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Determination of Mineral Abundances in Ordinary Chondrites Using Powder X-ray Diffraction:
Applications to Parent Body Processes and Asteroid Spectroscopy

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Degree
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DEDICATION

This is for the individuals who have dedicated their lives to the teaching of others.

You have all given me my most prized possession – my education.

For that, I thank you.

For the faculty and staff of:

Hendrix Drive Elementary (1983-1989),

Forest Park Middle School (1989-1992),

and

Forest Park High School (1992-1996)

“We think of the effective teachers we have had over the years with a sense of recognition, but those who have touched our humanity we remember with a deep sense of gratitude.”

- Anonymous student

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ABSTRACT

The ordinary chondrites, the most abundant group of meteorites, are divided into three chemical groups (H, L, and LL), which are distinguished based on variations in bulk composition and iron content. Although ordinary chondrites are relatively abundant, our understanding of their formation has been hampered by an inability to accurately measure the abundances of minerals that they contain. Here I use power x-ray diffraction (XRD) to quantify the modal abundances of 48 unbrecciated ordinary chondrite falls, which represent the complete petrologic range of equilibrated ordinary chondrites (types 4-6).

Although the degree of metamorphism varies within each ordinary chondrite group, many details regarding the geochemical and thermal changes that take place during this process are not well understood. Using XRD-measured modal mineral abundances and chemical analyses, we evaluate the redox state and peak metamorphic temperatures in ordinary chondrite parent bodies in order to develop quantitative thermal evolution models of ordinary chondrite parent asteroids. Modal abundances and mineral compositions measured in this study indicate that progressive oxidation of the ordinary chondrites likely occurred during metamorphism. Results also suggest that plagioclase crystallizes early in the metamorphic sequence, indicating that peak temperatures derived using the two-pyroxene geothermometer are more accurate than those calculated using the plagioclase geothermometer.

I also utilize ordinary chondrite modal abundances to develop new calibrations for deriving mineralogy from meteorite and asteroid spectra. Most previous studies examining the mineralogical characteristics of VISNIR asteroid spectra have focused on olivine and pyroxene proportions in single-pyroxene mixtures; therefore, current calibrations for deriving composition mineral abundances may be poorly suited for asteroids containing more than one pyroxene. It is

important that calibrations are correct, because mineral abundances derived from visible/near-infrared (VISNIR) spectra are used to classify asteroids, identify meteorite parent bodies, and understand the structure of the asteroid belt. Mineral abundances derived using my calibrations correlate well with measured data for all ordinary chondrites groups, and also appear to be valid for other meteorites and asteroids with mineral abundances and chemistries similar to those of the ordinary chondrites.

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PART I

INTRODUCTION

1. OVERVIEW

The ordinary chondrites are the most abundant group of meteorites, representing 80% of meteorite falls. Ordinary chondrites are divided into three chemical groups (H, L, and LL), which are distinguished based on variations in bulk composition, such as molecular ratios ($\text{FeO}/\text{FeO}+\text{MgO}$) in olivine and pyroxene (Mason 1963; Keil and Fredriksson 1964) and the ratio of metallic Fe to total Fe (Dodd et al. 1967). In addition to differences in bulk chemistry, textural variations and corresponding mineral and chemical trends present within each chemical group have been interpreted as evidence of different degrees of thermal metamorphism (Van Schmus and Wood 1967). Based on these variations, Van Schmus and Wood (1967) developed a petrologic classification scheme for ordinary chondrites consisting of petrologic types 3-6, each representing differing degrees of metamorphism. Type 3 (unequilibrated) ordinary chondrites are relatively unaltered or have experienced very slight heating, while type 6 (equilibrated) chondrites have undergone the highest degrees of thermal metamorphism (Van Schmus and Wood 1967; McSween et al. 1988).

Chondrites are distinguished from nonchondritic meteorites based on their primitive compositions and the presence of chondrules, spherical droplets of material that condensed from the solar nebula within a few million years of its formation. As some of the oldest material in the solar system, chondrules (and the chondrites in which they are found) contain the only tangible record of early solar system processes and conditions. Although ordinary chondrites are relatively abundant, our understanding of their formation has been hampered by an inability to accurately measure the abundances of minerals that they contain. In this dissertation, I attempt to resolve this problem by quantifying the mineral abundances of 48 ordinary chondrite samples, which represent the complete petrologic range of equilibrated

ordinary chondrites (types 4-6). The method for quantifying ordinary chondrite mineral abundances is presented in Part II, along with all the data referenced in subsequent parts. These mineral abundances are applied to questions regarding the geochemical evolution of the ordinary chondrite parent bodies in Part III, and are used to develop calibrations for deriving mineral abundances and chemistries from reflectance spectra of asteroids in Part IV.

This dissertation consists of four parts, three of which are publishable papers to be submitted to Meteoritics and Planetary Science. Part II of this dissertation, entitled “Analysis of ordinary chondrites using position sensitive X-ray diffraction: 1. Modal mineral abundances,” was prepared in conjunction with co-authors Gordon Cressey, Hap McSween, and Tim McCoy. Gordon Cressey provided assistance in collection and preliminary analysis of X-ray diffraction data, while Hap McSween and Tim McCoy offered thoughtful comments and suggestions in the final preparation of the manuscript. Part III, which was co-authored by the same three individuals, is a companion paper to Part II, entitled “Analysis of ordinary chondrites using position sensitive X-ray diffraction: Applications to parent body processes.” The final part of this dissertation is a paper entitled “Spectroscopic calibrations for ordinary chondrites and their parent asteroids.” This paper was co-authored by Hap McSween, Tim McCoy, and Tom Burbine. Hap McSween and Tim McCoy provided editorial comments and suggestions, and Tom Burbine acquired reflectance spectra for a large number of ordinary chondrites analyzed in this study.

2. ANALYSIS OF ORDINARY CHONDRITES USING POWDER X-RAY DIFFRACTION: 1. MODAL MINERAL ABUNDANCES (PART II)

Modal mineralogy is traditionally determined using optical point counting. Although it is an established technique, optical point counting is better suited for samples that contain large grains, because small grains are difficult to identify. In an attempt to accurately quantify

chondrite abundances, Bland et al. (2005) applied position-sensitive X-ray diffraction to several carbonaceous chondrites. This technique, developed by Cressey and Schofield (1996), differs from traditional XRD in that it uses a position-sensitive detector (PSD), which enables diffraction patterns to be collected simultaneously at all angles over a 120° arc. Accurate phase quantification can be carried out on patterns acquired in as little as 5 minutes (Cressey and Batchelder 1998); however, longer counts times are required for complex multiphase mixtures. Using PSD-XRD, well crystalline phases can often be detected at abundances as low as 1 wt%. The accuracy of the technique depends on several factors, the most significant of which is standard matching. Bland et al. (2004) suggested phase abundances can be determined within an accuracy of ~1 vol%, provided well matched standards are available.

The PSD-XRD technique was first applied to quantification of ordinary chondrite mineral abundances by Menzies et al. (2005), who determined the modes of six unequilibrated (relatively unaltered) type 3 ordinary chondrites and three equilibrated (thermally metamorphosed) type 4-6 ordinary chondrites. The success of the Menzies et al. (2005) study indicated that the PSD-XRD technique could be used to determine ordinary chondrite mineralogies on a much larger scale.

In Part II of this dissertation, I apply the PSD-XRD technique to 48 equilibrated ordinary chondrites and compare my results to modal and normative ordinary chondrite abundances determined in previous studies (e.g. Gastineau-Lyons et al. 2002, McSween et al. 1991). Part II is a comprehensive discussion of the XRD method - its limitations, and its accuracy - and contains all the data that are applied in current problems in planetary science in Parts III and IV.

3. ANALYSIS OF ORDINARY CHONDRITES USING POWDER X-RAY DIFFRACTION: 2. APPLICATIONS TO PARENT BODY PROCESSES (PART III)

Although the degree of metamorphism varies within each ordinary chondrite group (Van Schmus and Wood 1967; McSween et al. 1988), many details regarding the geochemical and thermal changes that take place during this process are not well understood. Part II of this dissertation addresses two long-standing questions have hindered our understanding of thermal metamorphism in the parent bodies of ordinary chondrites:

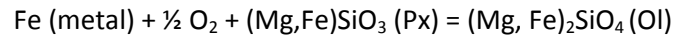
1. Does oxidation or reduction occur during progressive metamorphism in equilibrated ordinary chondrites?
2. What geothermometer is better-suited to constrain peak metamorphic temperatures in type 6 H, L, and LL ordinary chondrites?

Both of these questions must be resolved in order to develop quantitative thermal evolution models of ordinary chondrite parent asteroids. Redox state has important implications for understanding metamorphic conditions and fluid-rock interactions, and peak metamorphic temperatures (along with cooling rates and duration of heating) are critical input parameters in thermal calculations (McSween et al. 2002).

3.1. Redox State Variations

Along with bulk iron content, the oxidation state of iron varies systematically between ordinary chondrite groups, decreasing from LL to L to H. Chemical evidence, including intragroup variations in mean olivine Fa and low-Ca pyroxene Fs contents (McSween and Labotka 1993; Rubin 1990) and average Co and Ni concentrations in kamacite (Rubin 1990), suggest that oxidation state also changes within each chondrite group. McSween and Labotka (1993) linked these intragroup variations to metamorphic grade and suggested that equilibrated

ordinary chondrites were progressively oxidized during metamorphism, resulting in the following reaction.



Because olivine forms at the expense of pyroxene in this reaction, changes should occur in the relative proportions of olivine and low-Ca pyroxene (with increasing petrologic type). Systematic changes in the abundances of olivine and low-Ca pyroxene have been observed in CIPW norms McSween et al. (1991) calculated from bulk chemistries (Jarosewich 1990) and in modal abundances of a few chondrites (Gastineau-Lyons et al. 2002; Menzies et al. 2005). However, because modal abundances of ordinary chondrites have been difficult to quantify until now, previous studies are limited and may be unrepresentative. Using XRD-measured mineralogies and silicate mineral chemistries, I re-examine the question of intragroup redox state variations in the equilibrated ordinary chondrites in the first section of Part III.

3.2. Peak Temperature Estimates

Peak temperatures are determined by applying geothermometers to those chondrites that have experienced the highest degree of metamorphism (type 6). Because numerous geothermometers have been used to determine peak temperatures, current estimates for type 6 H, L, and LL chondrites range over several hundred degrees. The most common geothermometer used to determine peak metamorphic temperatures in ordinary chondrites is a two-pyroxene geothermometer, which is based on Ca partitioning between low-Ca and high-Ca pyroxene (Kretz 1982; Lindsley 1983).

As an alternative to pyroxene thermometry, Nakamuta and Motomura (1999) applied a plagioclase geothermometer, based on Si-Al ordering, to type 6 H, L, and LL ordinary chondrites. Peak temperatures estimated using the plagioclase geothermometer are lower than those

determined in previous studies using the two-pyroxene geothermometer (e.g. Olsen and Bunch 1984; McSween and Patchen 1989; Jones 1997), and are only valid if plagioclase continued to crystallize from chondrule glass through type 6 conditions. Petrologic observations used to develop the Van Schmus and Wood (1967) classification system suggest that all chondrule glass is crystallized to plagioclase by type 5 conditions, whereas previous investigations (Gastineau-Lyons et al. 2002) have suggested that plagioclase crystallization is complete by type 5 in LL chondrites and by type 6 in L chondrites.

The question of which geothermometer yields the most accurate peak temperatures can be addressed by determining the metamorphic grade at which plagioclase completely crystallizes, and I do so in Part III using XRD-measured and normative plagioclase abundances (calculated by McSween et al. 1991). Peak temperatures in several type 6 ordinary chondrites, which are calculated using the pyroxene geothermometer, are also presented in this section of Part III.

4. SPECTROSCOPIC CALIBRATIONS FOR ORDINARY CHONDRITES AND THEIR PARENT ASTEROIDS (PART IV)

One of the primary goals of asteroid spectroscopy is to determine compositions of asteroids using reflectance spectra. This is possible because ferromagnesian minerals commonly found in meteorites have diagnostic visible/near-infrared spectral properties that can be used for identification. Olivine and pyroxene are the two primary components of ordinary chondrites and are found extensively in many types of achondrites. Because of their abundance in extraterrestrial rocks, the spectral properties of these two minerals have been extensively studied (i.e. Adams 1975; Cloutis 1985; Cloutis and Gaffey 1991). In reflectance spectra, Band I

(~1- μm) and Band II (~2- μm) are sensitive to the relative proportions and compositions of olivine and pyroxene.

Existing calibrations for deriving mineral abundances (Cloutis et al. 1986) and silicate mineral compositions (Gaffey et al. 2002) from VISNIR spectra have focused on olivine and pyroxene proportions in single-pyroxene mixtures; therefore, current calibrations are poorly suited for asteroids containing more than one pyroxene. The ordinary chondrites, which consist of olivine, low-Ca pyroxene, and high-Ca pyroxene, would serve as an excellent suite for deriving new spectral calibrations for such asteroids, and these calibrations should yield more accurate mineralogical interpretations of asteroid spectra.

New calibrations for determining mineral abundances from reflectance spectra are presented in Part IV of this dissertation, along with a discussion of the applicability of these calibrations to different asteroid mineralogies, and a reexamination of the spectral classification for the S(IV) asteroids.

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PART II

ANALYSIS OF ORDINARY CHONDRITES USING POWDER X-RAY DIFFRACTION:

1. MODAL MINERAL ABUNDANCES

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Dunn T.L., Cressey G., McSween H.Y. Jr., and McCoy T.J. Analysis of ordinary chondrites using powder X-Ray diffraction: 1. Modal mineral abundances.

ABSTRACT

Powder X-ray diffraction is used to quantify the modal abundances (in wt%) of 18 H, 17 L, and 13 LL unbrecciated ordinary chondrite falls, which represent the complete petrologic range of equilibrated ordinary chondrites (types 4-6). The XRD technique presents an effective alternative to traditional methods for determining modal abundances, such as optical point counting and electron microprobe phase mapping. The majority of chondrite powders in this study were previously prepared for chemical characterization from 8 – 20 g of material, which is consistent with the suggested mass (10 g) necessary to provide representative sampling of ordinary chondrites. Olivine and low-Ca pyroxene are the most abundant phases present, comprising one-half to three-fourths of total abundances, while plagioclase, high-Ca pyroxene, troilite, and metal comprise the remaining XRD-measured mineralogy. XRD-measured abundances of primary phases (i.e. olivine and pyroxene) compare well with calculated normative abundances, with modal olivine and low-Ca pyroxene within 5.0 wt% and plagioclase within 2.0 wt% of normative values. Modal diopside abundances, however, are systematically higher than normative abundances by 1.0-5.0 wt%. Olivine compositions calculated from XRD fittings agree well with the range of measured olivine compositions in ordinary chondrites, although total wt% Fe calculated from fluorescence backgrounds of XRD patterns are typically lower than measured values, especially in the H chondrites. With the exception of Ca/Si, elemental ratios calculated from XRD-derived compositions are comparable to elemental ratios

of measured bulk chemistries, supporting the hypothesis that XRD-measured modal abundances represent realistic ordinary chondrite mineralogies.

1. INTRODUCTION

Ordinary chondrites are not only the most abundant type of meteorite (representing more than 80% of all observed falls), but are also among the solar system's most primitive material. Most aspects of these meteorites have been thoroughly characterized, from bulk chemical (Kallemeyn et al. 1989; Jarosewich 1991) and isotopic compositions (Clayton et al. 1991) to mineral chemistry (e.g. Keil and Fredriksson 1964; Rubin 1990) and metamorphic petrology (Van Schmus and Wood 1967; Dodd 1969; McSween et al. 1988). However, our understanding of ordinary chondrite formation and parent body processes has been hampered by an inability to determine precise abundances of the minerals that comprise them. Few credible determinations of phase abundances in ordinary chondrites exist because of the difficulty associated with quantifying modal abundances of fine-grained samples.

Modal mineralogy is traditionally determined using optical point counting. Although it is an established technique, optical point counting is better suited for samples that contain large grains, as small grains are difficult to identify. An energy dispersive spectrometer (EDS) phase mapping technique (Taylor et al. 1996), which detects, measures, and analyzes phases present in a backscattered electron image has been applied to ordinary chondrites (Gastineau-Lyons et al. 2002). The EDS phase-mapping technique with the electron microprobe is well-suited for determining the modal abundances of 2D slices of material (i.e. thin sections) at a precision that is user-dependent. Such 2D slices, however, may not be representative of entire samples. This phase-mapping method is typically time-consuming (6-8 hrs.), particularly if multiple determinations are required. Quantification of a large number of modal abundances may be

better accomplished using a less time-consuming method, which measures a more representative sample of the bulk material.

In an attempt to accurately quantify chondrite modal abundances, Bland et al. (2005) applied a new powder X-ray diffraction method to several carbonaceous chondrites. This technique, developed by Cressey and Schofield (1996), differs from traditional XRD in that it uses a position-sensitive detector (PSD), which enables diffraction patterns to be collected simultaneously at all angles over a 120° arc. Accurate phase quantification can be carried out on patterns acquired in as little as 5 minutes (Cressey and Batchelder 1998); however, longer counts times are required for complex multiphase mixtures. Well crystalline phases can often be detected at abundances as low as 1 wt%. The accuracy of the technique depends on several factors, the most significant of which is standard matching. Bland et al. (2004) suggested phase abundances can be determined within an accuracy of ~1 vol%, provided well matched standards are available.

This powder XRD technique was first applied to quantification of ordinary chondrite modal abundances by Menzies et al. (2005), who determined the modes of six unequilibrated (relatively unaltered) type 3 ordinary chondrites and three equilibrated (thermally metamorphosed) type 4-6 ordinary chondrites (Van Schmus and Wood 1967). The success of the Menzies et al. (2005) study indicated that powder XRD could be used to determine ordinary chondrite modal mineralogies on a much larger scale. In this study we use powder X-ray diffraction to quantify the modal abundances of 18 H, 17 L, and 13 LL ordinary chondrite samples, representing the complete petrologic range of equilibrated ordinary chondrites (types 4-6). We introduce this technique, report the modal abundances of all 48 ordinary chondrite

samples, and compare our results to modal and normative ordinary chondrite abundances determined in previous studies (e.g. Gastineau-Lyons et al. 2002; McSween et al. 1991).

2.0 METHODOLOGY

2.1. X-ray Diffraction

XRD data were collected using an INEL curved position-sensitive detector (PSD) at the Natural History Museum in London. With this PSD, diffracted intensity is measured simultaneously at all angles, around an arc of approximately 120° 2θ , resulting in rapid data collection. The angular range was calibrated using NIST silicon (SRM640) standard powder and the linearization of the detector was performed using a least-squares cubic spline function, resulting in an output array of 4017 channels each of 0.031° 2θ . Experimental configurations in this study are similar to those implemented by Bland et al. (2004) and Menzies et al. (2005). Samples were radiated using $\text{CuK}\alpha 1$ radiation, which was selected from the primary beam using a single-crystal Ge111 monochromator. Post-monochromator slits were used to restrict the beam size to 0.24×3.0 mm. Diffraction patterns were recorded in reflection geometry from the sample smear surface, which was set at an angle 7.5° to the incident beam. Because the detector remains fixed, the only movement is the sample itself, which spins slowly in its own plane. The absence of movement allows for very precise reproducibility of geometry from one sample to the next.

This powder method for quantification of multi-phase samples was first introduced by Cressey and Schofield (1996), further developed by Batchelder and Cressey (1998), and first applied to meteorites by Bland et al. (2004) and Menzies et al. (2005). These studies suggest that powder XRD can accurately quantify modal abundances of a variety of mineralogies, including those of complex extraterrestrial samples. In the procedure developed by Cressey and

Schofield (1996), modal abundances are determined by fitting peak intensities of a mineral standard to those present in a mixture. The intensity of the whole-pattern standard phase is decreased by a factor to match the intensity of that phase in the mixture and then subtracted, effectively removing that component from the mixture pattern. This procedure is repeated until all phases have been removed. The percentages of phases determined by this technique are termed “percentages of fit.”

In previous studies (e.g. Bland et al. 2004; Menzies et al. 2005) an ideal fit (i.e. all phases are accounted for) was indicated by a total fit of 100%, because the irradiated volumes of sample and standard phases were identical. This is not the case in this study, because the amount of chondrite powder available was insufficient to fill 1mm deep wells, which requires 180 mm³ of material. Instead, diffraction patterns of the chondrites in this study were recorded from thin smears, which require only 1-2 mm³ of material, while standard patterns were determined from powders in 1 mm-deep wells. As a result, the irradiated volume of the samples is less than that of the standards, and consequently a 100% total fit is not achieved, even after all standard phases have been subtracted. This does not present a problem because the fitting procedure actually measures ratios of phases present in a sample, and therefore the volume of the standards and the volume of the sample need not be equal. However, the standard patterns must form an internally-consistent data set with correct whole-pattern intensities relative to each other. This was achieved by recording the standards under identical conditions in the same volume deep well mounts. Since fitting each sample with the standard patterns determines the relative proportions of phases present, the fit proportions can simply be normalized to 100% after the total fit has been performed. Total fits vary among samples as a result of small differences between sample volumes, which cannot be avoided when preparing

thin smears. Because the sum of each sample's percentage of fit is unknown prior to fitting, a degree of uncertainty is added to the fitting procedure. The accuracy of each fit can be confirmed by examining residual XRD patterns, which should have near-zero residual counts.

Actual weight percentages of each mineral present are determined by correcting for the deadtime of the detector and for the mass absorption coefficient (μ/ρ). The deadtime correction is made by applying a multiplication factor of $100/(100-x)$, where x is the percent deadtime. The mass absorption coefficient is different for each mineral (Cressey and Batchelder 1998). Minerals with low absorption, such as plagioclase, when in a mixture with higher-absorbing phases, will be underestimated by the fit relative to its actual wt%. Conversely, minerals with high absorption (e.g. forsterite-rich olivine) will be overestimated by the fit. Using compositional data, the mass absorption coefficient for each mineral was calculated from the weighted average of the mass absorption coefficients of its constituent elements, from values given in *International Tables for X-Ray Crystallography*. Using the pattern-fit fraction of a single phase and the calculated mass absorption coefficients for each mineral in the mixture, the actual weight percent of each mineral can be determined (Batchelder and Cressey 1998). Weight percentages can be converted to volume percents if the density of each mineral phase is known. In this study all results are presented in weight percent to allow for comparison with previously calculated normative and measured modal abundances (McSween et al. 1991 and Gastineau-Lyons et al. 2002, respectively).

The detection limits for any particular phase will depend on many factors, such as the scattering power for X-rays (i.e. whether the phase is a good diffractor or not), the state and perfection of its crystallinity, the particle size, the total matrix absorption characteristics. For well crystalline phases these can often be detected and quantified at the 0.5 to 1% level. For

the final quantification results, structural inhomogeneities, the degree of near-matching of standards and any uncertainties in the assumed phase chemistries (leading to errors in the applied absorption corrections), will lead to compounded errors. However, blind tests on known mixtures and exact-match standards (e.g. the international round robin commissioned by the International Union of Crystallography, Madsen 1999, Madsen et. al 2001) demonstrated that powder XRD method yields quantitative results to within ~1% of the actual proportions. Many other complex multiphase mixtures have now been quantified at the Natural History Museum in London using the this method, and in such cases (where less-perfect, but near-matching of standards was achieved) the phase quantification results obtained are commonly within 2-3% of the actual values present. This situation can always be improved, given time, as a more comprehensive choice of standards are sought and characterized.

2.2. Samples

A total of forty-eight ordinary chondrite samples representing each of the ordinary chondrites groups (H, L, and LL) and petrologic categories 4-6 (Van Schmus and Wood 1967) were selected for analysis (Table 2.1). (All Tables and Figures are located in Appendix I.) Unequilibrated (type 3) chondrites are not included in this study, as modal abundances of type 3 chondrites were determined using PSD-XRD by Menzies et al. (2005), who examined the issue of redox state in the unequilibrated ordinary chondrites. All samples selected for analysis are unbrecciated falls with minimal terrestrial weathering. Unbrecciated meteorites were chosen to minimize the chance of analyzing monomict breccias (containing more than one petrologic type of the same group). Representative powders of thirty-seven of these samples were originally prepared for bulk chemical analysis by E. Jarosewich as part of the Smithsonian Institution's Analyzed Meteorite Powder Collection (chemical analyses published by Jarosewich 1990). Small

chips (0.1 – 0.5 g) of the remaining eleven chondrites were acquired from the Natural History Museum in London and the Smithsonian Institution. Samples obtained from the NHM were powdered on-site by museum personnel, while samples from the Smithsonian Institution were prepared for analysis at the University of Tennessee. These samples were ground with mortar and pestle to an approximate grain size of 35 μm . This grain size is necessary to provide a smooth surface for XRD experiments, which is important for minimizing preferred orientation effects and microabsorption (beam attenuation due to surface roughness), as demonstrated by Cressey and Batchelder (1998).

The presence of Fe-Ni metal in a sample can hinder XRD analyses because it tends to sink into less dense silicate material during sample preparation (Menzies et al. 2004). As a result, XRD-derived metal abundances may not represent the actual abundance of metal in a sample. To resolve this problem, Menzies et al. (2004) magnetically separated metal from the silicate portion of each powdered meteorite sample prior to analysis and weighed both fractions to determine the wt% metal present. XRD-derived silicate abundances were then re-proportioned to account for amount of metal in a given sample. Fe-Ni metal in most samples analyzed in this study was removed and weighed by E. Jarosewich (1990) prior to our acquisition of the samples. In all other samples, Fe-Ni metal was removed magnetically and weighed following procedures outlined by Menzies et al. (2004).

Powdered samples were analyzed on a single-crystal quartz substrate cut at an angle to prevent Bragg reflection, resulting in “zero background.” Using this substrate, diffraction patterns can be obtained from very small sample volumes if necessary. Immediately prior to analyses, a portion of each powdered sample was placed on the substrate and a drop of acetone was added to allow the sample to be spread in situ with a needle point to form a thin smear of

uniform thickness (approximately 30-40 μm). Acetone, which quickly evaporates, does not contaminate the sample or alter the XRD pattern. After preparation, most samples acquired counts for 60 minutes. A few samples were analyzed overnight, acquiring counts for a total of 600 minutes. Although accurate phase quantification can be carried out on patterns acquired in as little as 5 minutes (Cressey and Batchelder 1998), longer counts times are required for complex multiphase mixtures, such as the ordinary chondrites analyzed in this study. Longer count times ensure that peak intensities are recorded accurately and that the ratio of background noise to peaks is reduced. Silicon was used as an external calibration standard, as described by Cressey and Schofield (1996).

The availability of sample material is a critical aspect of meteorite analysis, as the amount is usually limited. The majority of chondrite powders in this study were prepared from 8 – 20 g of material (Jarosewich 1990), which is in line with the amount of material (10 g) required to provide a representative sampling of ordinary chondrites (Keil 1962). For chondrites not prepared as part of the Jarosewich (1990) study, availability of material was limited, and only small amounts (0.1 – 0.5 g) could be obtained. It is likely that these samples may not be as representative as those prepared by Jarosewich (1990), but these samples were necessary to ensure that the H, L, and LL ordinary chondrite groups were equally represented. In this study it is also essential that the thin smears provide a representative sampling of the powders. Although the volume of material used in a thin smear is small ($\sim 1\text{-}2\text{ mm}^3$), we believe that this amount is sufficient to accurately measure modal mineralogies of ordinary chondrites. Modal heterogeneity in the CI meteorite Orgueil was investigated by Bland et al. (2004), who used PSD-XRD to measure 10 different aliquots of Orgueil in a micro-well with a volume (0.07 mm^3) that is significantly lower than that of a thin smear. The average mineralogy of these 10 aliquots was

the same as modal mineralogy obtained using a standard well with a volume of 180 mm³ (Bland et al. 2004). In this study, two different thin smears of the L5 chondrite Guibja were analyzed, one for 600 minutes and the other for 60 minutes. All phase abundances agree within 1 wt% except for olivine, which correlates within 2 wt%. The accuracy of this technique will be further addressed in the Methods section by comparing XRD-measured modal abundances with abundances calculated from normative mineralogies.

