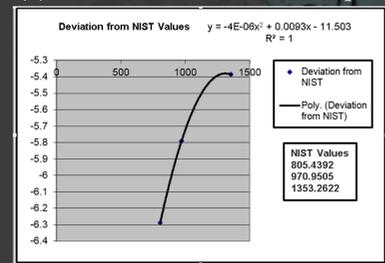
Spectra are calibrated as follows:

1. Peak position of neon lines are found using a Lorentzian fit with GRAMS software. The difference between measured values and NIST standard spectral lines is calculated and used to determine linear and nonlinear miscalibration.
2. The original spectrum is adjusted using a correction formula derived from the measured neon peak positions (b).
3. The olivine lines are fit along with nearby neon lines using the multiple peak fit routine in GRAMS software, using Voigt (mixed Lorentzian/Gaussian) peak profiles (c). This gives us the olivine peak position from which Fa values may then be calculated.

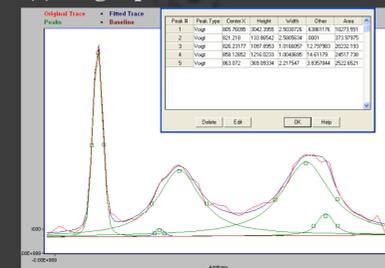
(a) Ne spectra with NIST values



(b) Correction formula from slope

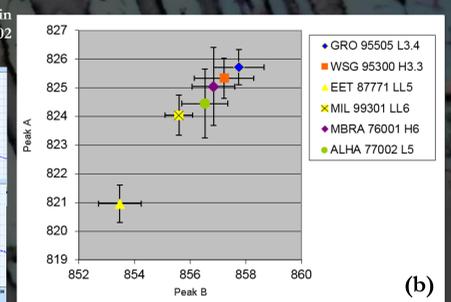
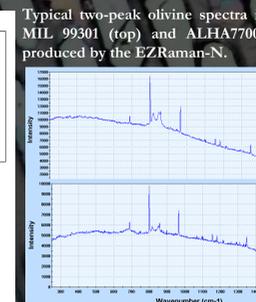
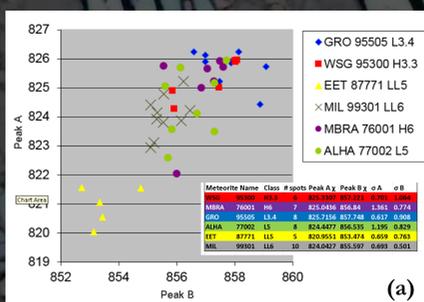


(c) Voigt peak Profiles



## Preliminary Data:

Ten spots were scanned for 60 seconds and 3 integrations each. Focus proved difficult, resulting in 5-8 spectra ideal for peak fitting. Few pyroxene spectra were observed. Wavenumber plots for all peaks are shown in (a). The average wavenumber (b) shows potential cluster of chemical classes, with the exception of GRO, likely due to unequilibrated olivine grains (see spread in (a) and in EMPA data from the table above). The low standard deviation (b)(inset) in Raman shift measurement show that the peak fits are good and that the I<sup>3</sup>C technique is effective.



## Conclusions:

- The I<sup>3</sup>C technique is sound and should be employed for every individual instrument as opposed to the more typical practice of periodic alignment of the spectrometer with a spectral standard.
- Care should be taken when using RRUFF data. We noted shifts between 532 and 785 peaks that could impact calculation of best fit olivine calibration curves.
- Our data are not yet sufficient to calculate the Raman shift that correlates to the compositional range of H, L, LL chondrites. However, based on EMPA classified meteorites, data can be grouped by class.
- The portable Raman analyzer will need automation of spectra collection and/or peak fitting to be a rapid method.
- Samples need to have a ground or at least cut surface with at least a 5mm<sup>2</sup> area.