Sequel to “White paper report for the Nomenclature Committee on the composition of olivine and pyroxene in equilibrated ordinary chondrites.”

Classification of Ordinary Chondrites Based on Mean and Standard Deviation of Fa and Fs contents of Mafic Silicates

Jeff Grossman, 24 April 2011

1) INTRODUCTION

The problem: we have modern methods to assign petrologic types to ordinary chondrites (OCs), but most people still use a 40+ year old method, and don’t even follow that. How do we evaluate this?

Since Dodd et al. (1967) and Van Schmus and Wood (1967), the composition and heterogeneity of olivine and low-Ca pyroxene (henceforth just called pyroxene) have been used to assign OCs into groups, H, L and LL, and to assign petrologic types from 3 to 6. Sears et al. (1980) refined the 1967 methods, and subdivided type 3 into types 3.0-3.9, mainly on the basis of thermoluminescence (TL) sensitivity. Huss et al. (1980) also found that matrix mineral and textural properties correlate with metamorphic grade in type 3s. Grossman and Brearley (2005) further subdivided the lowest part of type 3 into types 3.00-3.15, mainly on the basis of the Cr$_2$O$_3$ content of ferroan olivine. Recent work by Bonal and coworkers uses Raman spectroscopy to assign petrologic types, and Kimura and coworkers use the properties of metal to make further refinements in this area.

Although there are more modern ways to assign OCs to chemical groups (e.g., O isotopes and bulk chemistry), it is still most commonly done using microprobe data on olivine and pyroxene. The earlier White Paper report showed how this should be done for metamorphosed ordinary chondrites, in which the olivine and pyroxene have equilibrated (types 4-6 for olivine, and 5-6 for pyroxene). Although discussed in the 1967 papers, mineralogical trends exist that can be used to assign chemical groups to some unequilibrated chondrites. But these trends are not widely appreciated.

Likewise, although the Sears, Huss, Grossman, Bonal, and Kimura methods have superseded the 1967 methods for assigning petrologic types of unequilibrated OCs, it is still common for classifiers to apply (or attempt to apply) the old methods. Most frequently, classifiers report the mean and standard deviation (σ) of olivine (Fa) and pyroxene (Fs) data, and combine this with some sort of visual “guess” to assign OCs to one of the petrologic subtypes. This practice is complicated by the fact the most of the literature, including the 1967 papers, report the non-standard statistical parameter Percent Mean Deviation (PMD) of the FeO content of olivine and pyroxene, whereas new data are usually reported as mean Fa or Fs ± σ. Here, I will also discuss the proper way to do this kind of classification, based on the 1967 methods, but modified for the use with the modern statistical parameters. This conversion is based on unpublished data from a forthcoming paper by Grossman, Rubin, and Sears (2012).

Note on parameters: PMD is a relative measurement, the average difference of a set of measurements (here, the FeO contents of olivine or pyroxene) from its mean, divided by the mean, and reported as a percentage. The σ-Fa and σ-Fs parameters are absolute errors in the same units as Fa and Fs (mol%).
II) CONVERTING BETWEEN PMD AND SIGMA

One cannot compare data reported as Fa or Fs ± σ to the literature, which uses PMD-FeO, to evaluate petrologic types. In this section, it is shown how to approximate one parameter from the other.

A) Olivine

The Grossman et al. (2012) dataset contains olivine and pyroxene data for 54 OCs of all petrologic types above 3.5. The Dodd et al. (1967) method was used to select random points for analysis, and 100 combined olivine and pyroxene analyses were obtained on each sample. For H chondrites, this means ~50 grains of each mineral were analyzed, and for LL chondrites, ~65 olivine and ~35 pyroxene grains were analyzed (LL chondrites have more modal olivine than H chondrites; L chondrites are intermediate).

Because we have complete probe analyses in this dataset, unlike the 1967 dataset, it is possible to compute all the relevant parameters and intercompare them. In this case, σ-Fa and σ-Fs were computed along with the Dodd parameters PMD-FeO in olivine and pyroxene. For olivine, there is a nearly linear relationship, where the slope is different for H and L+LL chondrites (Fig 1, solid lines). Regression lines have been forced through the origin, although only small intercepts would be present if this was not done. Regression results are:

- L and LL chondrites: \( \sigma\text{-Fa (mol\%)} = 0.45 \cdot \text{PMD-FeO (\%)} \).
- H chondrites: \( \sigma\text{-Fa (mol\%)} = 0.32 \cdot \text{PMD-FeO (\%)} \).