2.3. Application to Ordinary Chondrite Mineralogy

To test the accuracy of the XRD method in mixtures with compositions similar to ordinary chondrites, we used the full pattern fitting procedure (Cressey and Schofield 1996) to determine modal abundances of five powder mixtures (prepared by T. J. McCoy at the Smithsonian Institution), consisting of varying proportions of plagioclase (An₁₁Ab₈₄), low-Ca pyroxene (En₇₈Fs₂₀Wo₁), high-Ca pyroxene (En₄₇Fs₈Wo₄₅), and olivine (Fo₉₂). These compositions are representative of the major mineral phases present in ordinary chondrites. To ensure consistency with our ordinary chondrite fittings, these unknown patterns were fitted using the same standards used to fit the ordinary chondrites. Table 2.2a compares XRD-derived modal abundances of the unknown mixtures with measured abundances, while Table 2.2b lists the compositions of standards used in this study. Overall, all XRD-derived phases are within +/-2.2 wt% of actual abundances, suggesting that, because the standards used are imperfect matches to the phases in the mixtures, the uncertainty of ordinary chondrite mineral abundances determined in this study is likely to be similar, i.e. to within about ~2 wt% of the actual values.

So, I wonder if anyone will actually read this thesis in the years to come, and I am adding this sentence to find out. If you are reading this, please email me and let me know. I'm sure I can be found using Google.

3. RESULTS

3.1. XRD Pattern Fitting

Figure 2.1 shows representative XRD patterns of the LL4 chondrite Greenwell Springs. A detailed fitting of all phases in Greenwell Springs is presented in Appendix II. Three XRD patterns are shown in figure 2.1: the measured pattern, the calculated pattern (the composite of all measured standards phases), and the residual pattern (the measured pattern minus the calculated pattern). A zero residual indicates that all phases have been accounted for in the fitting procedure. Some intensity may remain in the residual because of slight differences in solid solution between the standards and the sample phases. Such residuals show up as paired negative-positive deviations in the residual. In other cases a strong diffraction peak of a phase may be enhanced in the standard or in the sample owing to preferred orientation in the mount, and this extra intensity will show in the residual. However, because the whole pattern is used in the total fitting rather than just the main diffraction peaks, which is the practice used by most other methods employing scanning diffractometers, a strong peak can be excluded from the fitting procedure without affecting the final quantification result. A similar situation can arise because one larger single-crystal grain is oriented exactly at a Bragg angle, so a strong peak results. Again this can be recognized as it does not conform to the fit value for that phase established for the majority of the pattern, and can again be ignored. These basic rules for assessing phase quantities from multiphase patterns have been addressed and demonstrated by Cressey and Schofield (1996).

Olivine abundances were determined using a series of standards with compositions ranging from Fo₆₀ to Fo₁₀₀. Olivine compositions, which are derived using XRD-measured modal abundance and the forsterite content of each standard, are presented in Table 2.3, along with

electron microprobe-measured olivine compositions. XRD-derived olivine compositions are consistent with the range of olivine compositions present in ordinary chondrites (Fo₈₀₋₈₄: H chondrites, Fo₇₄₋₇₈: L chondrites, Fo₆₈₋₇₄: LL chondrites) (Brearley and Jones 1998, and references therein). In the H chondrites, 83% of samples have XRD-derived olivine compositions between Fo₇₈ and Fo₈₆, and the average composition in the H chondrites is Fo₈₂. In the L chondrites, the average composition is Fo₇₉, and olivine compositions in 65% of the samples fall in the range of Fo₇₂ to Fo₇₈. Derived olivine compositions in the LL chondrites are typically more forsteritic than measured olivine compositions, resulting in an average composition of Fo₈₂. Only four LL chondrites have derived olivine compositions that fall into a range (Fo₆₉₋₇₅) that is comparable to measured compositions. Most olivine compositions in the LLs are between Fo₇₇ and Fo₈₇. These higher than average olivine compositions are a direct result of the standards used in the fittings, which were most often Fo₇₀ and Fo₈₀.

An olivine composition can be obtained readily from its d₁₃₀ value measured from the 130 reflection in the X-ray diffraction pattern, as long as the peak is singular. However, in these meteorite samples the olivine peaks are not singular; their asymmetric profiles are made up of overlapping, compositionally-shifted peaks of different intensities. The fitting (deconvolution) can be achieved with a set of olivine standards, but these may not accurately reflect the continuous zoning or variability in composition of the olivine. The standards used for fitting were of fixed composition, and effectively any fit result bins the compositions accordingly, so these may not be the true compositions. Olivine compositions are best obtained by microprobe, but their phase proportions cannot be readily assessed this way. Absorption coefficients are best calculated from the microprobe compositions and then used together with the phase fit XRD data to yield a close estimate of the phase proportions.

All low-Ca pyroxene abundances were determined using an enstatite standard with a composition of $\text{En}_{86}\text{Fs}_{12}\text{Wo}_3$. The Fs content of this standard is slightly lower than that of typical orthopyroxene in ordinary chondrites, which ranges from $\text{Fs}_{14.5-18}$ in H chondrites, from Fs_{19-22} in L chondrites, and from Fs_{22-26} in LL chondrites (Brearley and Jones 1998, and reference therein). Because the composition of a mineral affects peak positions and peak intensities, an error in fitting is expected when a standard composition differs from the actual composition present. In orthopyroxene, peak positions of the 0k0 and hkl peaks shift to lower angles with increasing Fe, while the h00, 001, and h01 peaks remain in similar positions for all compositions. Because the number of Fe atoms in the Mg sites of a structure affect X-ray scattering, changes in Fe content also alter peak intensities. Determining the fit is more problematic when the enstatite-ferrosilite solid-solution is far from the standard composition, as in the case of the LL chondrites. However, because only limited orthopyroxene standards are available, only a best estimate can be made. Measured abundances would likely be more accurate if a more appropriate range of standards was available.

High-Ca pyroxene abundances and plagioclase abundances were determined using a diopside standard with a composition of $\text{En}_{47}\text{Fs}_6\text{Wo}_{47}$ and a pure anorthite (An_{100}) standard, respectively. In ordinary chondrites high-Ca pyroxene is diopsidic in composition, with an average Wo content of ~45 and mean Fs contents ranging from Fs_7 to $\text{Fs}_{8.5}$ to Fs_{10} in the H, L, and LL groups (Brearley and Jones 1998, and reference therein). Therefore, the diopside standard used in this study is a good compositional match for high-Ca pyroxene in ordinary chondrites. In type 4-6 ordinary chondrites, plagioclase is typically albitic ($\text{An}_{10}\text{-An}_{12}$) and shows little compositional variation between groups (Brearley and Jones 1998). Two plagioclase standards were obtained for this study, labradorite (An_{68}) and pure anorthite (An_{100}). XRD pattern fittings

using the labradorite standard yielded unrealistic plagioclase abundances (often >15 wt%), which suggested this standard was not well-suited for pattern fittings. Like pyroxene, composition and structural state (i.e. Al-Si order/disorder) affect XRD patterns of plagioclase, although the intensity of the main plagioclase peak ($31^\circ 2\theta$) is not especially affected by compositional variations. As a result, anorthite can be used in place of a more compositionally suitable standard. Using anorthite rather than a more albitic standard does result in an unquantifiable error when the correction for absorption is considered, as the mass absorption coefficient of plagioclase decreases with increasing Na content.

Because the fluorescence background of a multi-phase sample is equal to the sum of the fluorescence background of each component phase, the total wt% Fe in a sample can be calculated by adding the Fe weight fractions of all component phases in proportion to their abundances. Calculated wt% Fe values of all H, L, and LL chondrites are given in Table 2.4a, along with XRD-measured modal abundances. Most calculated wt% Fe values are lower than measured values (Jarosewich 1990). Mean absolute differences are 4.1 wt% in the H chondrites, 2.8 wt% in the L chondrites, and 1.5 wt% in the LL chondrites. The difference between measured and calculated values may be the result of a few factors, the first being the compositions of the olivine standards used in each fitting. Most samples were fitted with Fo₇₀ or Fo₈₀, which contain less Fe than more fayalitic olivine, which results in lower wt% Fe values. Those samples that were fitted with some Fo₇₀ and Fo₆₀ (primarily the L and LLs) have higher wt% Fe than samples that were fitted using Fo₈₀ and Fo₉₂ (the Hs). The second factor influencing calculated wt% Fe is the uncertainty associated with in wt% Fe in metal. The proportion of kamacite (low-Ni metal) to taenite (high-Ni metal) in each sample is unknown, because measured metal abundances (Jarosewich 1990) are presented as total wt% metal only. As a

result, kamacite and taenite cannot be incorporated in the wt% Fe calculation as separate phases. Instead, we used average taenite/kamacite ratios, which increase from 0.1 in H chondrites, to 0.3 in L chondrites, to 0.9 in LL chondrites (Afiattalab and Wasson 1980), to estimate the Fe weight fraction of metal in each chondrite group (0.73 wt% Fe for H chondrites, 0.78 for L chondrites, and 0.93 for LL chondrites). These values are not exact, as the ratio of taenite to kamacite varies slightly within the H, L, and LL groups. Finally, XRD-derived wt% Fe values will be lower than measured values because of the absence of chromite and ilmenite XRD-measured modes. Although abundances of chromite and ilmenite are low, the percentage of Fe in each is high. The absence of chromite and ilmenite from XRD-measured modes is discussed in section 3.3.

3.2. Modal Mineralogy

Olivine, low and high-Ca pyroxene, plagioclase, and troilite were identified in all samples using the PSD-XRD method. Olivine is the most abundant phase present, comprising one-third to one-half the total mode of each sample. At one-fifth to one-fourth of total abundances, low-Ca pyroxene is the second most common phase present. Plagioclase, high-Ca pyroxene, troilite, and metal comprise the remaining XRD-measured mineralogy of each sample. Metal abundances are from bulk chemical analyses compiled by Jarosewich (1990). Average modal abundances and standard deviations of the H, L, and LL chondrites are presented in Figure 2.4b. Detailed fitting information for each sample is presented in Appendix III.

3.2.1. *H chondrites*

The average abundance of olivine present in the H chondrites is 33.0 wt%; however, abundances range from 29.1 wt% to 39.9 wt%. The average abundance of low-Ca pyroxene is 25.6 wt%, with abundances ranging from 21.5 wt% to 28.2 wt%. Plagioclase is present at an

average abundance of 9.0 wt%, while average high-Ca pyroxene and troilite abundances are 6.7 wt% and 5.8 wt%, respectively.

3.2.2. *L* chondrites

Olivine is present at an average abundance of 42.1 wt%, and ranges from 38.4 wt% to 44.7 wt%. The average abundance of low-Ca pyroxene is 23.2 wt%; however, low-Ca pyroxene abundances range from 20.1 wt% to 25.9 wt%. The average abundance of plagioclase in the *L* chondrites is 9.4 wt%, whereas average high-Ca pyroxene and troilite abundances are 8.1 wt% and 7.2 wt%, respectively.

3.2.3. *LL* chondrites

The average abundance of olivine is 51.1 wt%, and olivine abundances range from 47.6 wt% to 57.2 wt%. Low-Ca pyroxene is present at an average abundance of 21.2 wt%; abundances range from 17.6 wt% to 24.1 wt%. Of the remaining phases, plagioclase is present at an average abundance of 9.9 wt%, high-Ca pyroxene at an average abundance of 7.5 wt%, and troilite at an average abundance of 7.1 wt%.

3.3. Comparison of XRD Modal Abundances and Normative Abundances

McSween et al. (1991) calculated CIPW normative mineral abundances of 27 *H* chondrites, 55 *L* chondrites, and 12 *LL* chondrites from bulk rock chemistries determined by Jarosewich (1990). In the norm calculation procedure, metal and sulfide are removed from the bulk sample, normative mineralogy is calculated (as a set of anhydrous minerals) using the standard CIPW algorithm, metal and sulfide are added back in, and normative abundances are renormalized to 100%. Normative data for all but nine samples analyzed in this study are presented in McSween et al. (1991), allowing for a thorough comparison with modal data. Normative abundances cannot be calculated for the remaining nine samples, because bulk

chemical data are not available. Bulk chemical analyses are necessary to calculate norms properly, as a distinction between metallic Fe and Fe^{2+} must be made in the CIPW algorithm. On the basis of normative mineralogy, olivine is the most abundant phase present in all ordinary chondrite groups, followed by low-Ca pyroxene (hypersthene), plagioclase, and high-Ca pyroxene (diopside). Normative olivine is present at average abundances of 34.9 wt% in the Hs, 45.2 wt% in the Ls, and 55.2 wt% in the LLs. Average low-Ca pyroxene abundances decrease from 26.0 wt% in the Hs, to 23.7 wt% in the Ls, to 19.4 wt% in the LLs. There is very little variation in plagioclase abundances between the H, L, and LL groups, with abundances averaging 9.0 wt% in the Hs, 9.4 wt% in the Ls, and 9.7 wt% in the LLs. Diopside abundances average 4.2 wt% in the Hs, 4.8 wt% in the Ls, and 5.3 wt% in the LLs. The average abundance of troilite present among all ordinary chondrite groups is 5.6 wt%.

Figure 2.3 compares modal and normative abundances of olivine, low-Ca pyroxene, high-Ca pyroxene, and plagioclase in 18 H, 15 L, and 6 LL chondrites. Apatite, chromite, ilmenite, and metal (Table 2.4a), which were not measured as part of this study, are not included in this comparison. Abundances of apatite, chromite, and ilmenite are taken from normative mineralogies (McSween et al. 1991) and metal from bulk chemical analyses (Jarosewich 1990). Two L and seven LL chondrites, for which bulk compositions have not been measured, are not included in this comparison. The solid diagonal lines represent equivalent values. Overall, modal abundances agree relatively well with normative abundances in H, L, and LL chondrites (Figure 2.3). Of the two most abundant phases, olivine abundances and norms are comparable within 5.0 wt% in all but six samples. Modal low-Ca pyroxene abundances are within 5.0 wt% of normative abundances in all samples except Andura (H6), which differs from normative values by 5.6 wt%. Although modal olivine is lower than normative olivine in all

chondrites except five H6 samples, there is no consistent trend in modal low-Ca pyroxene abundances, which are only higher than normative abundances in 50% of samples. Modal plagioclase abundances correlate well with normative abundances, with differences of <1.5 wt% in all but three L chondrites (Ausson, Messina, and Aumale). In 50% of the samples, modal and normative plagioclase abundances agree within 1.0 wt%. Modal diopside abundances are systematically higher than normative abundances, with differences ranging from 0.7 to 4.4 wt%. Average differences between modal and normative diopside abundances are 2.1 wt% in the Hs, 3.3 wt % in the Ls, and 2.5 wt% in the LLs.

Although there is some disagreement, most measured and normative abundances correlate well. Discrepancies between normative and modal abundances are present in olivine, diopside, and plagioclase, which may be due to way in which CIPW norms are calculated. A comparison of normative plagioclase compositions (McSween et al. 1991) with measured compositions (Brearley and Jones 1998, and references therein) indicates that normative compositions are higher in Ca and lower in Na than measured compositions. This suggests that the CIPW norm is assigning too much CaO to plagioclase, thus overestimating the normative abundance of plagioclase. We propose that this could also explain the discrepancy between measured and normative diopside abundances. If excess CaO is incorporated into normative plagioclase, then the amount of CaO remaining will be too low, and normative diopside will be underestimated. Olivine is the last mineral calculated in a silica-undersaturated CIPW norm, and it determined by based on the silica deficiency and the abundance of provisional hypersthene. Because hypersthene (low-Ca pyroxenes) and olivine are created provisionally from MgO and FeO, it is possible that the MgO and FeO oxides could be are incorrectly combined or allocated, leading to inaccurate normative values.

The disagreement between modal and normative diopside abundances is the most systematic discrepancy between the two data sets. Because we would not expect minor errors in normative calculations to yield such large differences, there may be an additional source of error. It is possible that the absence of an appropriate pigeonite standard may have an effect on measured pyroxene abundances. Pigeonite (low-Ca pyroxene with $>Wo_3$) has been identified in ordinary chondrites in previous studies (e.g. Keil 1978; McSween and Patchen 1989). Because a pigeonite standard was not available, any pigeonite present would have been measured as either low- or high-Ca pyroxene. Pigeonite is compositionally and structurally similar to clinoenstatite, the monoclinic form of low-Ca pyroxene. (Clinoenstatite, which is the predominant low-Ca pyroxene in type 3 ordinary chondrites (~30-34%), inverts progressively to the orthorhombic form with increasing metamorphism. Most low-Ca pyroxene in type 5 and type 6 is orthorhombic, although some lamellae of clinoenstatite do exist at these petrologic types (Brearley, personal communication).) Because clinopyroxene is also monoclinic, it is possible that any pigeonite present may have been misidentified as clinopyroxene.

3.4. Comparison of XRD Modal Abundances and Electron Microprobe Modal Abundances

Gastineau-Lyons et al. (2002) determined the modal abundances of three L and four LL ordinary chondrites using an electron microprobe phase mapping technique (Taylor et al. 1996), which uses user-defined “windows” of the energy dispersive spectrum to identify phases present in a sample. Several windows are used as identification criteria for a specific mineral (such as Si, Mg, and Ca, which are typically used to identify olivine and orthopyroxene), and each window varies depending on known elemental abundances in a given mineral phase. For example, Gastineau-Lyons et al. (2002) define olivine as 36-55% Si, 18-55% Mg, and 0-2% Ca, whereas the criteria for orthopyroxene are 55-70% Si, 13-30% Mg, and 0-3% Ca.

Modal abundances of five samples analyzed by Gastineau-Lyons et al. (2002) were also measured in this study. These samples are Bald Mountain (L4), Greenwell Springs (LL4), Olivenza (LL5), Tuxtuac (LL5), and Saint-Severin (LL6). Figure 2.4 compares the XRD-derived modal abundances of these five samples with abundances determined using the microprobe phase mapping technique. The electron microprobe-measured Olivenza mode used here is an average of the two sets of abundances (based on two separate thin sections) reported in Gastineau-Lyons et al. (2002). Both sets of data are presented in weight percent.

Comparison of electron microprobe abundances with XRD abundances appears to suggest that the probe mapping microprobe technique agrees better the XRD-technique as the ordinary chondrites become more equilibrated. However, because only five samples are compared, this correlation may not be valid for a larger number of samples. Of the samples compared here, modal phase abundances in the type 4 chondrites Bald Mountain and Greenwell Springs do not correlate well with probe abundances. Modal olivine abundances in Greenwell Springs (LL4) are 7.4 wt% higher than probe abundances, while the remaining phases are only within 3.7 wt% of probe abundances. In Bald Mountain (L4) the largest difference between XRD and probe abundances is seen in diopside, in which XRD-derived abundances are 6.2 wt% higher than probe abundances. XRD-measured olivine is also higher than probe abundances, but by a slightly smaller margin (4.2 wt%), and plagioclase abundances disagree by 3.6 wt%. In the type 5 chondrite Olivenza (LL5), olivine and low-Ca pyroxene are within 1.6 wt% of probe abundances. In Tuxtuac (LL5) these phases are within 3.6 wt%. In both of these samples, plagioclase abundances agree within 1.5 wt%. A discrepancy is present in diopside, as modal high-Ca pyroxene abundances are higher than probe values by ~3.2 wt%. In St. Severin (LL6), the most equilibrated chondrite examined by both techniques, all phases except for high-

Ca pyroxene are within 1.1 wt% of probe values. This is convergence of XRD modal abundances and electron microprobe-measured abundances at type 6 is not unexpected, as mineral phases become progressively more equilibrated and grain sizes increase with increasing petrologic type.

3.5. Bulk Chemistry

Bulk chemistry was calculated from XRD-derived modal abundances by combining known mineral chemistries of phases in proportion to their measured abundances and recalculating to wt% oxides. Abundances of apatite, ilmenite, and chromite used in bulk chemistry calculations are from CIPW norms calculated by McSween et al. (1991). Average normative abundances of apatite, ilmenite, and chromite were used for samples in which normative data was not available. Metal and troilite were not used in bulk chemistry calculations, but were reincorporated into the overall bulk chemistry after chemistry was derived. Derived bulk chemistry provides an additional check on the XRD method when measured bulk chemistry is available for comparison. Measured chemistry (from Jarosewich 1990) is available for all the chondrites analyzed in the study, with the exception of Bernares (a), Hamlet, Witsand Farm, Aldsworth, Alta'ameem, Paragould, Tuxtuac, Blackwell, and Cilimus.

To accurately convert XRD modal abundances to bulk chemistry, best fit standards representing known ordinary chondrite mineral compositions must be selected. Because olivine and low-Ca pyroxene compositions vary between H, L, and LL chondrites, a different standard composition was used in bulk chemistry calculations for each group. Olivine and low-Ca pyroxene compositions used in bulk chemistry calculations are presented in Table 2.5. These best fit standard compositions are averages of electron microprobe-measured olivine and low-Ca pyroxene analyses taken from several chondrites in this study. Compositions were determined with a Cameca SX50 electron microprobe, using standard operating conditions of 15

kV potential, 20 nA beam current, and a 2 μm beam size. An average high-Ca pyroxene composition of $\text{Mg}_{0.9}\text{Ca}_{0.9}\text{Fe}_{0.2}\text{Si}_2\text{O}_6$ was determined from analyses by McSween and Patchen (1989) and Slater-Reynolds and McSween (2005), while an endmember composition of $\text{Ab}_{84}\text{An}_{11}\text{Or}_5$ was used as a representative plagioclase standard (Brearley and Jones 1998). Ilmenite and chromite compositions are averages of H, L, and LL analyses from Snetsinger and Keil (1969) and Bunch et al. (1967), respectively. Our apatite standard is an average chloroapatite composition from the H6 chondrite Seoni (Bunch et al. 1972).

Using XRD-derived bulk chemistries, we calculated elemental ratios of major elements in the H, L, and LL chondrites in this study. Elemental ratios calculated from bulk chemistries are listed in Table 2.6. A comparison of elemental ratios derived from XRD modal abundances and those calculated from measured bulk chemistry (Jarosewich 1990) is presented in Figure 2.5. Overall there is good agreement between measured and XRD-derived elemental ratios in all chondrite groups. Table 2.6 lists mean relative differences and 1σ standard deviations for each ratio. Ca/Si has the highest mean relative differences (0.216 in the LLs to 0.494 in the Ls), while the lowest differences are in Mg/Si (<0.035 in all groups). The large Ca/Si errors in all groups are due to the higher than expected abundances of high-Ca pyroxene, which is the main source of CaO in ordinary chondrites. Mean differences in Fe/Si increase significantly from the LL chondrites to the H chondrites (0.031 in the LLs, 0.057 in the Ls, 0.192 in the Hs). This increasing trend is also present in Al/Si, Mg/Si, and Na/S, whereas the reverse trend is present in K/Si. Because the differences between most measured and XRD-derived elemental ratios are higher in the H chondrites, it is likely that XRD-measured modal abundances of the H chondrites are not as well determined as those of the L and LL chondrites. The main source of error is likely olivine abundances. Despite these discrepancies, the overall accuracy of derived chemistries in all

three chondrite groups suggests that our modal abundances represent reasonable approximations of actual ordinary chondrite mineralogy.

4. CONCLUSIONS

1. Ordinary chondrites are comprised primarily of olivine and low-Ca pyroxene (50-75 wt% total), with some high-Ca pyroxene, plagioclase, metal, and troilite. Olivine abundances increase from the H to the LL chondrites, whereas low-Ca pyroxene and metal abundances decrease. High-Ca pyroxene, plagioclase, and troilite abundances are relatively consistent between the three ordinary chondrite groups. These conclusions reinforce those of previous mineralogic studies of ordinary chondrites.

2. XRD-derived modal mineralogies compare well with calculated normative abundances. Olivine and low-Ca pyroxene modal abundances are within 5.0 wt% of normative abundances in all but a few samples, whereas plagioclase and troilite are within 2.0 wt%. Modal high-Ca pyroxene modal abundances are consistently higher than normative abundances by as much as 3.0-4.0 wt%. Although some systematic differences do exist, most modal abundances correlate well with normative abundances.

3. XRD modal abundances of five L and LL chondrites were compared to modal abundances determined using electron microprobe phase mapping. Comparison of electron microprobe abundances with XRD abundances suggests that the probe mapping microprobe technique and the XRD-technique correlate more closely as the ordinary chondrites become more equilibrated. However, only five samples are compared in this study, and this correlation may not be valid for a larger number of samples.

4. Total wt% Fe values calculated from XRD pattern background fluorescence in our ordinary chondrites are lower than measured values (Jarosewich 1990), especially in the H

chondrites. This discrepancy is due to the forsterite content of olivine standards, as standards with high forsterite contents contain less Fe than more fayalitic olivine. Consequently, samples that were fitted with Fo₇₀ and Fo₆₀ have higher wt% Fe than samples that were fitted using Fo₈₀ and Fo₉₂.

5. Elemental ratios calculated from XRD-derived chemistries agree well with those determined from measured chemistries (Jarosewich 1990). The largest relative differences are Ca/Si, due to higher than expected XRD-measured high-Ca pyroxene abundances. Because differences between measured and XRD-derived elemental ratios are typically higher in the H chondrites than in the L and LLs, there is likely a large degree of uncertainty associated with the H chondrite modal abundances. Relatively low differences in most other elemental ratios indicate that the XRD-derived chemistries are reasonably accurate. This suggests that modal abundances determined using the XRD-fitting procedure are representative of actual ordinary chondrite mineralogies.

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Appendix I

Table 2.1. Chondrites analyzed in this study using PSD-XRD

Sample	Class	Source	Sample	Class	Source	Sample	Class	Source
Benares (a)	LL4	NHM ^a	Atarra	L4	AMPC	Farmville	H4	AMPC
Greenwell Springs	LL4	AMPC ^b	Bald Mountain ^d	L4	AMPC	Forest Vale	H4	AMPC
Hamlet	LL4	NHM	Rio Negro	L4	AMPC	Kabo	H4	AMPC
Witsand Farm	LL4	NHM	Rupota	L4	AMPC	Marilia ^d	H4	AMPC
Aldsworth	LL5	NHM	Ausson	L5	SI	São Jose do Rio Preto	H4	AMPC
Alat'ameem	LL5	NHM	Blackwell	L5	SI	Allegan	H5	AMPC
Olivenza	LL5	NHM	Cilimus	L5	AMPC	Ehole	H5	AMPC
Paragould	LL5	NHM	Guibga ^d	L5	AMPC	Itapicuru-Mirim ^d	H5	AMPC
Tuxtuac	LL5	SI ^c	Mabwe-Khoywa	L5	AMPC	Lost City	H5	AMPC
Bandong	LL6	AMPC	Malakal	L5	AMPC	Pribram	H5	AMPC
Cherokee Spring	LL6	AMPC	Messina	L5	AMPC	Schenectady	H5	AMPC
Karatu	LL6	AMPC	Apt	L6	AMPC	Uberaba	H5	AMPC
Saint-Severin	LL6	AMPC	Aumale	L6	AMPC	Andura	H6	AMPC
			Karkh	L6	AMPC	Butsura ^d	H6	AMPC
			Kunashak	L6	AMPC	Canon City	H6	AMPC
			Kyushu	L6	AMPC	Chiang Khan	H6	SI
			New Concord ^d	L6	AMPC	Guareña	H6	AMPC
						Ipiranga	H6	AMPC

^aNatural History Museum, London, England

^bSmithsonian Institution's Analyzed Meteorite Powder Collection

^cSmithsonian Institution - sample chip, not part of the Analyzed Meteorite Powder Collection

^dCounts acquired for 600 minutes

Table 2.2a. XRD-measured modal abundances of five silicate powder mixtures

Composition of powder mixture ^a	Mineral phase	XRD fit ^b	% Deadtime correction ^c	μ/ρ ^d	XRD wt%
OLV ₄₀ LCP ₄₉ HCP ₁₁	Forsterite 92	0.45	1.06	48.6	38.2
	Enstatite	0.65	1.09	53.4	50.1
	Diopside	0.15	1.05	63.3	11.6
LCP ₅₀ HCP ₅₀	Enstatite	0.80	1.09	53.4	52.2
	Diopside	0.90	1.05	63.3	47.8
LPC ₈₅ HCP ₁₅	Enstatite	0.90	1.09	53.4	84.7
	Diopside	0.15	1.05	63.3	15.3
OLV ₈₀ LCP ₉ HCP ₂ PLG ₁₀	Forsterite 92	1.60	1.06	48.6	79.7
	Enstatite	0.20	1.09	53.4	10.0
	Diopside	0.00	1.05	63.3	0.0
	Anorthite	0.20	1.00	52.7	10.3
OLV ₇₀ LCP ₃₀	Forsterite 92	0.80	1.06	48.6	71.1
	Enstatite	0.30	1.09	53.4	28.9

^aPhases are reported in wt%; OLV - olivine, LCP - low-Ca pyroxene, HCP - high-Ca pyroxene, PLG - plagioclase

^bRaw fit data before corrections are made.

^cMultiplication factor of 100/ (100-x), where x is the percent deadtime

^dMass absorption coefficient (linear absorption coefficient/density)

Table 2.2b. Compositions of standards used in this study

Mineral	Composition
Olivines	Fo ₆₀ , Fo ₇₀ , Fo ₈₀ , Fo ₉₂ , Fo ₁₀₀
Low-Ca pyroxene	En ₈₆ Fs ₁₂ Wo ₃
High-Ca pyroxene	En ₄₇ Fo ₆ Wo ₄₇
Plagioclase	An ₁₀₀
Troilite	FeS (63.5 wt% Fe)

Table 2.3. Measured and XRD-derived olivine compositions (as mol% Fo)^a

H Chondrites			Measured	XRD	L Chondrites			Measured	XRD	LL Chondrites			Measured	XRD
Farmville	H4		82.4	83.2	Atarra	L4		76.8	76.1	Benares (a)	LL4		71.1	94.6
Forest Vale	H4		81.7	78.1	Bald Mountain	L4		77.1	79.2	Greenwell Springs	LL4		71.6	74.9
Kabo	H4		81.8	83.7	Rio Negro	L4		75.5	76.1	Hamlet	LL4		73.5	87.7
Marilia	H4		n.m. ^b	83.5	Rupota	L4		75.5	78.4	Witsand Farm	LL4		n.m.	93.7
São Jose do Rio Preto	H4		81.1	79.2	Ausson	L5		75.9	88.3	Aldsworth	LL5		71.8	85.6
Allegan	H5		82.3	83.0	Blackwell	L5		n.m.	74.6	Alat'ameem	LL5		70.3	92.6
Ehole	H5		80.7	79.2	Cilimus	L5		n.m.	86.3	Olivenza	LL5		70.0	79.3
Itapicuru-Mirim	H5		81.7	83.0	Guibga	L5		75.3	76.5	Paragould	LL5		72.3	79.6
Lost City	H5		81.3	83.7	Mabwe-Khoywa	L5		n.m.	79.4	Tuxtuac	LL5		69.6	80.3
Pribram	H5		81.5	80.5	Malakal	L5		75.2	76.7	Bandong	LL6		69.5	73.8
Schenectady	H5		81.0	80.0	Messina	L5		75.5	72.2	Cherokee Spring	LL6		71.7	74.9
Uberaba	H5		n.m.	83.0	Apt	L6		74.9	69.7	Karatu	LL6		68.9	68.7
Andura	H6		80.7	86.1	Aumale	L6		75.5	73.7	Saint-Severin	LL6		70.3	76.9
Butsura	H6		80.9	83.4	Karkh	L6		75.2	77.8					
Canon City	H6		80.8	75.9	Kunashak	L6		75.4	83.7					
Chiang Khan	H6		n.m.	92.0	Kyushu	L6		75.5	83.7					
Guareña	H6		80.8	85.5	New Concord	L6		75.7	83.9					
Ipiranga	H6		81.3	77.2										

^aOlivine compositions are from part 2 of this study (Dunn et al. 2008b). Additional sources: Forest Vale and Alta'ameem (Rubin 1990), Greenwell Springs (Slater-Reynolds and McSween 2005)

^bn.m. indicates not measured

Table 2.4a. XRD-derived modal abundances and total Fe% of ordinary chondrites analyzed in this study

Sample	Class	Olivine	Low-Ca pyroxene	High-Ca pyroxene	Plagioclase	Troilite	Metal ^a	Other ^b	Total Fe% (lit.) ^c	Total Fe% (calc.) ^d
Farmville	H4	30.3	27.9	7.6	8.7	5.6	18.5	1.6	27.6	23.1
Forest Vale	H4	30.1	25.5	7.4	8.5	5.4	21.4	1.7	27.5	26.7
Kabo	H4	29.1	27.0	6.8	9.7	6.2	19.5	1.7	28.1	23.9
Marilia	H4	29.7	28.2	6.5	9.4	6.0	18.7	1.6	27.8	23.4
São Jose do Rio Preto	H4	29.8	26.4	8.2	9.4	6.8	17.8	1.6	26.8	24.1
Allegan	H5	30.1	26.5	7.2	8.2	6.6	19.8	1.7	28.5	24.6
Ehole	H5	34.7	26.2	7.1	8.1	4.6	17.8	1.6	27.4	24.6
Itapicuru-Mirim	H5	32.9	23.2	6.3	9.0	5.8	21.3	1.6	29.6	25.2
Lost City	H5	31.4	25.4	7.4	10.1	5.4	18.5	1.8	27.6	22.8
Pribram	H5	32.3	25.9	7.7	8.8	7.0	16.7	1.6	26.2	22.5
Schenectady	H5	35.7	24.8	6.2	8.9	5.7	16.9	1.7	27.5	21.4
Uberaba	H5	34.7	24.5	8.3	9.5	6.1	15.3	1.6	26.1	20.9
Andura	H6	36.2	26.8	5.1	8.8	5.9	15.5	1.8	26.7	20.9
Butsura	H6	34.1	27.2	5.9	8.4	4.1	18.5	1.8	27.9	22.4
Canon City	H6	35.0	23.8	6.0	8.5	6.1	18.8	1.8	27.8	25.7
Chiang Khan	H6	34.4	24.8	6.0	9.2	6.0	18.0	1.6	27.0	21.0
Guareña	H6	39.9	21.5	4.7	9.3	4.8	18.2	1.7	27.7	22.3
Ipiranga	H6	34.3	25.3	6.3	9.1	6.5	16.9	1.6	26.3	24.3
Atarra	L4	39.9	21.0	10.7	9.8	7.8	8.7	1.6	21.4	20.4
Bald Mountain	L4	38.4	23.9	8.1	9.3	8.9	9.8	1.6	23.5	21.1
Rio Negro	L4	42.0	25.2	8.5	9.8	4.7	8.1	1.7	21.4	18.6
Rupota	L4	42.6	24.4	7.9	9.1	6.4	8.1	1.7	21.9	18.9
Ausson	L5	38.7	24.9	7.2	12.3	5.5	9.9	1.5	23.8	16.7
Blackwell	L5	44.6	25.9	9.6	8.8	2.6	6.9	1.6	n.m.	18.1
Cilimus	L5	44.3	25.0	6.8	9.3	5.6	7.6	1.6	n.m.	16.0
Guibga	L5	40.9	22.1	8.0	9.1	9.1	9.4	1.4	23.0	21.9
Mabwe-Khoywa	L5	42.2	24.8	6.1	9.2	8.3	7.8	1.6	21.8	19.7
Malakal	L5	41.8	23.2	8.1	9.3	7.4	8.8	1.4	22.3	20.5
Messina	L5	42.9	23.4	8.4	7.2	8.7	7.9	1.5	21.5	25.3
Apt	L6	40.0	22.7	8.2	9.4	10.3	7.8	1.6	21.6	23.0
Aumale	L6	42.4	21.5	7.8	8.9	8.9	8.9	1.6	21.7	22.3
Karkh	L6	43.4	22.5	7.8	9.0	7.2	8.6	1.6	22.4	20.2
Kunashak	L6	43.9	21.9	7.6	10.2	7.0	7.7	1.6	21.8	17.6
Kyushu	L6	43.4	20.1	8.2	9.3	9.3	8.2	1.4	21.9	19.3
New Concord	L6	44.7	21.6	8.8	10.0	5.0	8.4	1.5	22.2	16.9
Benares (a)	LL4	47.6	24.1	9.8	11.2	5.3	0.5	1.6	n.m.	7.8
Greenwell Springs	LL4	50.5	22.0	6.4	8.8	6.5	4.3	1.5	19.8	19.8
Hamlet	LL4	49.9	23.2	7.3	10.0	4.7	3.4	1.6	n.m.	12.6
Witsand Farm	LL4	50.8	20.9	6.8	8.7	4.2	7.1	1.6	n.m.	13.5
Aldsworth	LL5	52.1	21.1	6.6	9.0	4.8	4.8	1.6	n.m.	14.8
Alat'ameem	LL5	51.1	23.3	7.9	9.0	5.1	2.0	1.6	n.m.	9.9
Olivenza	LL5	51.0	21.9	6.8	9.4	6.3	3.0	1.7	18.9	16.2
Paragould	LL5	49.4	19.9	6.7	10.3	4.9	7.2	1.6	n.m.	15.3
Tuxtuac	LL5	51.9	22.7	7.9	10.1	3.6	2.2	1.6	n.m.	13.6
Bandong	LL6	50.4	18.6	7.5	10.8	8.6	2.4	1.7	19.6	18.6
Cherokee Spring	LL6	51.2	19.1	6.6	10.1	8.1	3.3	1.5	20.4	19.0
Karatu	LL6	57.2	17.6	8.2	9.4	4.7	1.6	1.4	18.6	18.4
Saint-Severin	LL6	51.3	20.1	7.4	9.5	6.8	3.2	1.6	21.2	17.6

^aMetal abundances from bulk chemistry (Jarosewich, 1990)^bNormative abundances of apatite, ilmenite, and chromite (McSween and Bennett, 1991); Average abundances were used when individual norms were not available^cTotal Fe weight percent from Jarosewich (1990)^dTotal Fe weight percent calculated using final modal abundances (in wt%) and weight fraction Fe of each standard

Table 2.4b. Average XRD-measured abundances and standard deviations^a

Chondrite Group	Number of samples	Olivine	Low-Ca pyroxene	High-Ca pyroxene	Plagioclase	Troilite
H4	5	29.8 (1.4)	27.0 (1.9)	7.3 (0.2)	9.1 (0.1)	6.0 (0.7)
H5	7	33.1 (2.0)	25.2 (1.1)	7.2 (0.7)	8.9 (0.7)	5.9 (0.8)
H6	6	35.7 (2.2)	24.9 (2.1)	5.7 (0.6)	8.9 (0.4)	5.6 (0.9)
L4	4	40.7 (1.9)	23.6 (1.8)	8.8 (1.3)	9.5 (0.4)	7.0 (1.8)
L5	7	42.2 (2.0)	24.2 (1.3)	7.7 (1.2)	9.3 (1.5)	6.8 (2.3)
L6	6	43.0 (1.6)	21.7 (0.9)	8.1 (0.4)	9.5 (0.5)	8.0 (1.9)
LL4	4	49.7 (1.5)	22.6 (1.4)	7.6 (1.5)	9.7 (1.2)	3.8 (1.0)
LL5	5	51.1 (1.1)	21.8 (1.4)	7.2 (0.7)	9.6 (0.6)	3.8 (0.9)
LL6	4	52.5 (3.1)	18.9 (1.0)	7.5 (0.6)	9.8 (0.7)	2.6 (1.8)

^aNumbers in parentheses represent 1 σ standard deviationsTable 2.5. Average olivine and low-Ca pyroxene compositions from several H, L, and LL chondrites analyzed in this study^{ac}

	Olivine			Low-Ca Pyroxene		
	H [147] ^b	L [186]	LL [70]	H [118]	L [170]	LL [71]
SiO ₂	39.4 (4)	38.1 (4)	37.3 (3)	29.9 (7)	35.7 (4)	54.7 (5)
TiO ₂	n.m.	n.m.	n.m.	0.09 (7)	0.11 (5)	0.20 (7)
Al ₂ O ₃	n.m.	n.m.	n.m.	0.13 (19)	0.14 (13)	0.20 (11)
Cr ₂ O ₃	0.03 (6)	0.04 (7)	0.03 (7)	0.10 (17)	0.12 (15)	0.14 (13)
MgO	42.6 (2)	39.0 (4)	35.7 (2)	16.4 (4)	18.8 (5)	27.5 (4)
CaO	0.03 (2)	0.04 (2)	0.05 (2)	0.36 (10)	0.58 (24)	0.98 (27)
MnO	0.46 (3)	0.46 (4)	0.45 (4)	0.26 (3)	0.31 (19)	0.45 (4)
FeO	17.6 (3)	22.3 (4)	27.1 (5)	11.1 (2)	8.8 (6)	16.2 (4)
Na ₂ O	n.m.	n.m.	n.m.	<0.03	<0.03	0.04 (4)
Total	100.1	99.9	100.6	100.4	99.8	100.5

Cations based on 3 oxygens (olivine) and 4 oxygens (pyroxene)

Si	1.00	0.99	0.99	1.99	1.98	1.97
Ti	n.m.	n.m.	n.m.	0.00	0.00	0.01
Al	n.m.	n.m.	n.m.	0.01	0.01	0.01
Cr	0.00	0.00	0.00	0.01	0.01	0.00
Mg	1.61	1.52	1.41	1.62	1.55	1.48
Ca	0.00	0.00	0.00	0.03	0.03	0.04
Mn	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.37	0.49	0.60	0.33	0.41	0.49
Na	n.m.	n.m.	n.m.	0.00	0.00	0.00
Total	3.00	3.01	3.01	4.00	4.01	4.01

^aValues are in wt% oxides.^aNumbers in parentheses represent 1 σ precision expressed as the least digit cited.^cNumbers in parentheses are 1 σ standard deviations.

Table 2.6. Major elemental ratios calculated from XRD-derived bulk chemistries

Meteorite	Type	Fe/Si	Mg/Si	Mn/Si	Al/Si	Ca/Si	Na/Si	K/Si
Farmville	H4	0.508	0.804	0.013	0.073	0.115	0.045	0.004
Forest Vale	H4	0.511	0.810	0.013	0.074	0.120	0.046	0.004
Kabo	H4	0.499	0.784	0.013	0.082	0.111	0.051	0.005
Marilia	H4	0.505	0.795	0.013	0.079	0.105	0.049	0.005
São Jose do Rio Preto	H4	0.495	0.785	0.013	0.079	0.121	0.049	0.005
Allegan	H5	0.495	0.787	0.013	0.078	0.122	0.048	0.005
Ehole	H5	0.530	0.853	0.014	0.067	0.106	0.041	0.004
Itapicuru-Mirim	H5	0.517	0.834	0.013	0.078	0.102	0.048	0.005
Lost City	H5	0.496	0.792	0.013	0.083	0.116	0.051	0.005
Primbram	H5	0.510	0.819	0.013	0.073	0.117	0.045	0.004
Schenectady	H5	0.529	0.855	0.014	0.073	0.100	0.045	0.004
Uberaba	H5	0.506	0.821	0.013	0.076	0.116	0.047	0.005
Andura	H6	0.541	0.866	0.014	0.072	0.088	0.044	0.004
Bustura	H6	0.534	0.851	0.014	0.070	0.099	0.043	0.004
Cannon City	H6	0.532	0.860	0.014	0.072	0.100	0.044	0.004
Chiang Khan	H6	0.522	0.842	0.014	0.076	0.096	0.047	0.005
Guareña	H6	0.543	0.893	0.014	0.076	0.082	0.046	0.005
Ipiranga	H6	0.522	0.840	0.014	0.075	0.100	0.046	0.005
Attarra	L4	0.558	0.788	0.014	0.071	0.129	0.044	0.004
Bald Mountain	L4	0.568	0.799	0.014	0.070	0.107	0.043	0.004
Rio Negro	L4	0.573	0.808	0.014	0.069	0.108	0.043	0.004
Rupota	L4	0.587	0.827	0.014	0.065	0.105	0.040	0.004
Ausson	L5	0.538	0.761	0.013	0.086	0.101	0.053	0.005
Blackwell	L5	0.582	0.828	0.014	0.060	0.115	0.038	0.004
Cilimus	L5	0.595	0.839	0.014	0.066	0.094	0.041	0.004
Guibga	L5	0.583	0.820	0.014	0.068	0.105	0.042	0.004
Mabwe-Khoywa	L5	0.597	0.834	0.014	0.068	0.087	0.042	0.004
Malakal	L5	0.583	0.820	0.014	0.068	0.102	0.042	0.004
Messina	L5	0.607	0.857	0.015	0.055	0.109	0.034	0.003
Apt	L6	0.575	0.808	0.014	0.070	0.108	0.043	0.004
Aumale	L6	0.595	0.834	0.014	0.066	0.106	0.041	0.004
Karkh	L6	0.596	0.836	0.014	0.066	0.102	0.041	0.004
Kunashak	L6	0.588	0.822	0.014	0.072	0.101	0.045	0.004
Kyushu	L6	0.595	0.832	0.014	0.069	0.104	0.043	0.004
New Concord	L6	0.586	0.822	0.014	0.070	0.106	0.043	0.004
Bernares (a)	LL4	0.675	0.747	0.013	0.065	0.101	0.040	0.004
Greenwell Springs	LL4	0.744	0.808	0.014	0.056	0.079	0.034	0.003
Hamlet	LL4	0.717	0.783	0.014	0.060	0.084	0.037	0.004
Witsand Farm	LL4	0.747	0.811	0.015	0.056	0.083	0.034	0.003
Aldsworth	LL5	0.751	0.812	0.015	0.056	0.082	0.035	0.003
Alta'ameem	LL5	0.730	0.797	0.014	0.055	0.090	0.034	0.003
Olivenza	LL5	0.737	0.800	0.014	0.058	0.083	0.036	0.004
Paragould	LL5	0.727	0.787	0.014	0.065	0.085	0.040	0.004
Tuxtuac	LL5	0.723	0.788	0.014	0.060	0.089	0.037	0.004
Bandong	LL6	0.723	0.782	0.014	0.068	0.092	0.042	0.004
Cherokee Spring	LL6	0.740	0.799	0.014	0.064	0.085	0.039	0.004
Karatu	LL6	0.766	0.826	0.015	0.057	0.087	0.035	0.003
Saint-Severin	LL6	0.739	0.801	0.014	0.060	0.087	0.037	0.004

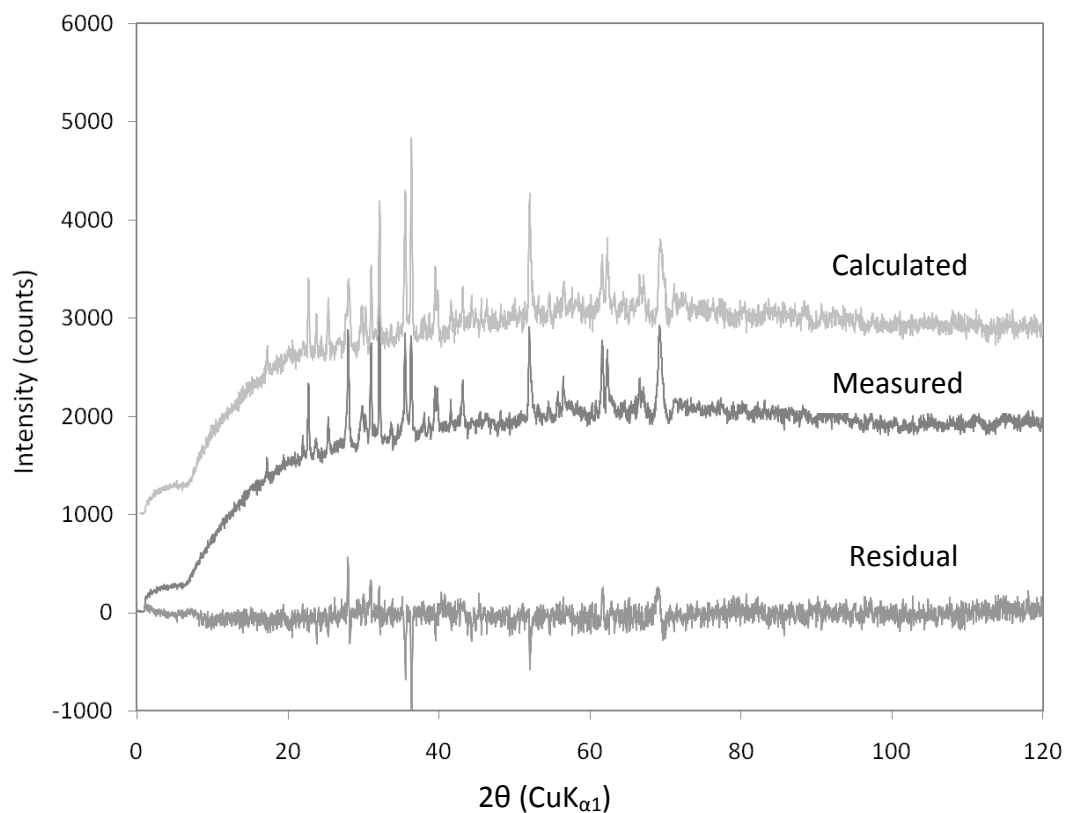


Figure 2.1. Measured, calculated, and residual X-ray diffraction patterns of Greenwell Springs (LL4). The calculated pattern has been offset by 1000 counts. Some peaks remain in the residual pattern due to enhanced reflections from large crystals; however, these peaks have no effect on the final quantification and can be disregarded.

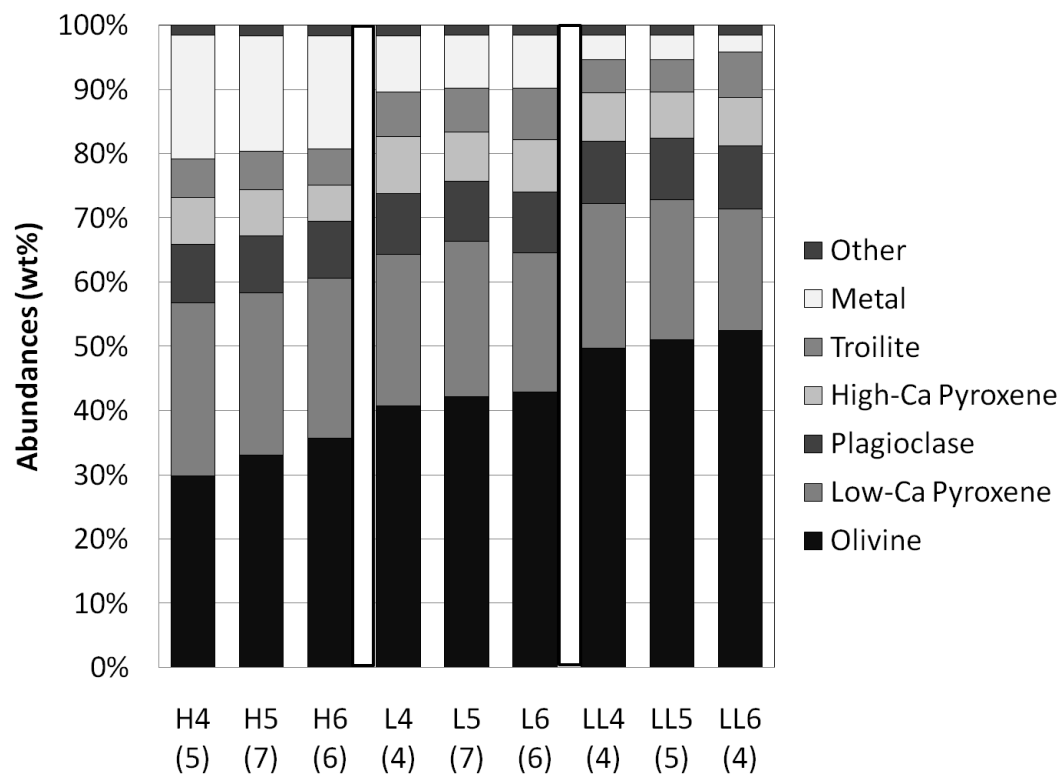


Figure 2.2. Average XRD-derived modal abundances (in wt%) of H, L, and LL ordinary chondrites at each petrologic type (4-6). Numbers in parentheses represent number of samples averaged.

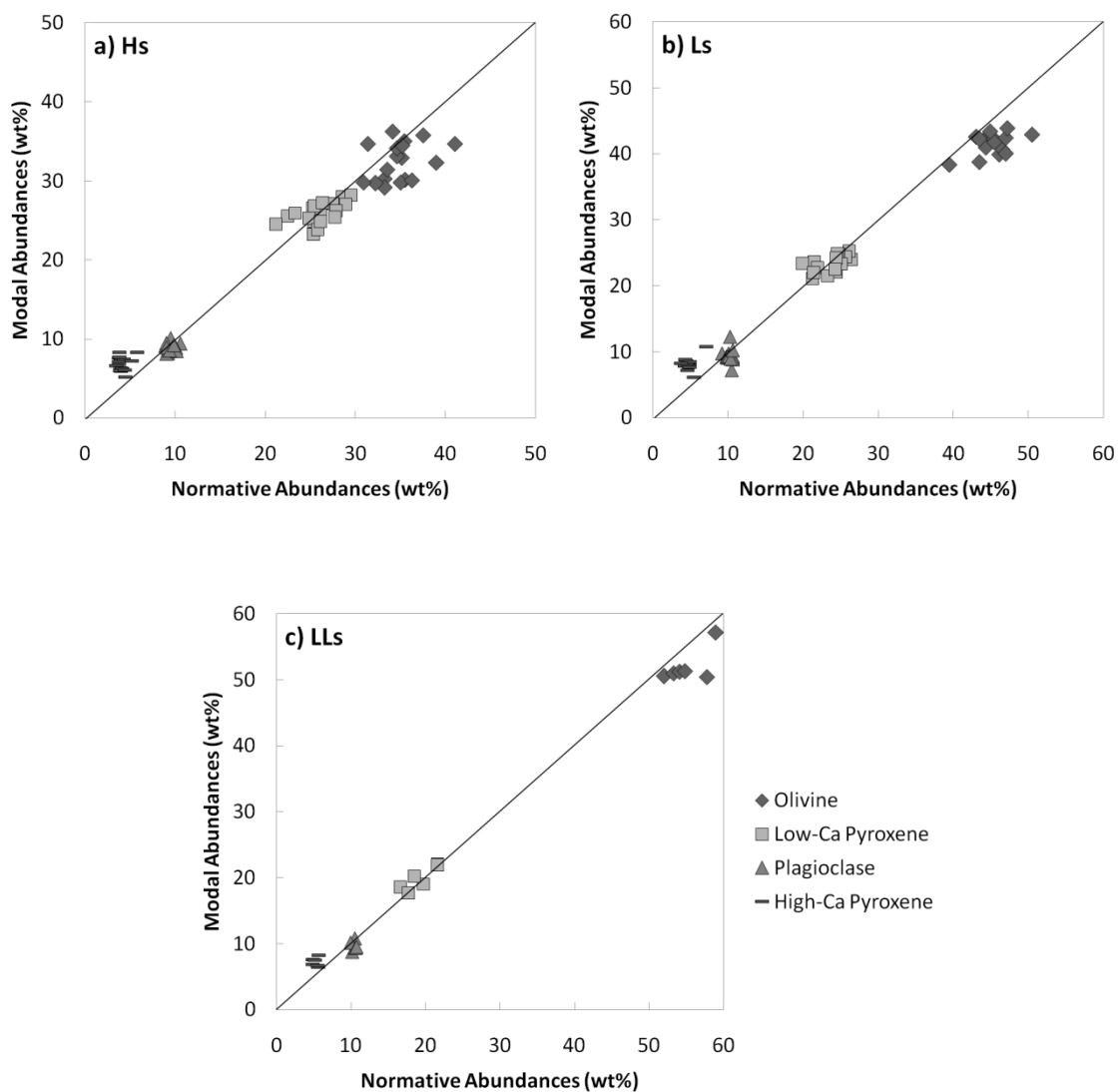


Figure 2.3. Comparison of normative abundances (McSween et al. 1991) with XRD-derived modal abundances in (a) H, (b) L, (c) LL ordinary chondrites. The diagonal lines represent a 1:1 normative to modal ratio.