![Figure 1. Relationship between σ-Fa and PMD-FeO for olivine.](image)
But note that these are only calibrated up to PMD-FeO = 25%, although much higher PMD values would be found in the very low-type-3 chondrites that were absent from the Grossman et al. (2012) dataset. A second dataset, based on data for type 3.0-3.4 chondrites in Grossman and Brearley (2005) can be used to estimate what happens at high PMD, although the points selected for analysis in this dataset were not chosen by the Dodd method, leading to possible bias. Thirteen UOCs all had PMD between 52 and 64, and σ-Fa between ~8 and ~12, indicating that the lines in Fig 1. give way to much shallower slopes between their terminations and PMD above 50% (dashed portions of curves).

B) Pyroxene.

The heterogeneity of pyroxene is was also discussed as a classification tool by Dodd et al. (1967), although this parameter is less commonly used. Nevertheless, using the same methods discussed above for olivine, it is possible to calibrate the relationship between the old PMD-FeO in pyroxene statistic and the currently reported σ-Fs statistic. In this case, the Grossman et al. (2012) dataset spans the entire range of PMD-FeO, so it is not necessary to supplement it with data from Grossman and Brearley (2005). Figure 2 shows the calibration curves, which have been fit with a 3rd order polynomial, giving the following fits:

L and LL chondrites: $\sigma$-Fs (mol%) = $5.17 \times 10^{-5} \cdot \text{PMD}^3 - 7.13 \times 10^{-3} \cdot \text{PMD}^2 + 0.382 \cdot \text{PMD}$.

H chondrites: $\sigma$-Fs (mol%) = $-4.12 \times 10^{-6} \cdot \text{PMD}^3 - 2.08 \times 10^{-3} \cdot \text{PMD}^2 + 0.260 \cdot \text{PMD}$.

Figure 2. Relationship between $\sigma$-Fs and PMD-FeO for low-Ca pyroxene.

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1 The Dodd method is: “Points were selected ... by traversing in 500 μm steps along traverses 1000 μm apart. Smaller intervals were used for small samples, in order to obtain about 100 olivine measurements and a comparable number of pyroxene measurements in each sample. A single measurement ... was made at each grid point. If there was no silicate grain at a point, or if there was a visible imperfection (inclusion, crack, or grain boundary) at the point, the sample was moved as much as 20 μm to reach a silicate grain. Where this was necessary, the sample was repositioned randomly to avoid biasing the data in favor of grain margins or centers. If there was no silicate grain within 20 μm of a grid point, the point was omitted.” Note that many analysts prefer to analyze the cores of large olivine grains, which can lead to very different results for unequilibrated chondrites.
III) The “traditional” classification scheme, recalibrated for sigma.

Huss et al. (2004) summarized the 1967 classification scheme for petrologic types, as modified by the work of Sears (1980) and subsequent papers, all calculated using PMD parameters. The Table 1 presents the Huss et al summary, and applies the relationships derived in section II.

Table 1: Traditional classification scheme for OCs based on PMD parameters, updated to show $\sigma$-Fa and $\sigma$-Fs. Dashed horizontal lines represent approximate boundaries.

<table>
<thead>
<tr>
<th>Pet type</th>
<th>OLIVINE</th>
<th>LOW-CA PYROXENE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PMD-FeO-ol (old scheme)</td>
<td>$\sigma$-Fa (mol %) [H] (new)</td>
</tr>
<tr>
<td>3.0</td>
<td>&gt;33</td>
<td>&gt;9</td>
</tr>
<tr>
<td>3.1</td>
<td></td>
<td></td>
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<tr>
<td>3.2</td>
<td></td>
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<td>3.3</td>
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<tr>
<td>3.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>15-33</td>
<td>5-9</td>
</tr>
<tr>
<td>3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>5-15</td>
<td>1.6-5</td>
</tr>
<tr>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>&lt;5</td>
<td>&lt;1.6</td>
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<td>6</td>
<td></td>
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</tr>
</tbody>
</table>

Important note #1: The only solid horizontal line in Table 1, i.e., the only definitive boundary, corresponds to the definition that type 3 chondrites have PMD-FeO in olivine above 5. This is still the definition of type 3 used for OCs today. This boundary corresponds to $\sigma \approx 2$ mol% Fa in all three OC groups.