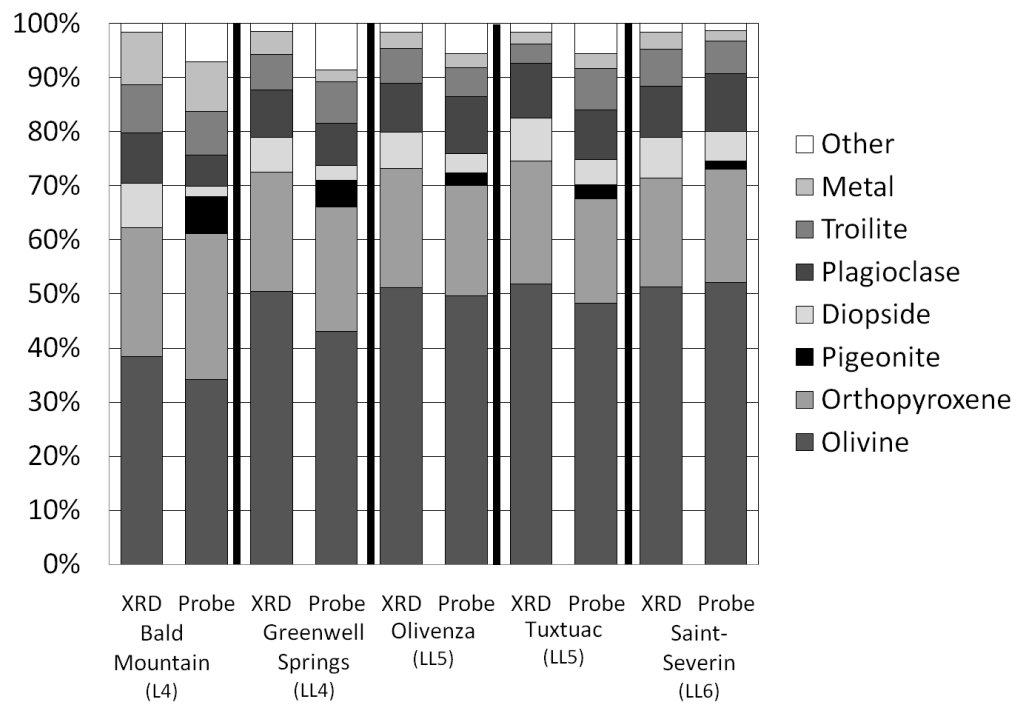


Figure 2.4. Comparison of XRD-derived modal abundances and electron microprobe-measured abundances (Gastineau-Lyons et al. 2002) of one L and four LL ordinary chondrites. Values are in wt%.

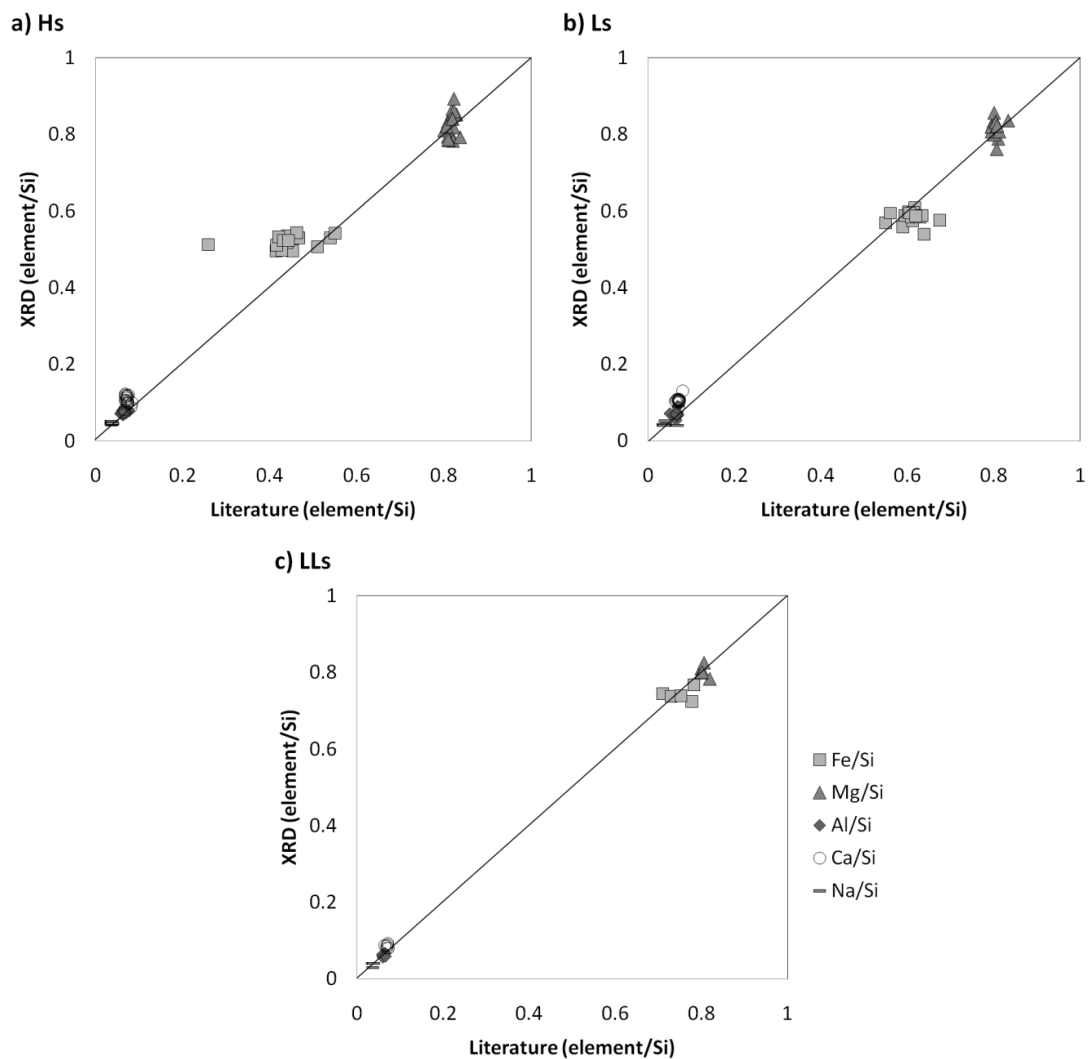
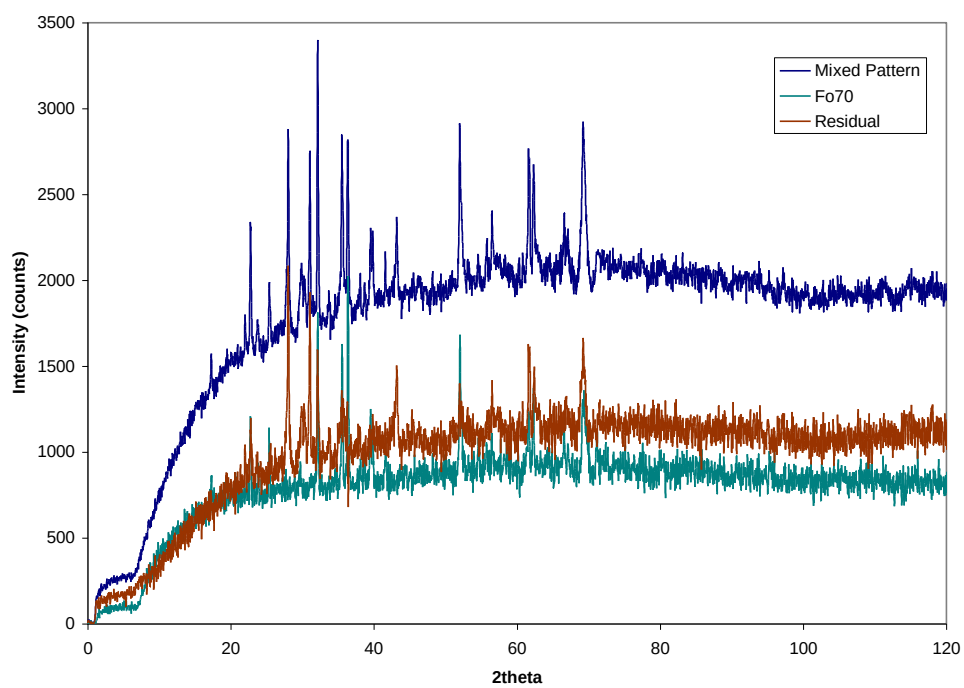


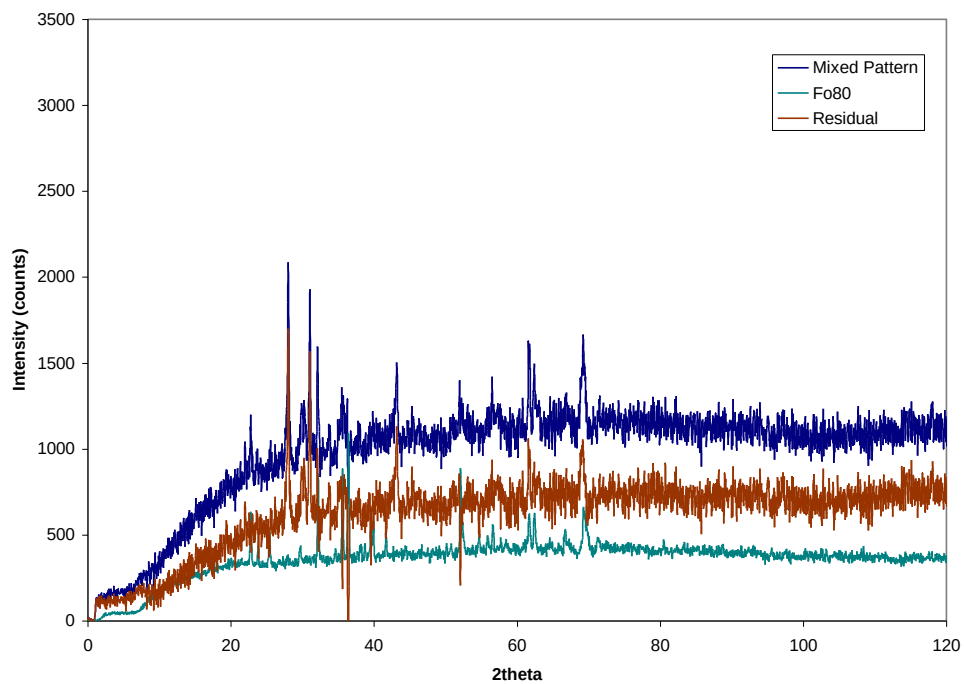
Figure 2.5. Elemental ratios calculated from XRD-derived chemistries (XRD) versus elemental ratios determined from Jarosewich (1990) (literature) in (a) H, (b) L, and (c) LL chondrites. The diagonal lines represent a 1:1 measured (literature) to modeled (XRD-derived) ratio. Uncertainties for each oxide (not illustrated for clarity) are listed in Table 2.6.

Appendix II

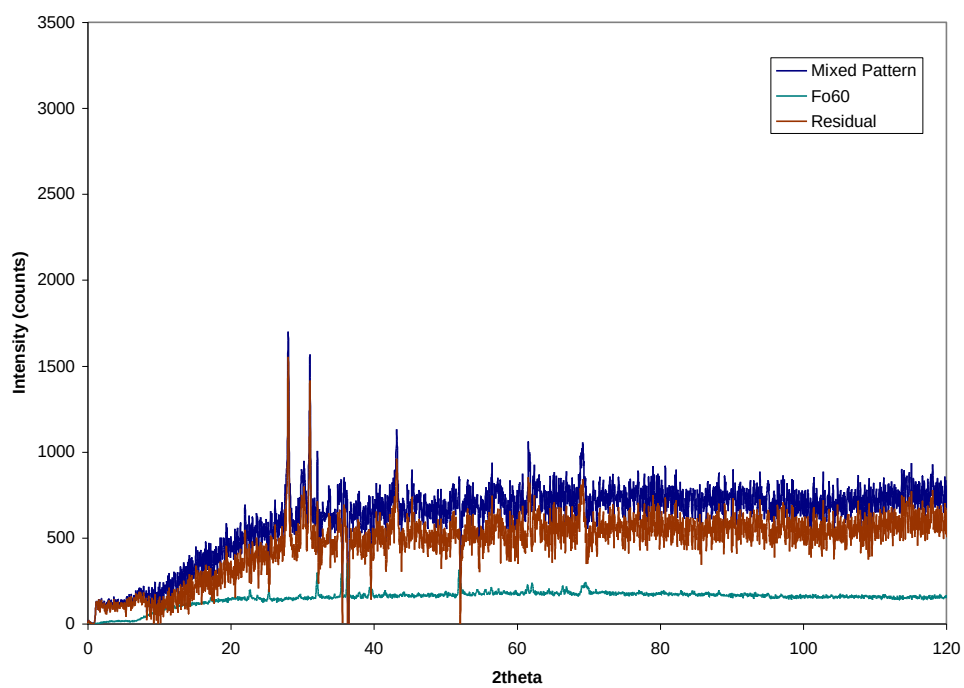
Fo70



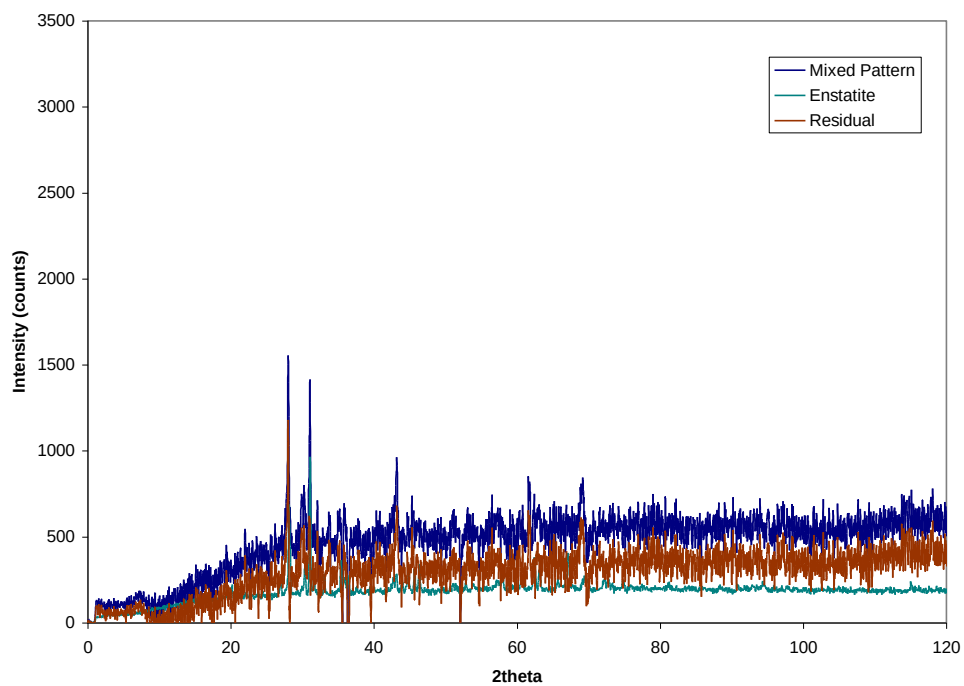
Fo80



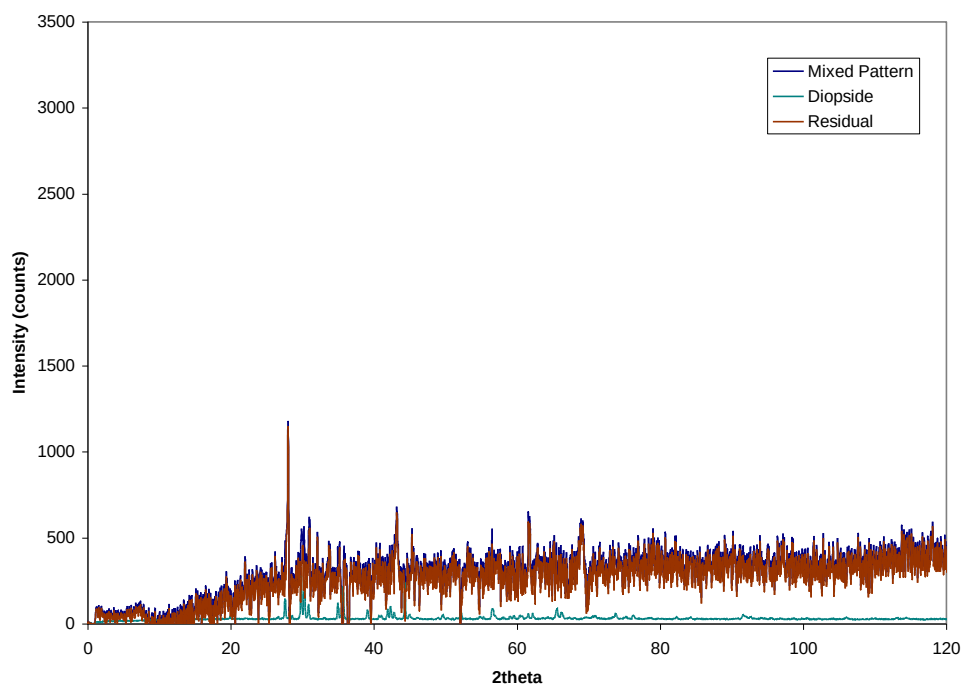
Fo60



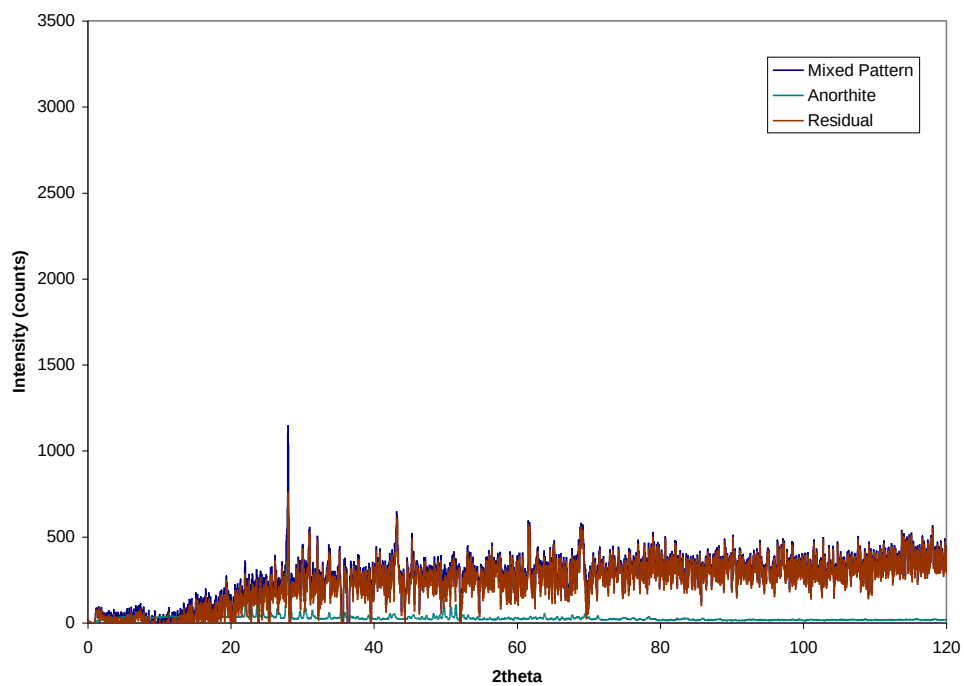
Enstatite

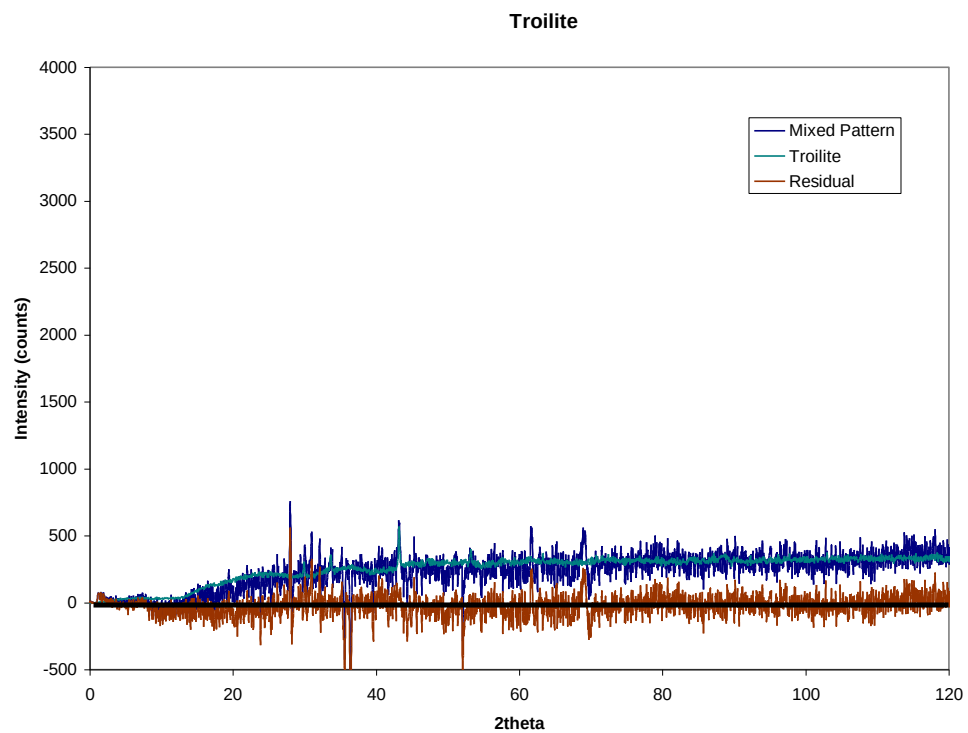


Diopside



Anorthite





Appendix III

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Farmville (H4)						
	Forsterite 80	16	1.09	71.3	0.15	27.9
	Forsterite 92	6	1.06	48.6	0.06	10.0
	Enstatite 86	15	1.09	53.4	0.08	34.9
	Diopside	5	1.05	63.3	0.03	9.5
	Anorthite	5	1.00	52.7	0.00	10.8
	Troilite	8	1.08	142.0	0.64	6.9
Forest Vale (H4)						
	Forsterite 70	5	1.10	88.5	0.21	7.2
	Forsterite 80	18	1.09	71.3	0.15	31.9
	Enstatite 86	14	1.09	53.4	0.08	33.2
	Diopside	5	1.05	63.3	0.03	9.6
	Anorthite	5	1.00	52.7	0.00	11.0
	Troilite	8	1.08	142.0	0.64	7.1
Kabo (H4)						
	Forsterite 80	13	1.09	71.3	0.15	25.7
	Forsterite 92	4	1.06	48.6	0.06	11.3
	Enstatite 86	13	1.09	53.4	0.08	34.3
	Diopside	4	1.05	63.3	0.03	8.6
	Anorthite	5	1.00	52.7	0.00	12.3
	Troilite	8	1.08	142.0	0.64	7.9
Marilia (H4)						
	Forsterite 80	14	1.09	71.3	0.15	26.5
	Forsterite 92	4	1.06	48.6	0.06	10.8
	Enstatite 86	14	1.09	53.4	0.08	35.3
	Diopside	4	1.05	63.3	0.03	8.2
	Anorthite	5	1.00	52.7	0.00	11.7
	Troilite	8	1.08	142.0	0.64	7.5
São Jose do Rio Preto (H4)						
	Forsterite 70	2	1.10	88.5	0.21	3.1
	Forsterite 80	18	1.09	71.3	0.15	33.9
	Enstatite 86	13	1.09	53.4	0.08	32.7
	Diopside	5	1.05	63.3	0.03	10.2
	Anorthite	5	1.00	52.7	0.00	11.7
	Troilite	9	1.08	142.0	0.64	8.4
Alegan (H5)						
	Forsterite 80	17	1.09	71.3	0.15	28.7
	Forsterite 92	4	1.06	48.6	0.06	9.6
	Enstatite 86	15	1.09	53.4	0.08	33.8
	Diopside	5	1.05	63.3	0.03	9.1
	Anorthite	5	1.00	52.7	0.00	10.5
	Troilite	10	1.08	142.0	0.64	8.4

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Ehole (H5)						
	Forsterite 70	8	1.10	88.5	0.21	10.6
	Forsterite 80	20	1.09	71.3	0.15	32.4
	Enstatite 86	15	1.09	53.4	0.08	32.5
	Diopside	5	1.05	63.3	0.03	8.8
	Anorthite	5	1.00	52.7	0.00	10.1
	Troilite	7	1.08	142.0	0.64	5.7
Itapicuru-Mirim (H5)						
	Forsterite 80	17	1.09	71.3	0.15	31.9
	Forsterite 92	4	1.06	48.6	0.06	10.7
	Enstatite 86	12	1.09	53.4	0.08	30.1
	Diopside	4	1.05	63.3	0.03	8.2
	Anorthite	5	1.00	52.7	0.00	11.7
	Troilite	8	1.08	142.0	0.64	7.5
	Metal				0.90	
Lost City (H5)						
	Forsterite 80	16	1.09	71.3	0.15	27.3
	Forsterite 92	5	1.06	48.6	0.06	12.2
	Enstatite 86	14	1.09	53.4	0.08	31.9
	Diopside	5	1.05	63.3	0.03	9.3
	Anorthite	6	1.00	52.7	0.00	12.7
	Troilite	8	1.08	142.0	0.64	6.8
Pribram (H5)						
	Forsterite 70	3	1.10	88.5	0.21	5.3
	Forsterite 80	13	1.09	71.3	0.15	28.1
	Forsterite 92	2	1.06	48.6	0.06	6.2
	Enstatite 86	11	1.09	53.4	0.08	31.8
	Diopside	4	1.05	63.3	0.03	9.4
	Anorthite	4	1.00	52.7	0.00	10.7
	Troilite	8	1.08	142.0	0.64	8.6
Schnectady (H5)						
	Forsterite 80	25	1.09	71.3	0.15	44.0
	Enstatite 86	13	1.09	53.4	0.08	30.5
	Diopside	4	1.05	63.3	0.03	7.6
	Anorthite	5	1.00	52.7	0.00	10.9
	Troilite	8	1.08	142.0	0.64	7.0
Uberaba (H5)						
	Forsterite 80	17	1.09	71.3	0.15	31.3
	Forsterite 92	4	1.06	48.6	0.06	10.5
	Enstatite 86	12	1.09	53.4	0.08	29.5
	Diopside	5	1.05	63.3	0.03	10.0
	Anorthite	5	1.00	52.7	0.00	11.4
	Troilite	8	1.08	142.0	0.64	7.2

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Andura (H6)	Forsterite 80	15	1.09	71.3	0.15	21.4
	Forsterite 92	11	1.06	48.6	0.06	22.4
	Enstatite 86	17	1.09	53.4	0.08	32.4
	Diopside	4	1.05	63.3	0.03	6.2
	Anorthite	6	1.00	52.7	0.00	10.6
	Troilite	10	1.08	142.0	0.64	7.1
Butsura (H6)	Forsterite 80	18	1.09	71.3	0.15	30.7
	Forsterite 92	5	1.06	48.6	0.06	12.2
	Enstatite 86	15	1.09	53.4	0.08	34.1
	Diopside	4	1.05	63.3	0.03	7.4
	Anorthite	5	1.00	52.7	0.00	10.6
	Troilite	6	1.08	142.0	0.64	5.1
Canon City (H6)	Forsterite 70	13	1.10	88.5	0.21	18.2
	Forsterite 80	15	1.09	71.3	0.15	25.9
	Enstatite 86	13	1.09	53.4	0.08	30.0
	Diopside	4	1.05	63.3	0.03	7.5
	Anorthite	5	1.00	52.7	0.00	10.7
	Troilite	9	1.08	142.0	0.64	7.7
Chiang Khan (H6)	Forsterite 92	26	1.06	48.6	0.06	42.8
	Enstatite 86	20	1.09	53.4	0.08	30.8
	Diopside	6	1.05	63.3	0.03	7.5
	Anorthite	8	1.00	52.7	0.00	11.5
	Troilite	13	1.08	142.0	0.64	7.5
Guareña (H6)	Forsterite 80	20	1.09	71.3	0.15	26.8
	Forsterite 92	12	1.06	48.6	0.06	22.9
	Enstatite 86	15	1.09	53.4	0.08	26.8
	Diopside	4	1.05	63.3	0.03	5.8
	Anorthite	7	1.00	52.7	0.00	11.6
	Troilite	9	1.08	142.0	0.64	6.0
Ipiranga (H6)	Forsterite 70	8	1.10	88.5	0.21	11.6
	Forsterite 80	17	1.09	71.3	0.15	30.4
	Enstatite 86	13	1.09	53.4	0.08	31.1
	Diopside	4	1.05	63.3	0.03	7.8
	Anorthite	5	1.00	52.7	0.00	11.1
	Troilite	9	1.08	142.0	0.64	8.0

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Atarra (L4)						
	Forsterite 70	14	1.10	88.5	0.21	25.1
	Forsterite 80	6	1.09	71.3	0.15	13.3
	Forsterite 92	2	1.06	48.6	0.06	6.3
	Enstatite 86	8	1.09	53.4	0.08	23.6
	Diopside	5	1.05	63.3	0.03	12.0
	Anorthite	4	1.00	52.7	0.00	11.0
	Troilite	8	1.08	142.0	0.64	8.8
Bald Mountain (L4)						
	Forsterite 70	13	1.10	88.5	0.21	17.8
	Forsterite 80	5	1.09	71.3	0.15	13.5
	Forsterite 92	5	1.06	48.6	0.06	12.0
	Enstatite 86	14	1.09	53.4	0.08	27.0
	Diopside	5	1.05	63.3	0.03	9.1
	Anorthite	5	1.00	52.7	0.00	10.5
	Troilite	12	1.08	142.0	0.64	10.1
Rio Negro (L4)						
	Forsterite 70	19	1.10	88.5	0.21	26.9
	Forsterite 80	7	1.09	71.3	0.15	12.2
	Forsterite 92	3	1.06	48.6	0.06	7.5
	Enstatite 86	12	1.09	53.4	0.08	27.9
	Diopside	5	1.05	63.3	0.03	9.5
	Anorthite	5	1.00	52.7	0.00	10.8
	Troilite	6	1.08	142.0	0.64	5.2
Rupota (L4)						
	Forsterite 70	15	1.10	88.5	0.21	24.7
	Forsterite 80	4	1.09	71.3	0.15	8.1
	Forsterite 92	5	1.06	48.6	0.06	14.4
	Enstatite 86	10	1.09	53.4	0.08	27.0
	Diopside	4	1.05	63.3	0.03	8.8
	Anorthite	4	1.00	52.7	0.00	10.0
	Troilite	7	1.08	142.0	0.64	8.1
Ausson (L5)						
	Forsterite 80	11	1.09	71.3	0.15	13.7
	Forsterite 92	17	1.06	48.6	0.06	30.1
	Enstatite 86	17	1.09	53.4	0.08	28.2
	Diopside	6	1.05	63.3	0.03	8.1
	Anorthite	9	1.00	52.7	0.00	13.9
	Troilite	10	1.08	142.0	0.64	6.2
Blackwell (L5)						
	Forsterite 70	20	1.10	88.5	0.21	31.4
	Forsterite 80	9	1.09	71.3	0.15	17.4
	Enstatite 86	11	1.09	53.4	0.08	28.3
	Diopside	5	1.05	63.3	0.03	10.5
	Anorthite	4	1.00	52.7	0.00	9.6
	Troilite	3	1.08	142.0	0.64	2.9

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Cilimus (L5)						
	Forsterite 80	17	1.09	71.3	0.15	23.3
	Forsterite 92	13	1.06	48.6	0.06	25.4
	Enstatite 86	15	1.09	53.4	0.08	27.5
	Diopside	5	1.05	63.3	0.03	7.4
	Anorthite	6	1.00	52.7	0.00	10.2
	Troilite	9	1.08	142.0	0.64	6.1
Guibga (L5)						
	Forsterite 70	16	1.10	88.5	0.21	26.8
	Forsterite 80	5	1.09	71.3	0.15	10.3
	Forsterite 92	3	1.06	48.6	0.06	8.8
	Enstatite 86	9	1.09	53.4	0.08	24.7
	Diopside	4	1.05	63.3	0.03	8.9
	Anorthite	4	1.00	52.7	0.00	10.2
	Troilite	10	1.08	142.0	0.64	10.2
Mabwe-Khoywa (L5)						
	Forsterite 70	6	1.10	88.5	0.21	10.0
	Forsterite 80	15	1.09	71.3	0.15	30.8
	Forsterite 92	2	1.06	48.6	0.06	5.9
	Enstatite 86	10	1.09	53.4	0.08	27.4
	Diopside	3	1.05	63.3	0.03	6.7
	Anorthite	4	1.00	52.7	0.00	10.2
	Troilite	9	1.08	142.0	0.64	9.2
Malakal (L5)						
	Forsterite 70	11	1.10	88.5	0.21	24.8
	Forsterite 80	5	1.09	71.3	0.15	13.9
	Forsterite 92	2	1.06	48.6	0.06	7.9
	Enstatite 86	7	1.09	53.4	0.08	25.9
	Diopside	3	1.05	63.3	0.03	9.0
	Anorthite	3	1.00	52.7	0.00	10.3
	Troilite	6	1.08	142.0	0.64	8.3
Messina (L5)						
	Forsterite 60	3	1.11	104.5	0.27	4.5
	Forsterite 70	16	1.10	88.5	0.21	27.9
	Forsterite 80	7	1.09	71.3	0.15	15.0
	Enstatite 86	9	1.09	53.4	0.08	25.8
	Diopside	4	1.05	63.3	0.03	9.3
	Anorthite	3	1.00	52.7	0.00	8.0
	Troilite	9	1.08	142.0	0.64	9.6

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Apt (L6)	Forsterite 60	10	1.11	104.5	0.27	14.5
	Forsterite 70	14	1.10	88.5	0.21	23.7
	Forsterite 92	2	1.06	48.6	0.06	6.0
	Enstatite 86	9	1.09	53.4	0.08	25.1
	Diopside	4	1.05	63.3	0.03	9.1
	Anorthite	4	1.00	52.7	0.00	10.4
	Troilite	11	1.08	142.0	0.64	11.4
Aumale (L6)	Forsterite 60	5	1.11	104.5	0.27	7.0
	Forsterite 70	14	1.10	88.5	0.21	22.8
	Forsterite 80	6	1.09	71.3	0.15	12.0
	Forsterite 92	2	1.06	48.6	0.06	5.7
	Enstatite 86	9	1.09	53.4	0.08	24.0
	Diopside	4	1.05	63.3	0.03	8.7
	Anorthite	4	1.00	52.7	0.00	9.9
Karkh (L6)	Troilite	10	1.08	142.0	0.64	10.0
	Forsterite 70	5	1.10	88.5	0.21	10.9
	Forsterite 80	14	1.09	71.3	0.15	37.5
	Enstatite 86	7	1.09	53.4	0.08	25.0
	Diopside	3	1.05	63.3	0.03	8.7
	Anorthite	3	1.00	52.7	0.00	10.0
	Troilite	6	1.08	142.0	0.64	8.0
Kunashak (L6)	Forsterite 80	13	1.09	71.3	0.15	33.7
	Forsterite 92	4	1.06	48.6	0.06	14.8
	Enstatite 86	7	1.09	53.4	0.08	24.2
	Diopside	3	1.05	63.3	0.03	8.4
	Anorthite	3.5	1.00	52.7	0.00	11.2
	Troilite	6	1.08	142.0	0.64	7.7
Kyushu (L6)	Forsterite 80	16	1.09	71.3	0.15	33.3
	Forsterite 92	5	1.06	48.6	0.06	14.8
	Enstatite 86	8	1.09	53.4	0.08	22.2
	Diopside	4	1.05	63.3	0.03	9.0
	Anorthite	4	1.00	52.7	0.00	10.3
	Troilite	10	1.08	142.0	0.64	10.3
New Concord (L6)	Forsterite 80	15	1.09	71.3	0.15	33.6
	Forsterite 92	5	1.06	48.6	0.06	16.0
	Enstatite 86	8	1.09	53.4	0.08	24.0
	Diopside	4	1.05	63.3	0.03	9.7
	Anorthite	4	1.00	52.7	0.00	11.1
	Troilite	5	1.08	142.0	0.64	5.6

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Benares (a) (LL4)						
	Forsterite 92	15	1.06	48.6	0.06	32.9
	Forsterite100	5	1.00	32.2	0.00	15.6
	Enstatite 86	12	1.09	53.4	0.08	24.6
	Diopside	6	1.05	63.3	0.03	10.0
	Anorthite	6	1.00	52.7	0.00	11.5
	Troilite	7	1.08	142.0	0.64	5.4
Greenwell Springs (LL4)						
	Forsterite 60	5	1.11	104.5	0.27	4.4
	Forsterite 70	30	1.10	88.5	0.21	30.5
	Forsterite 80	15	1.09	71.3	0.15	18.8
	Enstatite 86	14	1.09	53.4	0.08	23.4
	Diopside	5	1.05	63.3	0.03	6.8
	Anorthite	6	1.00	52.7	0.00	9.3
	Troilite	11	1.08	142.0	0.64	6.9
Hamlet (LL4)						
	Forsterite 80	20	1.09	71.3	0.15	28.2
	Forsterite 92	5	1.06	48.6	0.06	10.1
	Forsterite100	5	1.00	32.2	0.00	14.3
	Enstatite 86	13	1.09	53.4	0.08	24.5
	Diopside	5	1.05	63.3	0.03	7.6
	Anorthite	6	1.00	52.7	0.00	10.5
	Troilite	7	1.08	142.0	0.64	4.9
Witsand Farm (LL4)						
	Forsterite 92	27	1.06	48.6	0.06	44.0
	Forsterite100	5	1.00	32.2	0.00	11.6
	Enstatite 86	15	1.09	53.4	0.08	22.9
	Diopside	6	1.05	63.3	0.03	7.4
	Anorthite	6	1.00	52.7	0.00	9.5
	Troilite	8	1.08	142.0	0.64	4.6
Aldsworth (LL5)						
	Forsterite 80	23	1.09	71.3	0.15	29.8
	Forsterite 92	14	1.06	48.6	0.06	25.9
	Enstatite 86	13	1.09	53.4	0.08	22.5
	Diopside	5	1.05	63.3	0.03	7.0
	Anorthite	6	1.00	52.7	0.00	9.7
	Troilite	8	1.08	142.0	0.64	5.2
Alta'ameem (LL5)						
	Forsterite 80	5	1.09	71.3	0.15	7.6
	Forsterite 92	14	1.06	48.6	0.06	30.1
	Forsterite100	5	1.00	32.2	0.00	15.3
	Enstatite 86	12	1.09	53.4	0.08	24.2
	Diopside	5	1.05	63.3	0.03	8.2
	Anorthite	5	1.00	52.7	0.00	9.4
	Troilite	7	1.08	142.0	0.64	5.3

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Olivenza (LL5)						
	Forsterite 70	12	1.10	88.5	0.21	12.9
	Forsterite 80	25	1.09	71.3	0.15	33.0
	Forsterite92	4	1.06	48.6	0.06	7.5
	Enstatite 86	13	1.09	53.4	0.08	22.9
	Diopside	5	1.05	63.3	0.03	7.2
	Anorthite	6	1.00	52.7	0.00	9.8
	Troilite	10	1.08	142.0	0.64	6.6
Paragould (LL5)						
	Forsterite 80	10	1.09	71.3	0.15	13.6
	Forsterite 92	18	1.06	48.6	0.06	35.0
	Forsterite100	2	1.00	32.2	0.00	5.5
	Enstatite 86	12	1.09	53.4	0.08	21.8
	Diopside	5	1.05	63.3	0.03	7.4
	Anorthite	6	1.00	52.7	0.00	11.3
	Troilite	8	1.08	142.0	0.64	5.5
Tuxtuac (LL5)						
	Forsterite 70	26	1.10	88.5	0.21	26.7
	Forsterite 80	3	1.09	71.3	0.15	3.8
	Forsterite 92	13	1.06	48.6	0.06	23.4
	Enstatite 86	14	1.09	53.4	0.08	23.6
	Diopside	6	1.05	63.3	0.03	8.2
	Anorthite	6	1.00	52.7	0.00	10.5
	Troilite	6	1.08	142.0	0.64	3.8
Bandong (LL6)						
	Forsterite 60	5	1.11	104.5	0.27	6.3
	Forsterite 70	20	1.10	88.5	0.21	29.5
	Forsterite 80	5	1.09	71.3	0.15	9.1
	Forsterite 92	3	1.06	48.6	0.06	7.8
	Enstatite 86	8	1.09	53.4	0.08	19.3
	Diopside	4	1.05	63.3	0.03	7.9
	Anorthite	5	1.00	52.7	0.00	11.2
	Troilite	10	1.08	142.0	0.64	7.8
Cherokee Springs (LL6)						
	Forsterite 70	20	1.10	88.5	0.21	34.9
	Forsterite 80	6	1.09	71.3	0.15	12.9
	Forsterite 92	2	1.06	48.6	0.06	6.1
	Enstatite 86	7	1.09	53.4	0.08	20.0
	Diopside	3	1.05	63.3	0.03	7.0
	Anorthite	4	1.00	52.7	0.00	10.6
	Troilite	8	1.08	142.0	0.64	6.1
	Metal				0.72	

	Mineral phase	XRD % fit	Deadtime correction	μ/ρ	Weight fraction Fe	XRD wt% ^a
Karatu (LL6)						
	Forsterite 60	13	1.11	104.5	0.27	17.6
	Forsterite 70	20	1.10	88.5	0.21	31.6
	Forsterite 80	5	1.09	71.3	0.15	9.7
	Enstatite 86	7	1.09	53.4	0.08	18.2
	Diopside	4	1.05	63.3	0.03	8.4
	Anorthite	4	1.00	52.7	0.00	9.7
	Troilite	5	1.08	142.0	0.64	4.8
Saint-Severin (LL6)						
	Forsterite 60	3	1.11	104.5	0.27	3.0
	Forsterite 70	9	1.10	88.5	0.21	10.5
	Forsterite 80	28	1.09	71.3	0.15	40.3
	Enstatite 86	11	1.09	53.4	0.08	21.2
	Diopside	5	1.05	63.3	0.03	7.8
	Anorthite	5	1.00	52.7	0.00	10.0
	Troilite	10	1.08	142.0	0.64	7.2

^aWeight percent after correction for absorption but prior to correction for metal, (+/-3 wt%)

Part III

ANALYSIS OF ORDINARY CHONDRITES USING POWDER X-RAY DIFFRACTION:

2. APPLICATIONS TO ORDINARY CHONDRITE PARENT BODY PROCESSES

This chapter is a reformatted version of a paper, by the same name, to be submitted to Meteoritics and Planetary Science by Tasha L. Dunn, Harry Y. McSween Jr., Timothy J. McCoy, and Gordon Cressey.

Dunn T.L., McSween H.Y. Jr., McCoy T.J., and Cressey G. Analysis of ordinary chondrites using powder X-Ray diffraction: 2. Applications to ordinary chondrite parent body processes.

ABSTRACT

We evaluate the chemical and physical conditions of metamorphism in ordinary chondrite parent bodies using modal mineral abundances and chemical analyses. Several observations indicate that oxidation may have occurred during progressive metamorphism, including systematic changes with petrologic type in olivine and low-Ca pyroxene abundances, increasing ratios of $\text{MgO}/(\text{MgO}+\text{FeO})$ in olivine and pyroxene, mean Ni/Fe and Co/Fe ratios in bulk metal with increasing metamorphic grade, and linear Fe addition trends in molar Fe/Mn and Fe/Mg plots. Water, possibly incorporated as hydrous silicates or as ice, is the most plausible agent responsible for oxidation in ordinary chondrites. Based on mass balance calculations, a minimum of 0.3 – 0.4 wt% H_2O reacted with metal to produce oxidized Fe. Average plagioclase abundances increase slightly from the H to LL chondrites, but do not show any systematic changes with increasing petrologic type. Based on this observation and on a comparison of modal and normative plagioclase abundances, we suggest that plagioclase completely crystallized from glass by type 4 temperature conditions in the H and L chondrites and by type 5 in the LL chondrites. Because the validity of using the plagioclase thermometer to determine peak temperatures rests on the assumption that plagioclase continued to crystallize through type 6 conditions, we suggest that temperatures calculated using pyroxene geothermometry provide more accurate estimates of the peak temperatures reached in ordinary chondrite parent bodies.

1. INTRODUCTION

The ordinary chondrites consist of three groups (H, L, and LL) distinguished based on variations in bulk composition, such as molecular ratios ($\text{FeO}/\text{FeO}+\text{MgO}$) in olivine and pyroxene (Mason 1963; Keil and Fredriksson 1964) and the ratio of metallic Fe to total Fe (Dodd et al. 1967). Textural variations and corresponding mineral and chemical trends indicate that differing degrees of thermal metamorphism took place within each chondrite group. Based on these variations, Van Schmus and Wood (1967) developed a petrologic classification scheme for ordinary chondrites. Ordinary chondrites that are relatively unmetamorphosed, or have experienced very slight heating, are designated as type 3 (unequilibrated), whereas chondrites that have undergone the highest degrees of thermal metamorphism are designated as type 6 (equilibrated) (Van Schmus and Wood 1967; McSween et al. 1988). Although the degree of metamorphism varies within each chondrite group, many details regarding the geochemical and thermal changes that take place during this process are not well understood.

In this paper we use X-ray diffraction-measured modal abundances of olivine, low-Ca and high-Ca pyroxene, and plagioclase (Dunn et al. 2008), along with supplemental chemical analyses to address two long-standing questions have hindered our understanding of thermal metamorphism in the parent bodies of ordinary chondrites:

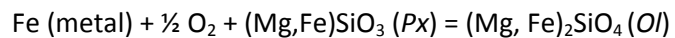
1. Does oxidation or reduction occur during progressive metamorphism in equilibrated ordinary chondrites?
2. What is the best geothermometer to constrain peak metamorphic temperatures in type 6 H, L, and LL ordinary chondrites?

Both of these questions must be resolved in order to develop quantitative thermal evolution models of ordinary chondrite parent asteroids. Redox state has important implications for

understanding metamorphic conditions and fluid-rock interactions, and peak metamorphic temperatures (along with cooling rates and duration of heating) are critical input parameters in thermal calculations (McSween et al. 2002).

1.1. Oxidation State

Along with bulk iron content, the oxidation state of iron also varies systematically between ordinary chondrite groups, decreasing from LL to L to H. Intragroup variations in mean olivine Fa and low-Ca pyroxene Fs contents (McSween and Labotka 1993), modal abundances of Fe-Ni metal, olivine, and low-Ca pyroxene (Afiattalab and Wasson 1980; McSween and Labotka 1993), and average Co and Ni concentrations in kamacite (Rubin 1990) suggest that oxidation state also changes within each chondrite group. McSween and Labotka (1993) linked these intragroup redox variations to metamorphic grade and suggested that the equilibrated ordinary chondrites became progressively oxidized during metamorphism by small amounts of aqueous fluid. They proposed the following reaction caused oxidation:



Because olivine forms at the expense of pyroxene in this reaction, changes should occur in the relative proportions of olivine and low-Ca pyroxene (with increasing petrologic type). Increasing olivine and decreasing low-Ca pyroxene abundances with petrologic type have been observed in CIPW norms calculated from bulk chemical data (McSween et al. 1991), electron microprobe-measured modal abundances (Gastineau-Lyons et al. 2002), and XRD-measured modal abundances (Menzies et al. 2005). Observations in the Gastineau-Lyons et al. (2002) and Menzies et al. (2005) study were based on very limited data sets, and until now there has been little convincing evidence that modal abundances of olivine and low-Ca pyroxene change systematically with petrologic type.

1.2. Peak Temperatures

Peak metamorphic temperatures reached within the interiors of ordinary chondrite parent bodies, along with cooling rates, are critical input parameters in asteroid thermal evolution models (McSween et al. 2002). Peak temperatures are determined by applying geothermometers to those chondrites that have experienced the highest degree of metamorphism (petrologic type 6). Because several different geothermometers have been used to determine peak temperatures, current estimates for type 6 H, L, and LL chondrites range over several hundred degrees. The most common geothermometer used for chondrites is a two-pyroxene geothermometer, based on Ca partitioning between low-Ca and high-Ca pyroxene (Kretz 1982; Lindsley 1983). Several calibrations of this thermometer have been applied to peak temperature estimates in ordinary chondrites (e.g. Olsen and Bunch 1984; McSween and Patchen 1989; Jones 1997; Slater-Reynolds and McSween 2005). However, because results differ depending on the calibration model used or the meteorite examined, estimates for peak metamorphic temperatures vary considerably. The interpretation of pyroxene thermometry is also complicated by apparent disequilibrium between coexisting low-Ca and high-Ca pyroxenes (McSween and Patchen 1989; Jones 1997; Gastineau-Lyons et al. 2002). Olivine-spinel geothermometry has also been used to estimate peak temperatures in ordinary chondrites (Kessel et al. 2007). However, estimated temperatures are low due to Fe-Mg exchange between olivine and spinel, which continues during cooling.

Alternatively, Nakamuta and Motomura (1999) applied a plagioclase geothermometer (based on Si-Al ordering) to type 6 ordinary chondrites. Nakamuta and Motomura (1999) found that feldspar grains in each chondrite recorded a range of temperatures and assumed that the highest temperature represented peak thermal conditions (~700°C for H6, 750°C for L6, and

725°C for LL6). Peak temperatures estimated using the plagioclase geothermometer, however, are only valid if plagioclase continued to crystallize from chondrule glass through type 6 conditions. Petrologic observations used to develop the *Van Schmus and Wood* (1967) classification system suggest that all chondrule glass is crystallized to plagioclase by type 5 conditions. Based on modal and normative abundances of plagioclase, Gastineau-Lyons et al. (2002) suggested that plagioclase crystallization was complete at type 5 in LL chondrites and at type 6 in L chondrites.

2. ANALYTICAL METHODS

2.1. Sample Selection

A total of forty-eight ordinary chondrite samples representing each of the ordinary chondrites groups (H, L, and LL) and corresponding petrologic categories 4-6 (Van Schmus and Wood 1967) were selected for modal analysis (3.1). (All Tables and Figures are located in Appendix IV.) All samples are unbrecciated falls with minimal weathering and low shock. Unequilibrated (type 3) chondrites are not included in this study, as the question of their redox state (using XRD-derived modal abundances) was already addressed by Menzies et al. (2005). Thirty-seven of these samples were originally prepared for bulk chemical analysis by E. Jarosewich as part of the Smithsonian Institution's Analyzed Meteorite Powder Collection. Small chips of the remaining eleven chondrites were acquired from the Natural History Museum (NHM) and from the Smithsonian Institution (SI). These samples were crushed to a powder consistency and prepared for analysis at the University of Tennessee and the NHM. (We refer the reader to Dunn et al. (2008) for a detailed description of XRD sample preparation.) Polished thin sections of 38 of the 48 ordinary chondrites analyzed using X-ray diffraction were acquired

from the NHM and from the SI, so that compositions of olivine and low-Ca pyroxene could be determined.

2.2. X-ray Diffraction

XRD data were collected using an INEL curved position-sensitive detector (PSD) at the Natural History Museum in London, England. The INEL PSD has an output of 4096 channels (each 0.03° 2θ wide), which represents a total arc of 120° 2θ . Using a fixed detector, diffracted intensity is simultaneously measured at all angles, resulting in rapid collection of diffraction patterns. The precision of diffraction patterns is improved by the use of an anode blade rather than a traditional anode wire. Experimental configurations in this study are similar to those implemented by Bland et al. (2004) and Menzies et al. (2005). Samples were radiated using $\text{CuK}\alpha 1$ radiation, which was selected from the primary beam using a single-crystal $\text{Ge}111$ monochromator. Post-monochromator slits were used to restrict the beam size to 0.24×3.0 mm. Diffraction patterns were recorded in reflection geometry from the top of the sample smear, which was set at an angle 7.5° to the incident beam.

The PSD-XRD method for quantification of multi-phase samples (hereafter referred to as powder X-ray diffraction) was first introduced by Cressey and Schofield (1996) and further developed by Batchelder and Cressey (1998). Modal abundances are determined by fitting peak intensities of a mineral standard to those present in a mixture. The intensity of the whole pattern standard phase is decreased by a factor to match the intensity of that phase in the mixture then subtracted, effectively removing that component from the mixture pattern. This procedure is repeated until all phases have been removed. After applying a simple correction for deadtime of the detector, actual weight percent of each mineral are determined using the pattern-fit fraction of a single phase and the calculated mass absorption coefficients for each

mineral in the mixture (Batchelder and Cressey 1998). Weight percentages can be converted to volume percents if the density of each mineral phase is known. However, in this study all results are presented in weight percent to allow for ease in comparison with previously determined normative abundances (McSween et al. 1991). For a detailed description of this powder X-ray diffraction technique and its application to ordinary chondrite modal abundances, see Dunn et al. 2008.

2.3. Electron Microprobe Phase Analysis

Olivine, low-Ca pyroxene, and high-Ca pyroxene compositions were determined with a Cameca SX-50 electron microprobe at the University of Tennessee, using synthetic and natural mineral standards. Data were corrected using ZAF (PAP) procedures. Standard operating conditions during analysis included 15 kV potential, 20-30 nA beam current, and a 2 μm beam size. Counting time was typically 20 seconds. Olivine and low-Ca pyroxene grains were chosen randomly for analysis by moving the sample stage in a grid pattern and analyzing grains in the backscatter image field of view, resulting in a representative sampling of the entire sample. Grains larger than 30 μm were selected to ensure quality analyses, and 15-20 olivine and low-Ca pyroxene grains were typically analyzed per thin section. Unlike low-Ca pyroxene, which comprises $\frac{1}{3}$ to $\frac{1}{4}$ of ordinary chondrite modes, high-Ca pyroxene is present at very low abundances and can be difficult to recognize and analyze. High-Ca pyroxene was identified in nine type 6 chondrites, and 1 – 8 analyses were collected per sample. High-Ca pyroxene was analyzed in type 6 chondrites only for the purpose of calculating peak metamorphic temperatures.