Important note #2: It is impossible to tell the difference between subtypes 3.0-3.4 based on iron heterogeneity in olivine and pyroxene. There is also little textural difference between these types.

Important note #3: Little research has been done on the relationship between pyroxene heterogeneity and metamorphic grade. The most important thing to observe in the right half of Table 1 is that pyroxene does not become homogeneous until petrologic type 5. Although some OCs classified as type 4 do have fairly homogeneous pyroxene, many do not.

IV) Changes in mean FeO content of silicates as they equilibrate.

Dodd et al. (1967) showed that there was a correlation between the heterogeneity of olivine and pyroxene, as measured by the PMD parameter, and the mean compositions of those phases, as measured by either the absolute Fe content or the calculated Fa/Fs component of the phase. In each group, H, L and LL, specimens that have highly heterogeneous olivine or pyroxene (i.e., PMD > 30), also have relatively low mean Fa or Fs, and differences between the chemical groups are small. Within groups and for each mineral, as PMD decreases toward 0, the iron content increases toward the equilibrium value (i.e., that seen in type 5 and 6 specimens).

Despite the fact that these relationships have been known for >40 years, few workers make use of them. Yet, for unequilibrated chondrites, the only way to attempt to assign a specimen to a chemical group based on iron contents of silicates is by analysis of these correlations. Part of the problem is that Dodd et al. (1967) never
made good plots of their own data, so this is done now, again transforming their PMD data to \( \sigma \) using the relationships in section II (Figs. 3a,b).

Figure 3a. Re-casting of olivine data from Dodd et al. (1967). \( \sigma \)-Fa has been estimated from PMD-FeO using relationships in section II. Modern classifications (which may still be inaccurate!) have been substituted for those used in the 1967 paper. Typical ranges for Fa in equilibrated chondrites (see earlier White Paper) are shown as solid, colored bars along the abscissa.

For olivine, Fig. 3a shows that the highly unequilibrated OCs, with \( \sigma \)-Fa > 9, corresponding to PMD > 30, generally corresponding to modern subtypes \( \leq 3.4 \), are indistinguishable from one another, regardless of chemical group (which, of course, may be uncertain). The H chondrite data are noisy, and there is actually no
evidence of any change in mean Fa during equilibration. However, there are very few known highly unequilibrated H chondrites: Dodd only analyzed Tieschitz and Sharps, and the former is now classified as H/L. L and LL chondrites do show a clear increase in mean Fa as σ-Fa decreases. Where σ-Fa is below 6-7, mean Fa is within the range shown by equilibrated members of the group.

Pyroxene trends in Fig. 3b are better defined than olivine trends. All type 3 chondrites have σ-Fs > 5, type 4 chondrites range from σ-Fs < 1 to ~5, and four of five type 5/6 chondrites have σ-Fs < 0.5. Changes in mean Fs are gradual and well-defined, as σ-Fs falls through types 3 and 4. Similar to the case with olivine, it is not possible to distinguish H from L or LL where σ-Fs is above ~7.5. Mean Fs does not rise to the equilibrated value in any group until σ-Fs falls below ~2. The group may be inferred from meteorites with σ-Fs between 2 and 7.5 by interpolation along the dashed curves in Fig. 3b, although L and LL are not well-resolved from each other, possibly because of the paucity of LL points along much of the range.

V) Applications to Nomenclature Committee Submissions.

*Type 5 and 6 OCs.* Most often, meteorites are submitted with only mean Fa and Fs values, and an assertion that the samples are type 5 or 6. Because the normal way of telling the difference between types 4 / 5 and 5 / 6 are petrographic in nature (disappearance of monoclinic low-Ca pyroxene and coarsening of feldspar, respectively, combined with the sharpness of chondrule boundaries), these submissions are fine as long as Fa and Fs are within the ranges stated in the earlier White Paper report. If, however, sigmas are reported with Fa and Fs, they should be low, as listed in Table 1. If they are high, something is amiss.