3. EVALUATION OF REDOX STATE

3.1. Olivine and Low-Ca Pyroxene Modal Abundances

Modal abundances of olivine and low-Ca pyroxene show subtle but systematic variations with petrologic type in all chondrite groups (H, L, and LL). Average abundances and standard deviations of olivine, low-Ca pyroxene are listed in Table 3.2. Figure 3.1 illustrates changes in mean olivine and low-Ca pyroxene abundances (with petrologic type) in the H, L, and LL chondrites. In all three chondrite groups, average olivine abundances increase with increasing metamorphic grade. In the H and LL chondrites, the converse trend is present in low-Ca pyroxene abundances. This trend of decreasing low-Ca pyroxene abundances is slightly askew in the L chondrites, as average low-Ca pyroxene abundances show an overall decrease from type 4 to type 6, but increase between type 4 and type 5. Of the L5 chondrites, Ausson, Blackwell, and Cilimus have low-Ca pyroxene abundances that are higher than expected (25.0-26.0 wt%), and it is the abundance of low-Ca pyroxene in these chondrites that drives the average abundance to a value higher than that of the L4 chondrites. It is possible that these abundances are inaccurate due to unrepresentative sampling. Powders of Ausson, Blackwell, and Cilimus were prepared from small chip weighing 0.1 to 0.5 g, which may not be enough material to provide representative modal mineralogies. For a detailed discussion of representative sampling in this study, refer to Dunn et al. (2008).

The trends present in mean abundances of olivine and low-Ca pyroxene are very subtle. This was expected, as previous studies examining normative abundances in ordinary chondrites (McSween et al. 1991) recognized only minor changes in mean abundances. In this study, the largest change in mean modal abundances is 3.5 wt%, whereas the smallest is 0.3 wt%. On average, olivine abundances increase by 1.9 wt% and low-Ca pyroxene abundances decrease by

1.5 wt% between petrologic types. Changes in modal abundances are within the error of powder X-ray diffraction technique, as measured by Dunn et al. (2008) (± 2.2 wt%), and trends are indistinct when 1σ standard deviations are considered. However, an ANOVA single factor test indicates that the differences between mean olivine abundances are statistically significant in the H chondrites, while differences between mean low-Ca pyroxene abundances are statistically significant in the L and LL chondrites at 95% confidence levels. Because these intragroup trends are also present in normative data (McSween et al. 1991) and in electron microprobe-measured modal abundances of L and LL chondrites (Gastineau-Lyons et al. 2002), we believe that these changes in mean abundances represent real physical trends.

The relationship between average olivine and low-Ca pyroxene abundances can also be expressed simply as a ratio of Ol/Opx. Ratios of olivine to low-Ca pyroxene (Ol/Px) in ordinary chondrites have been calculated from normative abundances (McSween et al. 1991), modal abundances (Gastineau-Lyons et al. 2002), and VIS/NIR reflectance spectra (Gastineau-Lyons et al. 2002; Burbine et al. 2003). XRD-measured modal Ol/Opx ratios for the chondrites in this study are shown in Figure 3.2, along with ratios calculated from normative data (McSween et al. 1991). As with normative ratios, our modal Ol/Opx ratios increase with increasing petrologic type in the H, L, and LL chondrites. However, these trends are indistinct when 1σ standard deviations are considered. Because Ol/Opx ratios also increase with petrologic type in both modal and normative data (McSween et al. 1991), we suggest that these trends are indeed present.

It is worth noting that the trends represented by changes in Ol/Opx ratios are not linear, which would appear to indicate that temperature intervals are not constant between each petrologic type. This suggestion is supported by olivine-spinel equilibration temperatures for

the ordinary chondrites (Kessel et al. 2007), which indicate that temperature intervals within each petrologic type vary from 22°C to 153°C. In addition, measured temperature ranges often overlap between petrologic types, as seen in the LL chondrites, where temperatures range from 648-670°C in type 4, 677-741°C in type 5, and 683-777°C in type 6 (Kessel et al. 2007). We must consider these temperature variations when interpreting mineralogical and chemical data, as samples within a petrologic type likely represent various peak temperatures and durations of metamorphism.

3.2. Olivine and Low-Ca Pyroxene Mineral Chemistry

Of the 48 ordinary chondrites examined in this study, 38 were analyzed using the electron microprobe to determine olivine and low-Ca pyroxene compositions. Average olivine analyses of H, L, and LL chondrites are reported in Tables 3.3-3.5 and low-Ca pyroxene in Tables 3.6-3.8. In this section, we examine compositional data of silicate minerals to look for chemical trends indicative of oxidation. As bulk geochemical analyses from previous studies (Kallemeyn et al. 1989) indicate that there are no systematic compositional differences among ordinary chondrites of differing petrologic types, we base our interpretations in this section on the fundamental assumption that thermal metamorphism was isochemical, and that chondrites from each group were derived from a common, unequilibrated starting material.

Intragroup variations in the molecular ratios of olivine (mol% Fa) and low-Ca pyroxene (mol% Fs) have been recognized in several previous studies (Scott et al. 1986; Rubin 1990; McSween and Labotka 1992) and have been attributed to progressive oxidation with increasing thermal metamorphism (Rubin 1990). Olivine (mol% Fa) and low-Ca pyroxene (mol% Fs) compositions of each ordinary chondrite analyzed in this study are presented in Figure 3.3. Mean compositions of olivine and low-Ca pyroxene at each petrologic type are represented by

open symbols. Although there is slight variation among individual data points, mean Fa content in olivine and mean Fs content in low-Ca pyroxene increase with petrologic type all three chondrite groups, in agreement with data from previous studies.

Redox state in the H, L, and LL chondrites can also be examined using molar Fe/Mn and molar Fe/Mg ratios in silicate minerals (Goodrich and Delany 2000). Fe addition (as a result of oxidation) is indicated by the presence of a linear trend, which passes through the origin (y intercept = 0) and is defined by constant Mn/Mg ratios. Molar Fe/Mn ratios and molar Fe/Mg ratios in olivine and low-Ca pyroxene are listed in Tables 3.3-3.8. Figures 3.4a, 3.4b, and 3.4c compare Fe/Mn ratios to molar Fe/Mg ratios in the H, L, and LL chondrites, respectively, to check for the presence of Fe addition trends. In the H and LL chondrites, linear regression analyses of data yield R^2 values ranging from 0.53 to 0.85. R^2 values and slopes do not change when the y-intercept is set at zero, indicating that data fall on lines that pass naturally through the origin (Figures 3.4a and 3.4c). However, R^2 values are less than 0.90 in both groups, suggesting that there is a poor correlation between variables. In the L chondrites, R^2 values are 0.23 (in olivine) and 0.34 (in pyroxene) and R^2 values decrease significantly when the y-intercept is set at zero, indicating that the L chondrite data is best fit with a line that does not pass through the origin. In all three chondrite groups, there is considerable overlap between molar Fe/Mn and Fe/Mg ratios at different petrologic types. However, averages of data at petrologic types 4, 5, and 6 generally plot in an Fe-enrichment sequence in all three chondrite groups.

Examination of mol% Fa, mol% Fs, and Mg/Fe vs. Mn/Fe appear to suggest that the silicate minerals are being enriched in Fe during metamorphism in the H and LL chondrites. Data from the L chondrites, however, do not show support this assertion. Average mol% Fa vs. mol% Fs values do not show an increase between petrologic type 5 and type 6, and Mg/Fe vs. Mn/Fe

data for the L chondrites do not fall on an Fe-enrichment trend. Oxidation trends in the L chondrites are expected, but have likely been erased by residual heating from an episode of extreme shock in the L chondrite parent body, which took place ~500 Ma after formation (Anders 1964; Heymann 1967; Schmitz et al. 2003). This shock event left many parts of the L chondrite parent body at high residual temperatures (up to 1500°C) for weeks to months (Smith and Goldstein 1977). As a result, the expected metamorphic sequence (from type 4 to type 6) was interrupted and compositions of mineral phases were altered (i.e. Dodd and Jarosewich 1979; Huston and Lipschutz 1979), accounting for the lack of oxidation trends in the L chondrites.

3.3. Oxidation State and Petrologic Type

Additional mineralogical and chemical trends in metal have also been cited as evidence of progressive oxidation in the ordinary chondrites. Rubin (1990) noted enrichment trends of Co and Ni in kamacite with increasing petrologic type, and McSween and Labotka (1993) observed an increase in mean ratios of Ni/Fe and Co/Fe in bulk metal. Although metal was not analyzed in this study, weight ratios of Ni/Fe and Co/Fe in thirty-nine of our sample were determined from bulk chemical analyses collected by Jarosewich (1990). Mean ratios of Ni/Fe and Co/Fe and standard deviations are listed in 3.9, and these data are presented graphically in Figure 3.5. Although mean ratios of Ni/Fe and Co/Fe increase with petrologic type in the H chondrites, this is not the case in the L and LL chondrites. As suggested previously, the absence of a trend in the L chondrites is due to shock events in the parent body. In the LL chondrites, there is insufficient data to determine if Ni/Fe and Co/Fe increase with increasing metamorphic type, because only one LL4 and one LL5 sample were analyzed by Jarosewich (1990). Based on our data, it is

unclear whether compositional ratios in metal support the oxidation hypothesis in all chondrite groups.

Oxygen isotopic compositions also change systematically with petrologic type, as mean $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ progressively decrease from type 4 to type 6 in all three chondrite groups (Clayton et al. 1991; Rubin 2005). These decreases in mean $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ correspond to increasing mol% Fa in olivine, suggesting that there is a correlation between oxygen isotope compositions and oxidation state (Rubin 2005). Rubin (2005) attributed the decreases in $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ with petrologic type to loss of chondritic water during thermal metamorphism. It has been suggested that chondritic water was enriched in heavy O isotopes (Choi et al. 1998). If this was the case, loss of water during progressive metamorphism would result in lower $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values in chondrites of higher petrologic types (i.e. those that have lost more water through oxidation.) Because oxygen isotope compositions have only been measured in seven of the chondrites analyzed in this study, we do not have sufficient data to address the relationship between oxygen isotopic compositions and oxidation in this study. We believe, however, that data from Rubin (2005) strongly support the hypothesis that oxygen isotope composition decreases with increasing petrologic type as a result of progressive oxidation.

3.4. Oxidizing Agent

3.4.1. Water as an oxidizing agent

If temperature changes took place in a liquid-free environment, reduction would be expected. Because the ordinary chondrites appear to have been oxidized, a liquid oxidizing agent must have been present. Previous studies have suggested that water is the most plausible agent responsible for oxidation in the ordinary chondrite parent bodies (e.g. McSween and Labotka 1993; Choi et al. 1998; Wasson 2000; Rubin 2005). The occurrence of water in type

3 ordinary chondrites has been inferred from the presence of minor alteration products, such as phyllosilicates and clay minerals (Hutchinson et al. 1987; Alexander et al. 1989), carbide-magnetite-sulfide veins cross-cutting fine-grained chondrule rims (Krot et al. 1997), and magnetite grains showing large mass-dependent isotopic fractionation of oxygen ($\delta^{18}\text{O} \sim 13\text{‰}$), which indicates Rayleigh fractionation under water-limited conditions (Choi et al. 1998). Because water was presumably lost during metamorphism, evidence of water in type 4-6 ordinary chondrites is limited. However, the presence of bleached chondrules (products of low-temperature aqueous alteration) in type 4-6 chondrites (Grossman et al. 2000) and the discovery of fluid-inclusions in halite grains from the H5 chondrite Monahans (1998) (Zolensky et al. 1999) indicate that small amounts of fluid were present ordinary chondrite parent bodies. Water has also been measured in recovered ordinary chondrites (Jarosewich 1990). However, it is unlikely that all of this water is indigenous, as some of it may have been absorbed from the terrestrial atmosphere.

Although there are several lines of evidence to suggest that water was present in the ordinary chondrite parent bodies (and is therefore the most plausible agent responsible for oxidation), the origin of water in the ordinary parent bodies is unclear. McSween and Labotka (1993) suggested that water was produced by melting small amounts of ice, which accreted in different abundances on each of the three ordinary chondrite parent bodies. This model, however, does not account for the metal-silicate fractionation trend, which distinguishes the three ordinary chondrite groups, nor can it explain systematic changes in elemental composition (such as siderophile abundances and volatile/refractory ratios) that occur through the H-L-LL sequence (Kallemeyn et al. 1989). The presence of ice on ordinary chondrite parent bodies is

also problematic, as asteroids believed to be ordinary chondrite parent material accreted inside the snow line, at heliocentric distances where ice is not expected to form (Bell 1986).

As an alternative hypothesis, Wasson (2000) suggested that water was incorporated as hydrous silicates. Rubin (2005) suggested that the abundance of phyllosilicates among fine-grained nebular material may have increased over time. As a result, the H chondrites, which agglomerated first, incorporated the lowest abundances of hydrated silicates, and the LL chondrites, which agglomerated last, incorporated the highest abundance. Because the abundance of water is a function of the abundance of phyllosilicates, water should increase from the LL to H chondrites (Wasson 2000). Phyllosilicates may have formed by direct condensation of a modified solar gas composition under optimal temperature conditions (Petaev and Wood 1998; Wasson and Trigo-Rodriguez 2004), or may have been produced in icy regions by shock waves (Ciesla et al. 2003) and transported into inner regions by gas drag (Ciesla and Lauretta 2005).

Neither of these hypotheses can account for our observation that the type 6 chondrites are more oxidized than the type 4 chondrites, and thus required a larger amount of the oxidizing agent. In the onion-shell model of the ordinary chondrite parent bodies, the inner-most region corresponds to the highest temperatures (petrologic type 6) and the outer region to the lowest temperatures (petrologic type 3). According to the phyllosilicate hypothesis (Wasson 2000; Rubin 2005), material that accreted first (type 6) would contain the lowest amount of water. Progressive oxidation, however, indicates that type 6 material must have reacted with more water than the type 4 and type 5 materials. If water did form from hydrous silicate minerals, the suggestion that they increased in abundance over time may not be valid. The suggestion that water may have formed from melting of accreted ice also fails to account for the increased

abundance of water in type 6 material. Ice, which would have likely accreted early, would serve as a source of water for type 3 (and possibly type 4) material, but could not have provided a substantial amount of water to material deeper in the parent body, such as type 5 and type 6. Even if water percolated through the parent by some mechanism, possibly along a system fractures, it is unlikely that more water would have reached the interior of the body than the surface.

Because neither hypothesis for water on the ordinary chondrite parent bodies readily explains the observed oxidation patterns, this may suggest that there are factors in addition to abundance of water that drive the oxidation reaction in the parent body. The activation energy of the reaction may be one such factor. It is possible that the energy required to initiate the reaction is barely attained in type 4, resulting in only a small amount of oxidation. Once the activation energy has been reached, the reaction may progress to completion. Temperature may also play a more dominant role in oxidation, and it may be that more oxidation is achieved in type 6 because temperature drives the oxidation reaction. This would seem likely, since oxidation increases as heating progresses, but the extent to which this would occur is unclear. Finally, the reaction itself may be a factor in the degree of oxidation, as water coming into contact with metal is more likely to produce $\text{FeO}(\text{OH})$ rather than FeO . This may suggest that an intermediate reaction between $\text{FeO}(\text{OH})$ and FeO is required to more accurately describe oxidation in the ordinary chondrite parent bodies.

3.4.2. Abundance of water required for oxidation

The minimum amount of water necessary to oxidize Fe in chondrites can be estimated using observed changes in mineral abundances. The change in the amount of O (expressed here as H_2O) is the amount necessary to convert measured mineral abundances in type 4 to those in

type 6 during the continuous reaction $\text{low-Ca pyroxene} + \text{Fe} + \text{O}_2 = \text{olivine}$. The mass balance assumes that the system is isolated and that the weights of Si, Fe, Mg, and Ni + Co are conserved. Changes in abundances determined using mass balance are presented in 3.10, along with actual measured abundances low-Ca pyroxene, olivine, and metallic Fe. In the H chondrites, mass balance of type 4 abundances yields a 3.6 wt% increase in olivine, consumes 1.2 wt% metallic Fe, and requires 0.4 wt% H_2O . In L chondrites, olivine increases in type 6 by 3.3 wt%, metallic Fe decreases by 1.1 wt%, and 0.3 wt% water is consumed. Mass balance of type 4 abundances in the LL chondrites produces 6.4 wt% olivine, consumes 2.1 wt% metallic Fe, and requires 0.7 wt% water.

Phase abundances determined using mass balance of the oxidation equation do not always correlate with measured phase changes. In the H chondrites, measured changes in olivine and Fe metal are slightly higher than mass balance values (by 0.4 wt % in metal and 2.3 wt% in olivine). The converse is true in the L and LL chondrites, as measured abundance changes are lower than those calculated using mass balance. In the L chondrites, measured changes in abundances are 0.7 wt% lower in metal and 1.0 wt% lower in olivine. In the LL chondrites, the difference between measured and mass balance-derived abundances is 0.9 wt% in metal and 3.6 wt% in olivine. Mass balance calculations should accurately model expected phase changes, and the inconsistency between XRD-measured abundance changes and those calculated using mass balance may be a consequence of the error associated with the XRD technique.

Based on mass balance in the H and L chondrites, the amount of water required to convert low-Ca pyroxene to olivine is between 0.3 and 0.4 wt%. In the LL chondrites, this abundance is 0.7 wt%. However, we believe that the mean measured decrease in low-Ca-

pyroxene abundances between petrologic type 4 LL chondrites and type 6 LL chondrites is too large, resulting in more water than expected being consumed during mass balance. It is more likely the abundance of water required for oxidation in the LL chondrites is also in the range of 0.3-0.4 wt%. These abundances are slightly higher than those suggested by McSween and Labotka (1993) (0.1 wt% in the H chondrites and 0.2 wt% in the L chondrites); however, they correlate well with measured abundances of water in ordinary chondrites, which provide a lower-limit estimate of ~0.7 wt% in type 4 chondrites and ~0.3 wt% in type 6 chondrites (Jarosewich 1990). It is important to note that these calculated abundances are minimum values, as we have assumed that all O is present as H₂O, whereas analyses of fluid inclusions in Monahans (1998) suggest a brine composition (Zolensky et al. 1999).

4. EVALUATION OF PYROXENE AND PLAGIOCLASE GEOTHERMOMETRY

4.1. Plagioclase Modal Abundances

Unlike olivine and low-Ca pyroxene abundances, plagioclase abundances do not show any systematic changes with increasing petrologic type. However, as in the case of olivine and low-Ca pyroxene, the presence or absence of trends is obscured by the error of the XRD-technique. Average plagioclase abundances increase slightly from the H to LL chondrites (from 9.0 ± 0.5 wt% in the Hs, to 9.4 ± 0.8 wt% in the Ls, to 9.7 ± 0.8 wt% in the LLs). Table 3.2 list average plagioclase abundances and standard deviations, while Figure 3.6 illustrates plagioclase abundances as a function of petrologic type. Although normative plagioclase abundances increase from petrologic type 4 to type 6, no corresponding trend is present in modal abundances. These data seem to suggest that plagioclase abundances do not change appreciably with increasing petrologic type. This is contrary to petrologic observations from

previous studies (Van Schmus and Wood 1967; Sears et al. 1980), which suggest that plagioclase continues to crystallize through type 5 conditions.

Gastineau-Lyons et al. (2002) suggested that the timing of plagioclase crystallization could be constrained by comparing normative and modal plagioclase abundances, which should converge when all available chondrule glass has recrystallized. A comparison of normative plagioclase abundances (McSween et al. 1991) with modal abundances of type 3 chondrites (Menzies et al. 2005) and type 4-6 chondrites (Dunn et al. 2008) is shown in Figure 3.7. Although modal and normative values do not converge absolutely, modal abundances do increase to near normative values at petrologic type 4. When 1σ standard deviations of modal and normative abundances are considered, values converge at type 4 in the H and L chondrites and at type 5 in the LL chondrites. Because of limited sampling in the LL4 and LL5 chondrites, our findings may not be representative of the entire LL group. It is possible that plagioclase abundances may converge at type 4 in the LL chondrites.

It is unclear why modal and normative plagioclase abundances do not converge absolutely. One possibility is that normative plagioclase abundances are too high. Normative plagioclase is calculated as abundances of albite (Na), orthoclase (K), and anorthite (Ca), which can be used to determine plagioclase composition. A comparison of normative plagioclase compositions (McSween et al. 1991) with measured compositions (Brearley and Jones 1998, and references therein) indicates that normative compositions are higher in Ca and lower in Na than measured compositions. This suggests that the CIPW norm assigns too much CaO to plagioclase, thus overestimating the normative abundance of plagioclase. This could also explain the discrepancy between measured and normative diopside abundances, as XRD-measured diopside abundances are higher than normative diopside (Dunn et al. 2008). If excess CaO is

incorporated into normative plagioclase, then the amount of CaO remaining will be too low, and diopside will be underestimated.

Our assessment of modal and normative plagioclase abundances yields a slightly different conclusion from that of Gastineau-Lyons et al. (2002), who examined plagioclase abundances in equilibrated L and LL chondrites. In the Gastineau-Lyons et al. (2002) study, L chondrite normative and modal plagioclase abundances did not converge until petrologic type 6. Plagioclase abundances in the LL chondrites converged at type 5. Observations in the Gastineau-Lyons et al. (2002) study are based on a single chondrite of each petrologic type, and therefore do not represent a statistically significant sampling of the L and LL chondrite groups. Based on observations from this study, we suggest that plagioclase may have completely crystallized from glass by type 4 temperature conditions in the H and L chondrites. In the LL chondrites, plagioclase appears to have crystallized by type 5 conditions. Additional normative abundances of the LL4 and LL5 chondrites may indicate that plagioclase crystallization was complete by type 4 in the LL chondrites.

4.2. Peak Temperature Estimates

The validity of using the plagioclase thermometer to determine peak temperatures rests on the assumption that plagioclase continued to crystallize through type 6 conditions. Our data indicate that crystallization was complete much earlier in the metamorphic sequence, and we suggest that temperatures calculated using pyroxene geothermometry provide more accurate estimates of the peak temperatures reached in ordinary chondrite parent bodies. To assess peak metamorphic temperatures in ordinary chondrite parent bodies, we performed pyroxene geothermometry on nine type 6 ordinary chondrites using QUILF95 (Anderson et al. 1993, modified for Windows 95), a computer model based on the graphical approach of Lindsey

(1983). QUILF95 incorporates improved experimental data for pyroxene equilibrium, eliminates errors associated with converting and plotting chemical analyses on the pyroxene quadrilateral, and eliminates difficulties associated with discerning temperature differences. Temperatures were calculated at a pressure of 1 bar. Average high-Ca pyroxene analyses used to calculate peak temperatures are listed in Table 3.11.

Peak temperature estimates for low-Ca pyroxene and high-Ca pyroxene pairs are presented in Table 3.12. Peak temperatures range from $866 \pm 63^{\circ}\text{C}$ to $967 \pm 25^{\circ}\text{C}$, with all but two temperatures below the Fe-Ni metal-FeS eutectic (950°C). Because chondrites did not experience melting or differentiation, peak temperatures should be below the metal-sulfide eutectic. Peak temperatures above 950°C may be higher than expected due to inadequate high-Ca pyroxene analyses. There is no appreciable difference in temperature estimates from each chondrite group, as the H, L, and LL chondrites yield similar results. The QUILF95 program yields an uncertainty of $\pm 50^{\circ}\text{C}$ for temperatures calculated from low-Ca pyroxene and high-Ca pyroxene pairs. The actual error can be larger if equilibrium has not been reached between the two pyroxene compositions. Because the calculated error in the model does not account for analytical error, we also determined the maximum temperature range due to analytical uncertainty. Minimum and maximum temperatures were calculated by increasing or decreasing the amount of CaO, the most sensitive component in the temperature determinations, by an amount equal to the 1σ standard deviation of low-Ca pyroxene and high-Ca pyroxene. All temperatures calculated from pyroxene pairs fall within the temperature range due to expected analytical error.

Slater-Reynolds and McSween (2005) used QUILF95 to calculate peak temperatures of 41 type 6 ordinary chondrites. Of the nine chondrites analyzed in this study, two (Kyushu and

Saint Severin) were also analyzed by Slater-Reynolds and McSween (2005). The remaining seven chondrites add to the database of peak temperatures estimated from pyroxene goethermometry. Temperatures calculated in this study for Kyushu and Saint Severin are higher than those determined by Slater-Reynolds and McSween (2005). However, most of our estimated temperatures fall within the range (812-945°C) established by Slater-Reynolds and McSween (2005). In this study and in Slater-Reynolds and McSween (2005), peak temperatures calculated using QUILF95 overlap between groups, suggesting that observations of lower temperatures in the H chondrites (Olsen and Bunch 1984; Nakamuta and Motomura 1999) are inaccurate. Like Slater-Reynolds and McSween (2005), our peak temperatures are also higher than those determined using plagioclase goethermometry (Nakamuta and Motomura 1999). We suggest that the plagioclase-derived temperatures are not representative of peak conditions because plagioclase does not continue to crystallize through type 6 conditions. Peak temperatures calculated using QUILF95 also agree with those determined using oxygen isotopes, which average $900 \pm 50^\circ\text{C}$ (Clayton 1993).

5. CONCLUSIONS

In this study we evaluated oxidation state and peak temperatures in ordinary chondrite parent bodies using mineral abundances determined using powder X-ray diffraction and supplemental chemical analyses. Based on our results, we suggest that oxidation occurred during progressive metamorphism, for which we cite the following observations as evidence:

1. Modal abundances of olivine and low-Ca pyroxene exhibit subtle but systematic changes with petrologic type. Ratios of olivine to low-Ca pyroxene abundances increase from type 4 to type 6 in all chondrite groups, suggesting that olivine was produced at the expense of pyroxene during progressive metamorphism.

2. In all three chondrite groups, mean Fa in olivine and mean Fs in low-Ca pyroxene increase with increasing petrologic type, indicating that silicate phases became progressively enriched in Fe as a result of oxidation.
3. Linear trends indicative of Fe addition in silicate minerals appear to be present in the H and LL chondrites, though not in the L chondrites. Although there is considerable overlap between data at different petrologic types, values generally plot in an Fe-enrichment sequence. Individual data are too variable to constitute convincing evidence for or against oxidation in the L chondrites.
4. Mean ratios of Ni/Fe and Co/Fe in bulk metal increase with petrologic type in the H chondrites. An increasing trend is also discernable in the L chondrites when standard deviations are considered; however, a trend cannot be distinguished in the LL chondrites due to limited sampling in the LL4s and LL5s.

The most plausible agent responsible for oxidation in the ordinary chondrite parent bodies is water, which was incorporated as accreted ice (McSween and Labotka 1993) or as hydrous silicates (Wasson 2000). Water reacted with metal to produce oxidized Fe, which was most likely incorporated into olivine and low-Ca pyroxene by grain boundary diffusion. Based on mass balance calculations of XRD-measured modal abundances, a minimum of 0.3 – 0.4 wt% H₂O was necessary to convert measured mineral abundances in type 4 chondrites to those in type 6.

Average plagioclase abundances increase slightly from the H to LL chondrites, but do not show any recognizable trends with petrologic type. Based on this observation and on a comparison of modal and normative plagioclase abundances, we suggest that plagioclase completely crystallized from glass by type 4 temperature conditions in the H and L chondrites

and by type 5 in the LL chondrites. It is possible that plagioclase crystallization was complete at a lower petrologic grade in the LLs, but this cannot be determined based on available data. Because the validity of using the plagioclase thermometer to determine peak temperatures rests on the assumption that plagioclase continued to crystallize through type 6 conditions, we suggest that temperatures calculated using pyroxene geothermometry provide more accurate estimates of the peak temperatures reached in ordinary chondrite parent bodies. Peak temperatures calculated using QUILF95 range from $866 \pm 63^{\circ}\text{C}$ to $967 \pm 25^{\circ}\text{C}$, and there is no appreciable difference in temperature estimates from each chondrite group.

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Appendix IV

Table 3.1. Chondrites analyzed in this study using X-ray diffraction

Sample	Class	Sample	Class	Sample	Class
Benares (a)*	LL4	Atarra*	L4	Farmville*	H4
Greenwell Springs	LL4	Bald Mountain*	L4	Forest Vale	H4
Hamlet*	LL4	Rio Negro*	L4	Kabo*	H4
Witsand Farm	LL4	Rupota*	L4	Marilia*	H4
Aldsworth*	LL5	Ausson*	L5	São Jose do Rio Preto*	H4
Alat'ameem	LL5	Blackwell	L5	Allegan*	H5
Olivenza*	LL5	Cilimus	L5	Ehole*	H5
Paragould*	LL5	Guibga*	L5	Itapicuru-Mirim	H5
Tuxtuac*	LL5	Mabwe-Khoywa	L5	Lost City*	H5
Bandong*	LL6	Malakal*	L5	Pribram*	H5
Cherokee Spring*	LL6	Messina*	L5	Schenectady*	H5
Karatu*	LL6	Apt*	L6	Uberaba	H5
Saint-Severin*	LL6	Aumale*	L6	Andura*	H6
		Karkh*	L6	Butsura*	H6
		Kunashak*	L6	Canon City*	H6
		Kyushu*	L6	Chiang Khan	H6
		New Concord*	L6	Guareña*	H6
				Ipiranga*	H6

*Denotes sample in which olivine and low-Ca pyroxene were analyzed using EMP

Table 3.2. Average abundances of olivine, low-Ca pyroxene, and plagioclase^{ab}

Chondrite Group	Number of analyses	Olivine	Low-Ca pyroxene	Plagioclase
H4	5	29.8 (0.4)	27.0 (1.1)	9.1 (0.5)
H5	7	33.1 (2.0)	25.2 (1.1)	8.9 (0.7)
H6	6	35.7 (2.2)	24.9 (2.1)	8.9 (0.4)
L4	4	40.7 (1.9)	23.6 (1.8)	9.5 (0.4)
L5	7	42.2 (2.0)	24.1 (1.3)	9.3 (1.5)
L6	6	43.0 (1.6)	21.7 (0.9)	9.5 (0.5)
LL4	4	49.7 (1.4)	22.6 (1.4)	9.7 (1.2)
LL5	5	51.1 (1.1)	21.8 (1.3)	9.6 (0.6)
LL6	4	52.5 (3.1)	18.9 (1.0)	9.9 (0.7)

^aValues are in wt%.

^b1 σ standard deviations are shown in parentheses.

Table 3.3. Average electron microprobe analyses for olivine in each H chondrite^{ab}

	Farmville	Kabo	São Jose do Rio Preto	Allegan	Ehole	Itapicura Mirim	Lost City	Pribram	Schnectady	Andura	Butsura	Canon City	Guareña	Ipiranga
	H4	H4	H4	H5	H5	H5	H5	H5	H5	H6	H6	H6	H6	H6
	[16]	[13]	[16]	[14]	[17]	[14]	[20]	[14]	[21]	[17]	[17]	[18]	[13]	[16]
SiO ₂	39.1 (4)	39.1 (3)	38.8 (6)	39.1 (5)	38.5 (3)	39.0 (4)	39.0 (2)	38.6 (4)	38.5 (6)	39.6 (4)	39.6 (4)	39.9 (3)	40.0 (4)	39.8 (3)
Cr ₂ O ₃	<0.03	<0.03	0.03 (8)	0.03 (3)	0.03 (3)	0.03 (4)	<0.03	0.08 (23)	0.04 (10)	<0.03	0.09 (35)	0.02 (3)	<0.03	<0.03
MgO	43.5 (3)	43.0 (4)	42.5 (4)	43.3 (4)	42.1 (4)	43.4 (3)	43.0 (3)	43.0 (3)	42.5 (2)	42.2 (3)	42.1 (3)	42.1 (2)	42.7 (2)	43.0 (3)
CaO	0.03 (1)	<0.03	0.04 (4)	0.08 (14)	<0.03	<0.03	0.03 (1)	<0.03	<0.03	0.03 (1)	0.04 (1)	0.03 (7)	<0.03	<0.03
MnO	0.45 (4)	0.47 (3)	0.50 (3)	0.48 (3)	0.46 (3)	0.47 (3)	0.47 (3)	0.46 (3)	0.45 (3)	0.47 (3)	0.45 (4)	0.46 (4)	0.47 (5)	0.46 (3)
FeO	16.5 (3)	17.1 (4)	17.6 (3)	16.7 (4)	18.0 (3)	17.4 (3)	17.6 (2)	17.4 (3)	17.7 (6)	18.0 (3)	17.7 (3)	17.8 (2)	18.1 (2)	17.7 (3)
Total	99.6	99.6	99.5	99.7	99.1	100.2	100.1	99.6	99.2	100.3	100.0	100.3	101.3	101.0
Cations based on 3 oxygens														
Si	0.99	1.00	0.99	1.00	0.99	0.99	0.99	0.99	0.99	1.00	1.01	1.01	1.00	1.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.65	1.63	1.63	1.64	1.62	1.64	1.63	1.64	1.63	1.60	1.60	1.59	1.60	1.61
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.35	0.36	0.38	0.35	0.39	0.37	0.37	0.37	0.38	0.38	0.38	0.38	0.38	0.37
Total	3.01	3.00	3.01	3.00	3.01	3.01	3.01	3.01	3.01	3.00	2.99	2.99	3.00	3.00
Fe/Mn	35.9	36.3	37.3	34.6	38.2	36.3	36.9	36.7	39.5	37.9	38.9	38.7	38.1	37.6
Fe/Mg	0.21	0.22	0.23	0.22	0.24	0.22	0.23	0.23	0.23	0.24	0.24	0.24	0.24	0.23

^aNumbers in brackets represent number of analyses averaged.^bNumbers in parentheses represent 1 σ precision of replicate analyses expressed as the least digit cited.

Table 3.4. Average electron microprobe analyses for olivine in each L chondrite^{ab}

	Atarra	Bald Mountain	Rio Negro	Rupota	Guibga	Ausson	Malakal	Messina	Apt	Aumale	Karkh	Kunashak	Kyushu	New Concord
	L4	L4	L4	L4	L5	L5	L5	L5	L6	L6	L6	L6	L6	L6
	[19]	[20]	[20]	[20]	[21]	[20]	[12]	[14]	[15]	[12]	[10]	[17]	[17]	[15]
SiO ₂	38.2 (4)	38.2 (4)	38.3 (4)	38.1 (2)	38.3 (2)	37.9 (2)	37.2 (5)	37.9 (5)	37.9 (3)	37.9 (3)	37.8 (6)	38.3 (4)	37.9 (4)	37.7 (3)
Cr ₂ O ₃	0.11 (38)	0.09 (23)	0.03 (3)	<0.03	0.04 (11)	<0.03	0.04 (5)	<0.03	<0.03	<0.03	<0.03	0.03 (2)	<0.03	0.03 (12)
MgO	39.7 (4)	40.1 (4)	38.9 (11)	38.8 (3)	39.2 (4)	38.8 (2)	38.8 (6)	39.0 (4)	38.4 (4)	38.9 (3)	38.6 (6)	39.2 (4)	38.8 (2)	38.6 (3)
CaO	0.03 (2)	<0.03	0.04 (3)	0.05 (2)	<0.03	<0.03	<0.03	0.04 (2)	0.03 (1)	<0.03	0.04 (1)	0.12 (21)	0.03 (1)	0.06 (3)
MnO	0.46 (3)	0.46 (4)	0.46 (4)	0.46 (4)	0.45 (4)	0.49 (3)	0.48 (4)	0.48 (3)	0.44 (4)	0.46 (3)	0.45 (3)	0.47 (4)	0.47 (4)	0.49 (24)
FeO	21.4 (3)	21.3 (3)	22.5 (15)	22.4 (4)	22.1 (4)	22.7 (2)	22.8 (7)	22.6 (4)	22.9 (4)	22.4 (3)	22.7 (6)	22.8 (4)	22.4 (3)	22.2 (4)
Total	99.9	100.1	100.3	99.9	100.2	100.0	99.3	100.0	99.8	99.7	99.7	100.9	99.6	99.0
Cations based on 3 oxygens														
Si	0.99	0.99	1.00	1.00	1.00	0.99	0.98	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.54	1.55	1.51	1.51	1.52	1.51	1.52	1.52	1.50	1.52	1.51	1.51	1.51	1.52
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.46	0.46	0.49	0.49	0.48	0.50	0.50	0.49	0.50	0.49	0.50	0.49	0.49	0.49
Total	3.01	3.01	3.00	3.00	3.00	3.01	3.02	3.01	3.01	3.01	3.01	3.01	3.01	3.01
Fe/Mn	46.2	46.2	46.2	48.9	48.5	46.2	47.9	46.0	51.2	48.9	50.5	48.5	47.2	46.7
Fe/Mg	0.30	0.30	0.30	0.32	0.32	0.33	0.33	0.33	0.33	0.32	0.33	0.33	0.32	0.32

^aNumbers in brackets represent number of analyses averaged.^bNumbers in parentheses represent 1 σ precision of replicate analyses expressed as the least digit cited.

Table 3.5. Average electron microprobe analyses for olivine in each LL chondrite^{ab}

	Bernares (a)	Hamlet	Aldsworth	Olivenza	Paragould	Tuxtuac	Bandong	Cherokee Springs	Karatu	Saint- Severin
	LL4	LL4	LL5	LL5	LL5	LL5	LL6	LL6	LL6	LL6
	[16]	[12]	[20]	[19]	[17]	[17]	[17]	[17]	[19]	[19]
SiO ₂	37.3 (3)	37.4 (4)	37.2 (5)	37.2 (2)	37.8 (3)	36.9 (3)	37.2 (3)	37.6 (3)	37.1 (5)	37.4 (4)
Cr ₂ O ₃	0.07 (18)	<0.03	0.17 (52)	<0.03	0.08 (9)	<0.03	0.03 (2)	0.04 (12)	0.03 (8)	0.01 (2)
MgO	35.9 (2)	38.6 (13)	36.3 (3)	35.4 (2)	36.8 (4)	34.9 (3)	35.3 (6)	36.7 (3)	34.9 (5)	35.8 (3)
CaO	0.05 (2)	0.04 (2)	0.04 (3)	0.04 (1)	0.08 (3)	0.05 (5)	0.05 (2)	0.04 (1)	0.04 (3)	0.06 (2)
MnO	0.51 (5)	0.46 (3)	0.47 (5)	0.44 (3)	0.46 (5)	0.44 (5)	0.44 (6)	0.45 (3)	0.45 (5)	0.45 (5)
FeO	26.0 (2)	25.3 (16)	25.4 (3)	27.1 (3)	25.2 (4)	27.1 (3)	27.6 (5)	25.8 (3)	28.1 (5)	27.0 (5)
Total	99.8	100.1	99.7	100.1	100.4	99.5	100.7	100.7	100.6	100.6
Cations based on 3 oxygens										
Si	0.99	0.990	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.42	1.45	1.44	1.41	1.44	1.40	1.40	1.44	1.39	1.41
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.58	0.56	0.57	0.60	0.55	0.61	0.61	0.57	0.63	0.60
Total	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01
Fe/Mn	50.0	53.7	53.9	60.9	54.1	60.9	63.2	55.3	62.6	59.9
Fe/Mg	0.41	0.39	0.39	0.43	0.38	0.44	0.44	0.40	0.45	0.42

^aNumbers in brackets represent number of analyses averaged.^bNumbers in parentheses represent 1 σ precision of replicate analyses expressed as the least digit cited.

Table 3.6. Average electron microprobe analyses for low-Ca pyroxene in each H chondrite^{ab}

	Farmville	Kabo	São Jose do Rio Preto	Allegan	Ehole	Itapicura Mirim	Lost City	Pribram	Schnectady	Andura	Butsura	Canon City	Guareña	Ipiranga
	H4	H4	H4	H5	H5	H5	H5	H5	H5	H6	H6	H6	H6	H6
	[12]	[18]	[16]	[14]	[16]	[14]	[19]	[14]	[12]	[13]	[13]	[12]	[9]	[13]
SiO ₂	55.9 (6)	55.9 (5)	55.7 (7)	56.3 (8)	55.3 (6)	56.1 (7)	56.1 (3)	55.8 (7)	55.4 (6)	57.1 (5)	56.8 (8)	57.1 (5)	57.6 (4)	57.0 (6)
TiO ₂	0.18 (9)	0.11 (8)	0.14 (7)	0.22 (11)	0.17 (8)	0.17 (5)	0.16 (7)	0.17 (5)	0.13 (5)	0.18 (4)	0.19 (6)	0.18 (5)	0.17 (4)	0.20 (6)
Al ₂ O ₃	0.36 (29)	0.33 (37)	0.23 (20)	0.25 (19)	0.15 (10)	0.35 (45)	0.20 (11)	0.21 (9)	0.22 (22)	0.25 (26)	0.20 (6)	0.21 (12)	0.16 (7)	0.20 (7)
Cr ₂ O ₃	0.40 (61)	0.20 (15)	0.39 (53)	0.24 (21)	0.13 (18)	0.29 (33)	0.19 (12)	0.12 (2)	0.11 (4)	0.12 (3)	0.15 (8)	0.15 (6)	0.11 (2)	0.13 (5)
MgO	31.3 (4)	30.8 (5)	31.0 (4)	31.3 (3)	30.4 (33)	30.9 (8)	31.2 (2)	31.0 (3)	31.0 (2)	30.8 (2)	30.5 (3)	30.7 (2)	30.9 (2)	31.1 (2)
CaO	0.58 (8)	0.59 (11)	0.59 (8)	0.67 (10)	0.74 (52)	0.81 (10)	0.70 (11)	0.70 (10)	0.67 (7)	0.71 (14)	0.82 (13)	0.80 (5)	0.72 (13)	0.71 (9)
MnO	0.51 (3)	0.48 (4)	0.50 (3)	0.50 (5)	0.50 (6)	0.50 (4)	0.49 (3)	0.49 (4)	0.51 (3)	0.48 (3)	0.47 (3)	0.59 (2)	0.52 (4)	0.50 (4)
FeO	10.6 (3)	10.9 (2)	11.1 (3)	10.6 (2)	11.3 (2)	11.1 (4)	11.0 (1)	11.3 (5)	11.3 (2)	11.2 (3)	11.3 (10)	11.2 (1)	11.4 (1)	11.3 (6)
Na ₂ O	<0.03	0.06 (13)	<0.03	<0.03	<0.03	0.07 (15)	0.03 (1)	<0.03	0.05 (10)	<0.03	<0.03	<0.03	<0.03	<0.03
Total	99.9	99.4	99.8	100.1	98.7	100.2	100.0	99.8	99.3	100.8	100.5	100.8	101.5	101.1
Cations based on 4 oxygens														
Si	1.98	1.99	1.98	1.98	1.98	1.98	1.98	1.98	1.98	2.00	2.00	2.00	2.00	1.99
Ti	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01
Al	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cr	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.60	1.63	1.64	1.64	1.63	1.62	1.64	1.64	1.65	1.61	1.60	1.60	1.60	1.62
Ca	0.03	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Mn	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01
Fe	0.30	0.32	0.33	0.31	0.34	0.33	0.32	0.34	0.34	0.33	0.33	0.33	0.33	0.33
Na	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	4.00	4.00	4.01	4.00	4.01	4.01	4.01	4.01	4.02	3.99	3.99	3.99	3.99	4.00
Fe/Mn	20.5	22.7	22.3	20.9	22.1	21.7	22.3	22.8	21.9	23.4	23.9	22.2	22.1	22.2
Fe/Mg	0.19	0.20	0.20	0.19	0.21	0.20	0.20	0.20	0.20	0.20	0.21	0.20	0.21	0.20

^aNumbers in brackets represent number of analyses averaged.

^bNumbers in parentheses represent 1 σ precision of replicate analyses expressed as the least digit cited.

Table 3.7. Average electron microprobe analyses for low-Ca pyroxene in each L chondrite^{ab}

	Attara	Bald Mountain	Rio Negro	Rupota	Ausson	Guibga	Malakal	Messina	Apt	Aumale	Karkh	Kunashak	Kyushu	New Concord
	L4	L4	L4	L4	L5	L5	L5	L5	L6	L6	L6	L6	L6	L6
	[16]	[17]	[18]	[18]	[18]	[18]	[12]	[14]	[12]	[12]	[13]	[20]	[13]	[12]
SiO ₂	55.6 (6)	55.5 (4)	55.4 (7)	55.4 (2)	55.0 (6)	55.4 (5)	54.7 (7)	55.1 (10)	54.9 (7)	54.9 (4)	54.7 (7)	55.3 (4)	55.2 (3)	55.0 (4)
TiO ₂	0.14 (8)	0.13 (7)	0.15 (6)	0.18 (6)	0.14 (6)	0.17 (4)	0.20 (11)	0.19 (2)	0.18 (2)	0.19 (4)	0.19 (3)	0.21 (5)	0.18 (2)	0.18 (3)
Al ₂ O ₃	0.16 (10)	0.18 (10)	0.36 (62)	0.23 (19)	0.13 (7)	0.17 (8)	0.33 (44)	0.18 (8)	0.19 (12)	0.16 (6)	0.24 (8)	0.24 (9)	0.20 (12)	0.22 (15)
Cr ₂ O ₃	0.15 (10)	0.19 (14)	0.40 (47)	0.21 (16)	0.11 (5)	0.21 (40)	0.17 (18)	0.12 (5)	0.10 (3)	0.11 (10)	0.19 (10)	0.18 (12)	0.11 (4)	0.11 (4)
MgO	29.9 (5)	29.8 (6)	29.4 (7)	29.0 (7)	29.0 (5)	29.2 (2)	28.8 (6)	29.1 (3)	28.5 (4)	28.9 (20)	28.6 (4)	29.2 (7)	28.9 (2)	28.8 (4)
CaO	0.41 (9)	0.80 (83)	0.7 (40)	1.02 (29)	0.72 (8)	0.64 (15)	0.79 (13)	0.84 (20)	0.77 (12)	0.74 (33)	1.11 (34)	1.04 (11)	0.85 (15)	0.91 (48)
MnO	0.45 (4)	0.49 (4)	0.46 (4)	0.46 (8)	0.48 (3)	0.46 (4)	0.47 (3)	0.48 (6)	0.47 (3)	0.48 (5)	0.49 (3)	0.49 (4)	0.48 (4)	0.48 (2)
FeO	13.2 (8)	13.0 (5)	13.4 (7)	13.4 (10)	13.7 (2)	13.7 (3)	13.9 (4)	13.8 (4)	14.3 (7)	13.9 (15)	14.2 (7)	13.8 (6)	13.6 (3)	13.5 (4)
Na ₂ O	0.03 (2)	<0.03	0.05 (3)	0.03 (2)	<0.03	0.03 (1)	0.08 (17)	0.03 (2)	<0.03	<0.03	0.04 (3)	0.04 (3)	0.03 (2)	<0.03
Total	100.0	100.1	100.2	99.9	99.4	100.0	99.4	99.9	99.5	99.4	99.7	100.6	99.6	99.3
Cations based on 4 oxygens														
Si	1.98	1.98	1.98	1.98	1.98	1.98	1.97	1.98	1.98	1.98	1.97	1.97	1.98	1.98
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00
Al	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cr	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Mg	1.59	1.59	1.56	1.55	1.56	1.56	1.55	1.56	1.53	1.55	1.54	1.55	1.55	1.55
Ca	0.02	0.03	0.03	0.04	0.03	0.02	0.03	0.03	0.03	0.03	0.04	0.04	0.03	0.03
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.39	0.39	0.40	0.40	0.41	0.41	0.42	0.42	0.43	0.42	0.43	0.41	0.41	0.41
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	4.01	4.01	4.01	4.01	4.01	4.01	4.02	4.01	4.01	4.01	4.02	4.02	4.01	4.01
Fe/Mn	28.9	26.3	29.2	29.2	28.0	29.4	29.2	28.4	30.4	28.3	28.8	27.7	27.9	27.9
Fe/Mg	0.25	0.24	0.26	0.26	0.27	0.26	0.27	0.27	0.28	0.27	0.28	0.26	0.26	0.26

^aNumbers in brackets represent number of analyses averaged.^bNumbers in parentheses represent 1 σ precision of replicate analyses expressed as the least digit cited.

Table 3.8. Average electron microprobe analyses for low-Ca pyroxene in each LL chondrite^a

	Benares (a)	Hamlet	Aldsworth	Olivenza	Paragould	Tuxtuac	Bandong	Cherokee Springs	Karatu	Saint-Severin
	LL4	LL4	LL5	LL5	LL5	LL5	LL6	LL6	LL6	LL6
	[12]	[14]	[15]	[18]	[17]	[14]	[16]	[19]	[17]	[19]
SiO ₂	54.3 (8)	54.7 (11)	54.6 (3)	54.7 (3)	55.2 (4)	54.5 (3)	54.6 (5)	55.1 (3)	54.5 (4)	54.8 (3)
TiO ₂	0.15 (9)	0.09 (9)	0.12 (6)	0.15 (5)	0.14 (7)	0.19 (10)	0.20 (3)	0.19 (5)	0.21 (2)	0.20 (2)
Al ₂ O ₃	0.42 (70)	0.70 (12)	0.30 (24)	0.13 (4)	0.16 (8)	0.17 (12)	0.23 (14)	0.16 (3)	0.22 (12)	0.18 (2)
Cr ₂ O ₃	0.31 (38)	0.46 (32)	0.21 (18)	0.11 (7)	0.17 (6)	0.10 (6)	0.17 (13)	0.10 (3)	0.15 (3)	0.16 (7)
MgO	27.2 (9)	28.0 (20)	27.9 (5)	27.4 (1)	27.9 (5)	27.2 (2)	27.3 (4)	28.1 (2)	26.9 (3)	27.7 (3)
CaO	1.20 (10)	0.98 (93)	0.81 (65)	0.79 (13)	0.87 (33)	0.76 (17)	1.04 (18)	0.87 (12)	1.12 (1)	0.89 (8)
MnO	0.44 (4)	0.44 (9)	0.44 (4)	0.44 (3)	0.45 (3)	0.45 (4)	0.43 (5)	0.46 (3)	0.44 (4)	0.45 (4)
FeO	15.1 (8)	14.5 (22)	15.3 (4)	16.1 (1)	15.4 (4)	16.3 (3)	16.5 (3)	15.4 (2)	17.0 (3)	16.0 (3)
Na ₂ O	0.08 (5)	0.06 (7)	0.04 (3)	<0.03	<0.03	<0.03	0.03 (1)	0.03 (2)	0.06 (6)	0.03 (2)
Total	99.2	99.9	99.7	99.9	100.3	99.8	100.5	100.5	100.6	100.4
Cations based on 4 oxygens										
Si	1.98	1.97	1.98	1.98	1.98	1.98	1.97	1.98	1.97	1.97
Ti	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01
Al	0.02	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cr	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.48	1.50	1.51	1.48	1.50	1.47	1.47	1.51	1.45	1.49
Ca	0.05	0.04	0.03	0.03	0.03	0.03	0.04	0.03	0.04	0.03
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.46	0.44	0.46	0.49	0.46	0.49	0.50	0.46	0.51	0.48
Na	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	4.01	4.01	4.01	4.01	4.01	4.01	4.02	4.01	4.02	4.01
Fe/Mn	33.5	33.1	33.9	35.7	33.7	35.7	38.5	33.3	35.7	35.3
Fe/Mg	0.31	0.29	0.31	0.33	0.31	0.34	0.34	0.31	0.34	0.32

^aNumbers in brackets represent number of analyses averaged.^bNumbers in parentheses represent 1 σ precision of replicate analyses expressed as the least digit cited.

Tabel 3.9. Mean weight ratios and standard deviations of bulk metal compositions from Jarosewich (1990)

Chondrite Group	Ni/Fe	Standard Deviation	Co/Fe	Standard Deviation
H4	0.102	0.007	0.0043	0.0012
H5	0.108	0.011	0.0048	0.0012
H6	0.109	0.006	0.0054	0.0006
L4	0.177	0.021	0.0087	0.0013
L5	0.169	0.017	0.0086	0.0012
L6	0.189	0.030	0.0096	0.0012
LL4	0.346	ind. ^a	0.0160	ind.
LL5	0.883	ind.	0.0325	ind.
LL6	0.779	0.386	0.0354	0.0188

^aIndeterminate, only one analyses available

Table 3.10. Measured and mass balanced changes in abundances from petrologic type 4 to 6^a

	Measured decrease in low-Ca pyroxene	Decrease in metallic Fe		Increase in Olivine		H ₂ O required
		Balanced	Measured	Balanced	Measured	
H4-H6	2.1%	1.2%	1.6%	3.6%	5.9%	0.4%
L4-L6	1.9%	1.1%	0.4%	3.3%	2.3%	0.3%
LL4-LL6	3.7%	2.1%	1.2%	6.4%	2.8%	0.7%

^aValues are in wt%.

Table 3.11. Average electron microprobe analyses for high-Ca pyroxene in type 6 chondrites^a

	Butsura	Ipiranga	Karkh	Kunashak	Kyushu	Bandong	Cherokee Springs	Karatu	St. Severin
	H6	H6	L6	L6	L6	LL6	LL6	LL6	LL6
	[3]	[1]	[13]	[1]	[1]	[3]	[4]	[8]	[3]
SiO ₂	54.6 (13)	54.8	53.4 (2)	54.0	53.4	53.1 (8)	53.7 (3)	53.5 (3)	53.4 (3)
TiO ₂	0.44 (3)	0.51	0.49 (2)	0.47	0.51	0.49 (3)	0.44 (3)	0.46 (3)	0.43 (5)
Al ₂ O ₃	1.32 (77)	0.50	0.51 (2)	0.50	0.52	0.90 (39)	0.53 (9)	0.56 (10)	0.50 (3)
Cr ₂ O ₃	0.75 (3)	0.80	0.88 (46)	0.91	0.98	0.91 (2)	0.66 (8)	0.82 (6)	0.79 (11)
MgO	16.5 (4)	17.2	16.7 (1)	16.9	16.7	16.3 (2)	16.6 (1)	16.3 (2)	16.4 (1)
CaO	21.6 (5)	23.0	21.9 (1)	21.1	21.7	20.7 (6)	22.1 (3)	21.0 (3)	21.3 (5)
MnO	0.24 (1)	0.18	0.24 (2)	0.24	0.23	0.29 (4)	0.21 (6)	0.24 (3)	0.22 (4)
FeO	4.44 (12)	3.42	5.05 (18)	5.14	4.97	6.51 (59)	4.96 (16)	6.76 (28)	6.47 (36)
Na ₂ O	0.64 (2)	0.54	0.59 (1)	0.60	0.57	0.61 (3)	0.53 (7)	0.55 (3)	0.50 (6)
Total	100.5	101.1	99.7	99.9	99.6	99.9	99.7	100.1	100.1
Cations based on 4 oxygens									
Si	1.98	1.98	1.97	1.98	1.97	1.96	1.98	1.97	1.97
Ti	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Al	0.06	0.02	0.02	0.02	0.02	0.04	0.02	0.02	0.02
Cr	0.02	0.02	0.03	0.03	0.03	0.03	0.02	0.02	0.02
Mg	0.89	0.93	0.92	0.93	0.92	0.90	0.91	0.89	0.90
Ca	0.84	0.89	0.86	0.83	0.86	0.82	0.87	0.83	0.84
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.14	0.10	0.16	0.16	0.15	0.20	0.15	0.21	0.20
Na	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Total	3.99	4.00	4.01	4.00	4.01	4.01	4.01	4.01	4.01

^aNumbers in parentheses represent 1σ precision expressed as the least digit cited.