*Type 4 OCs.* Type 4s are confusing, and were confusing to Van Schmus and Wood (1967), attempting to summarize Dodd et al. (1967)’s data. In the text, they say,

> Petrologic type 4 is defined by relatively ambiguous characteristics. This type represents the transition between the extremely variable chondrites and the uniform ones. As a result, many of the characteristics are not too explicit, having a wide range. These characteristics are: well-defined chondrules with a tendency toward noticeable recrystallization; igneous glass (turbid, birefringent) may be present; olivine and pyroxene are usually uniform in composition but may be variable to about 5% mean deviation; clinopyroxene is usually more abundant than orthopyroxene (it is always a major constituent); and low carbon contents. Of these properties, the presence of major amounts of clinopyroxene (approximately 20% of total pyroxene) is the most important and has been used in the absence of a diagnostic choice based on the other criteria in order to separate type 4 chondrites from type 5 chondrites.

They misread Dodd’s paper, in saying that type 4 chondrites have homogeneous pyroxene. As shown in the present report, type 4 chondrites have homogeneous Fa content of olivine, but pyroxene shows a wide range, from highly unequilibrated (σ-Fs around 5 mol%, or PMD of 20-30%; e.g., Barratta), to nearly homogeneous (σ-Fs < 0.5, or PMD < 1; e.g., Weston). In practice, a chondrite with homogeneous olivine and heterogeneous pyroxene is almost certainly type 4. But if both phases are equilibrated, the only way to demonstrate that a chondrite is type 4 is by structural analysis of the pyroxene, as explained in the Van Schmus and Wood quote above.
Type 4 chondrites can be accurately placed in groups based on mean Fa content, as is done with types 5 and 6. Mean Fs content will be lower than equilibrated group averages in specimens with heterogeneous pyroxene, but will plot on Fig. 3b along well-defined curves.

**Type 3 OCs.** The difference between type 3 and 4 is, by definition, marked by the homogenization of iron contents of olivine: PMD of FeO in olivine of 5%, corresponding to $\sigma$-Fa as shown in Table 1, forms the boundary. Pyroxene is always heterogeneous in type 3 OCs. Petrologic subtypes may be crudely estimated from olivine heterogeneity, as shown in Table 1, but the resolution is poor, and types 3.0-3.4 cannot be differentiated. Once homogenization of olivine begins, i.e., in subtypes $>3.4$ with $\sigma$-Fa below 6-7, classification into chemical groups is possible from mean Fa contents.

**VI) Final notes.**

*How many points do you have to analyze?* One cannot evaluate data for the mean and standard deviation of olivine and pyroxene data without knowing how many points were analyzed. If one is using an analytical method with good precision, then the uncertainty on a parameter like $\sigma$-Fa is $1/\sqrt{2N}$. Thus for $N=8$, $\sigma$-Fa is accurate within only ±25% relative. For $N=50$, $\sigma$-Fa should be known to within ±10%. If one is attempting to decide whether a borderline meteorite is type 3 or 4 based on $\sigma$-Fa, it makes sense to analyze $>30$ points. But for equilibrated chondrites, $\sigma$-Fa or -Fs are not important to know with great accuracy, so fewer points will suffice to determine the mean Fa/Fs values well enough to classify the meteorites.

*How important is it to use the Dodd et al. (1967) method?* For type 3 chondrites, it is VERY important!!! The Dodd method does not analyze cores or rims of grains preferentially. During metamorphism, the cores of large grains, especially forsterite and enstatite, are the last areas to equilibrate. If one is biased towards analyzing the centers of large, clear grains, partially equilibrated chondrites will appear much more heterogeneous than they actually are. Note also that the Dodd method is based on 1960s electron microprobe techniques. Tiny grains of olivine and pyroxene, such as might be present in chondrite matrix, could not be analyzed. Data taken using modern probes with FE guns, which may have higher spatial resolution, must exclude grains smaller than a few micrometers in size, or the results may not be comparable to literature data, such as are presented in this report.