Table 3.12. Peak metamorphic temperatures (°C) calculated from average low- and high-pyroxene compositions

			Maximum T	Minimum T
			Cpx - 1 σ CaO	Cpx + 1 σ CaO
			Opx + 1 σ CaO	Opx - 1 σ CaO
		Pyroxene pairs		
Butsura	H6	929 $\pm$ 20	950 $\pm$ 15	894 $\pm$ 20
Ipiranga	H6	866 $\pm$ 63	Indeterminate ^a	
Karkh	L6	967 $\pm$ 25	1022 $\pm$ 38	896 $\pm$ 15
Kunashak	L6	964 $\pm$ 39	Indeterminate	
Kyushu	L6	894 $\pm$ 64	Indeterminate	
Bandong	LL6	933 $\pm$ 50	984 $\pm$ 41	888 $\pm$ 70
Cherokee Springs	LL6	876 $\pm$ 66	910 $\pm$ 64	837 $\pm$ 66
Karatu	LL6	945 $\pm$ 44	974 $\pm$ 39	916 $\pm$ 49
St. Severin	LL6	904 $\pm$ 35	934 $\pm$ 24	884 $\pm$ 49

^aOnly one cpx analyses available

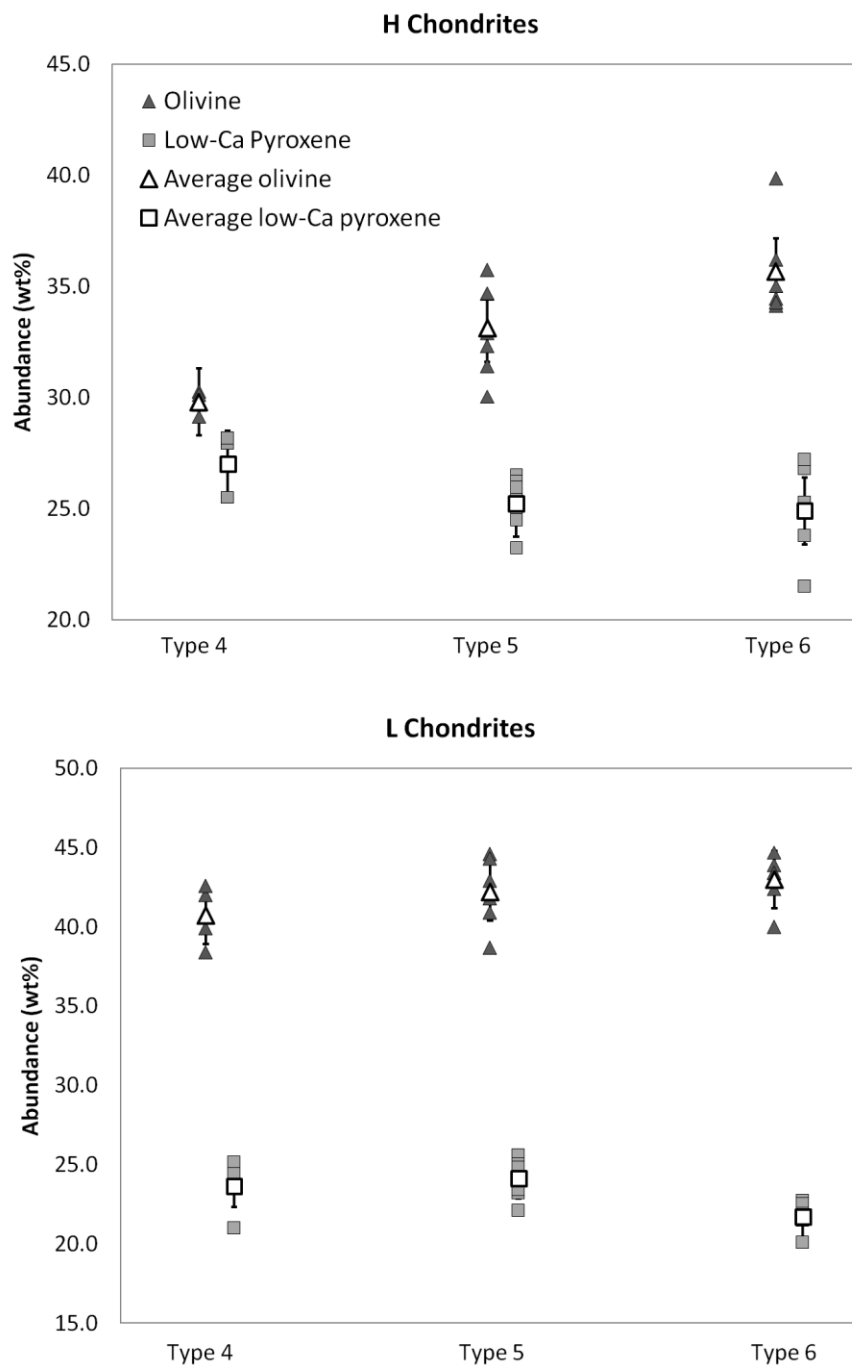


Figure 3.1. XRD-measured olivine and low-Ca pyroxene abundances of each chondrite measured in this study. Closed symbols represent average abundances. Error bars are 1σ standard deviations or mean abundances. Average abundances and standard deviations are listed in Table 3.2.

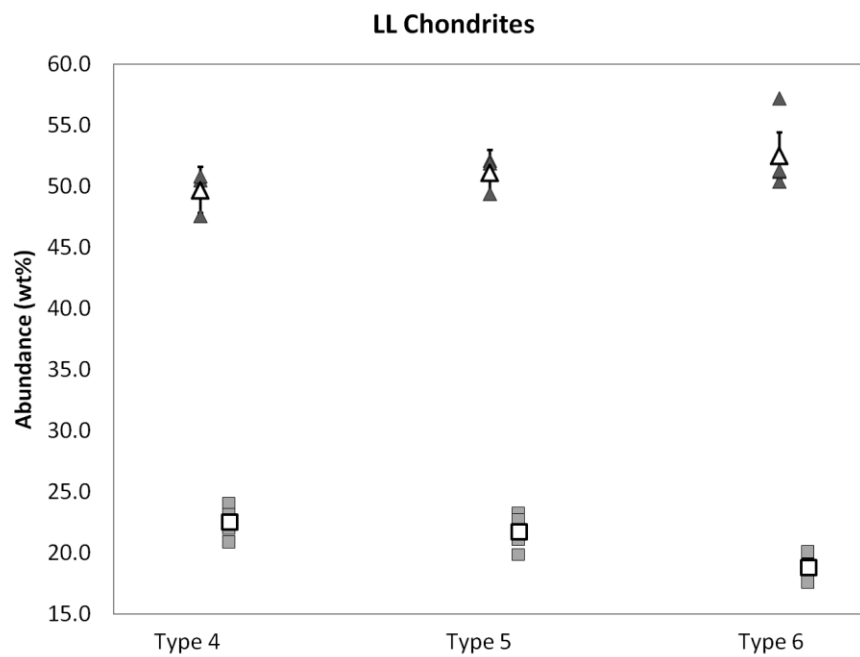


Figure 3.1. Continued.

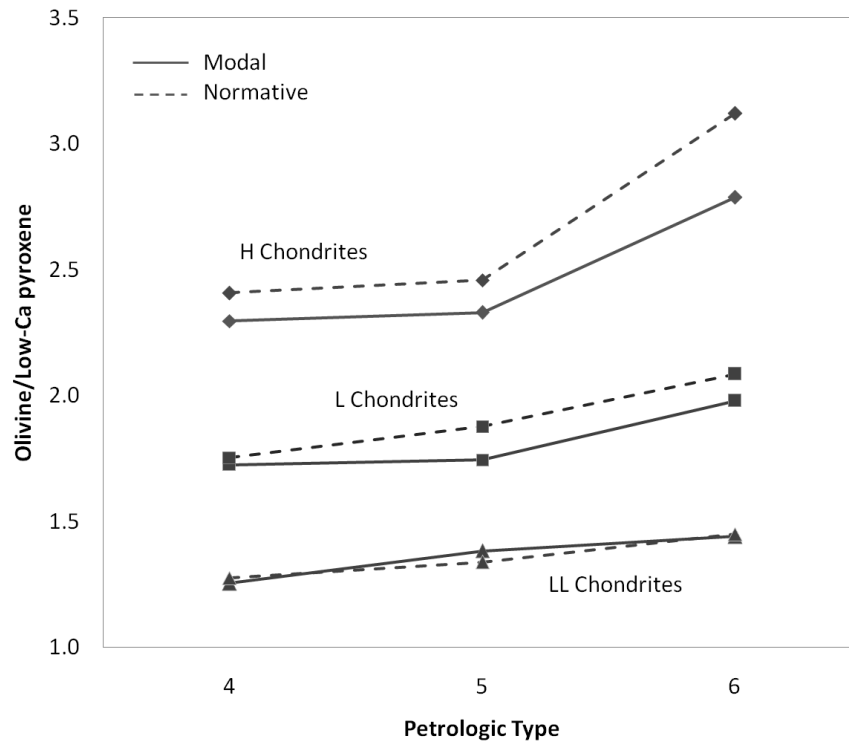


Figure 3.2. Ol/Px ratios of H, L, and LL chondrites determined from modal data (this study) and normative data (McSween et al. 1991). Ratios in both sets of data increase from petrologic type 4 to petrologic type 6.

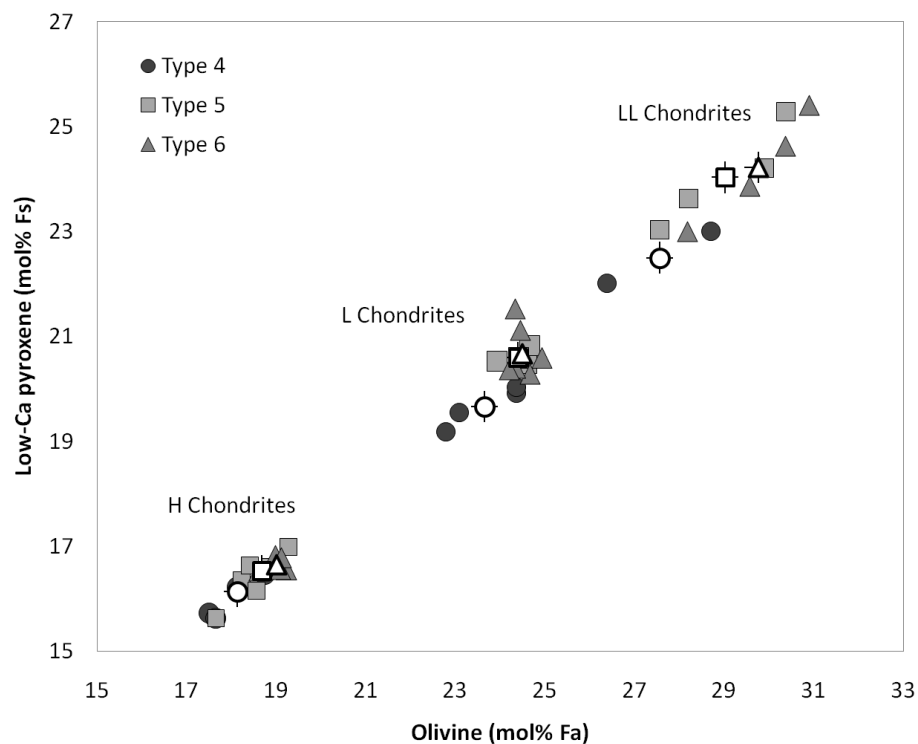


Figure 3.3. Olivine (as mol% Fa) versus low-Ca pyroxene (as mol% Fs) in the H, L, and LL chondrites. Symbols are average analyses from each chondrite analyzed in this study; circles are type 4 chondrites, squares are type 5, and triangles are type 6. Overall averages of all samples at each petrologic type are shown as open symbols with crosshairs. 1σ standard deviations are smaller than the symbols.

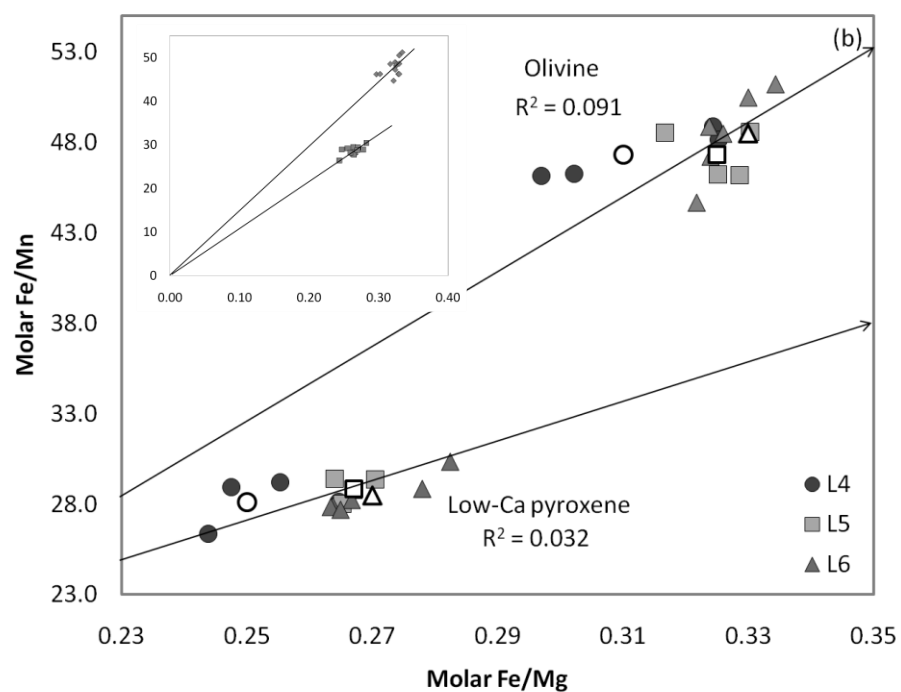
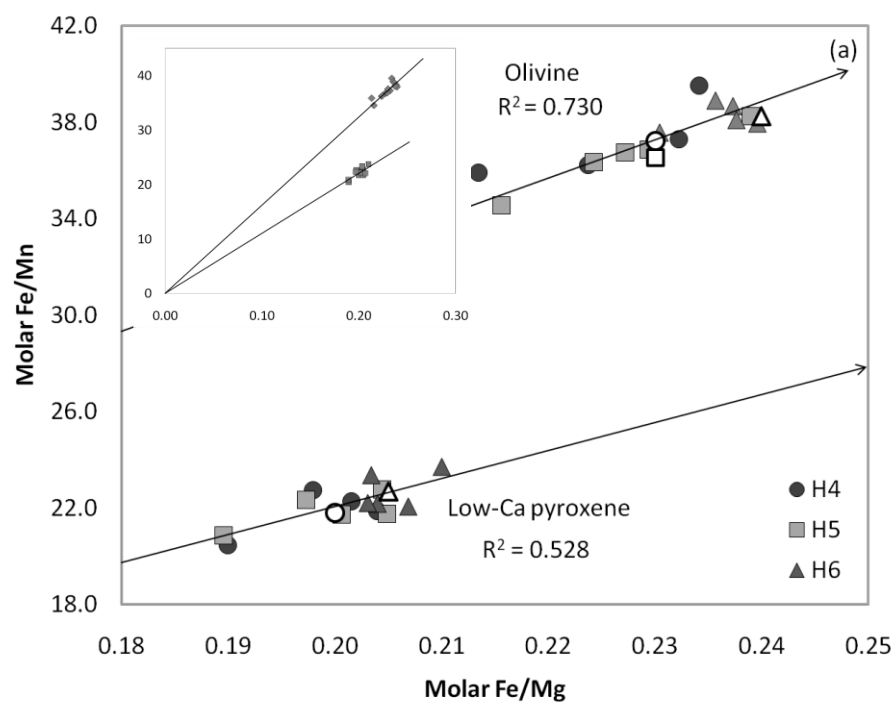


Figure 3.4. Molar Fe/Mn versus Fe/Mg ratios for olivine and low-Ca pyroxene in a) H, b) L, and c) LL chondrites. Solid symbols represent average analyses from each chondrite; Open symbols are averages for each petrologic type. Each insert shows a linear regression of data, where the y-intercept is zero.

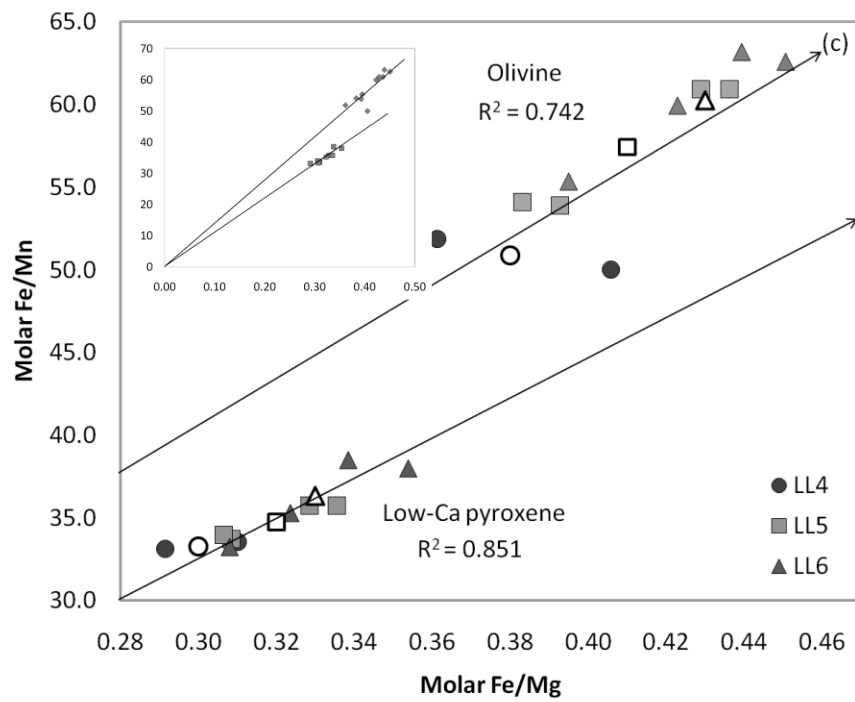


Figure 3.4. Continued.

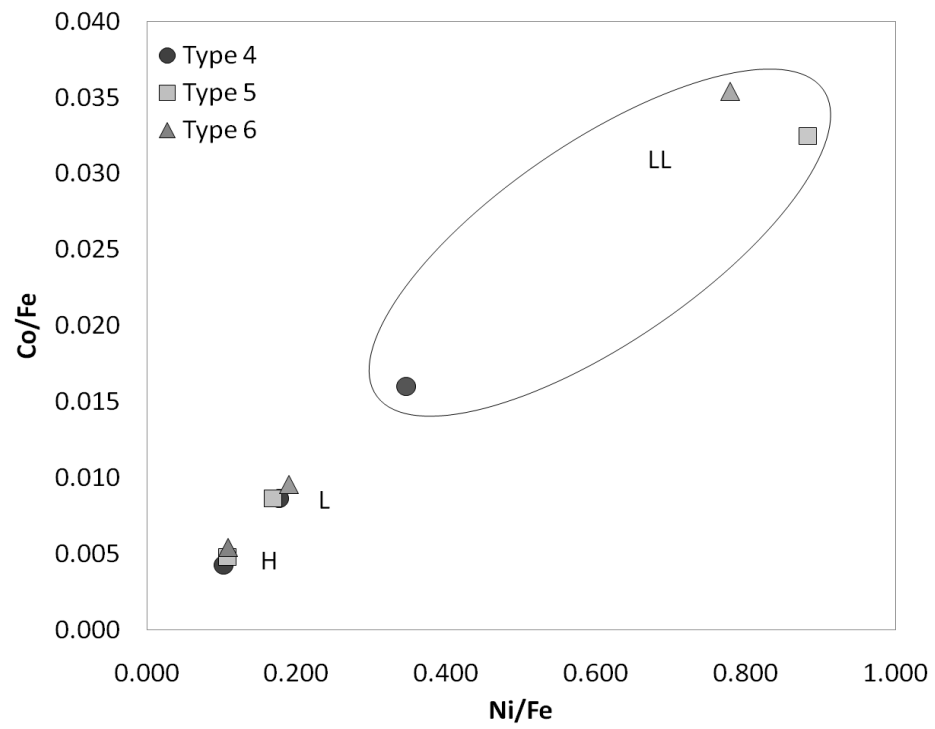


Figure 3.5. Weight ratios of Ni/Fe and Co/Fe (from Jarosewich 1990) in 18 H, 15 L, and 6 LL chondrites analyzed in this study.

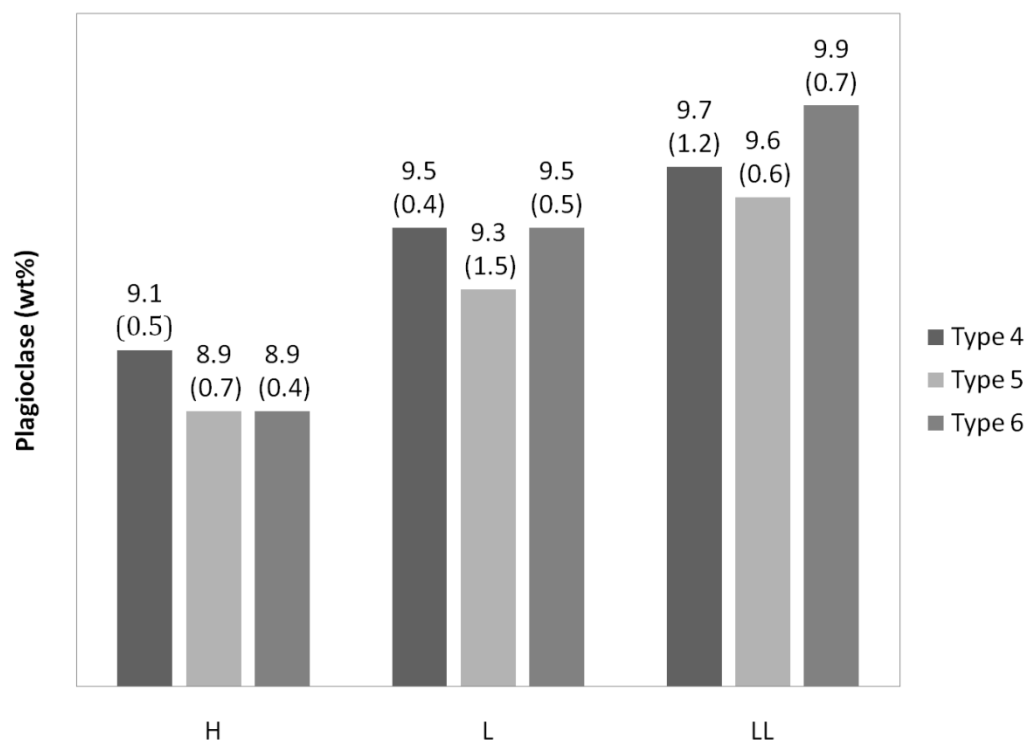


Figure 3.6. XRD-measured modal abundances (wt%) of plagioclase in the H, L, and LL chondrites at petrologic types 4, 5, and 6. 1 σ standard deviations are in parentheses.

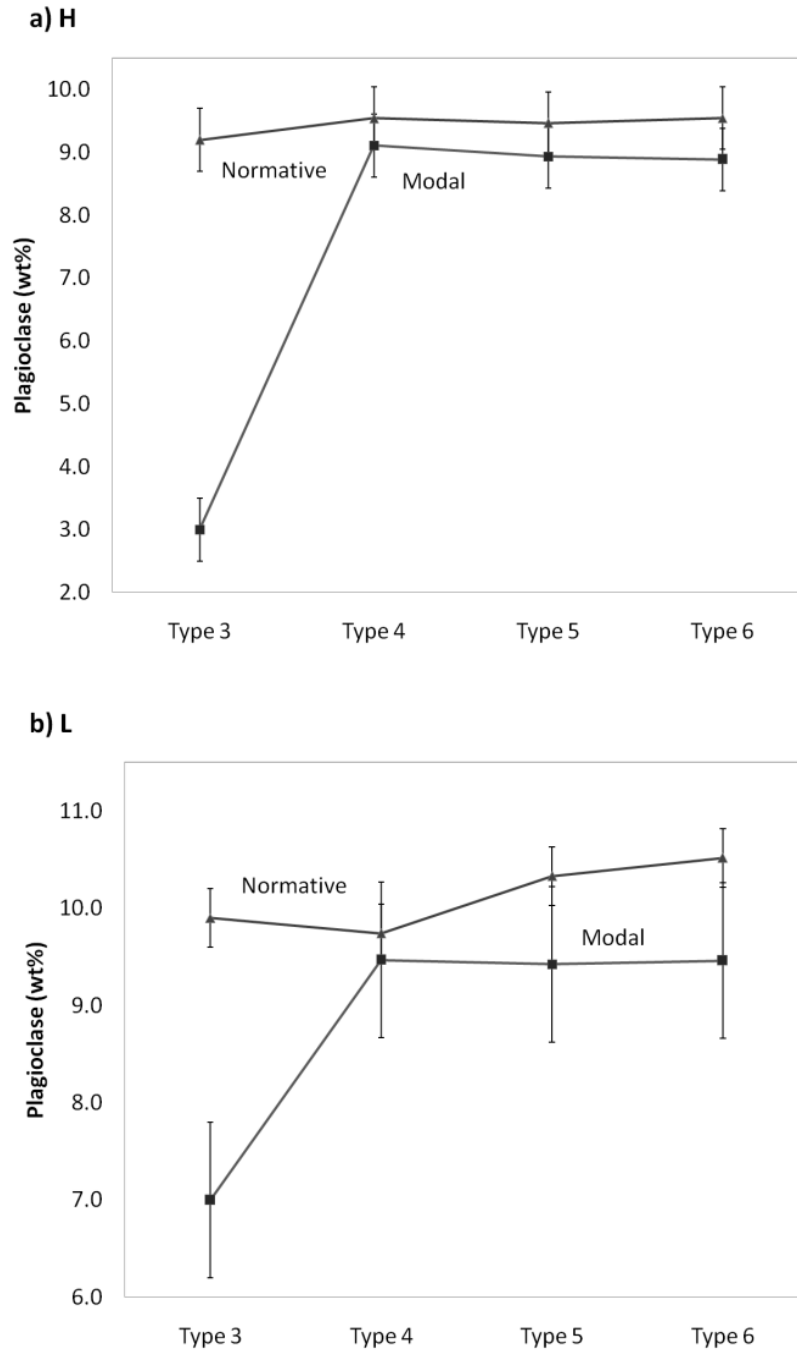


Figure 3.7. XRD-measured modal plagioclase abundances for the (a) H, (b) L, and (c) LL chondrites plotted against normative plagioclase abundances from McSween et al. (1991). Type 3 modal abundances are from Menzies et al. 2005. Standard deviations of modal plagioclase abundances are listed in Table 2. 1σ standard deviations for type 3 chondrites are 0.5 wt% for the Hs and 0.3 wt % for the Ls and LLs.

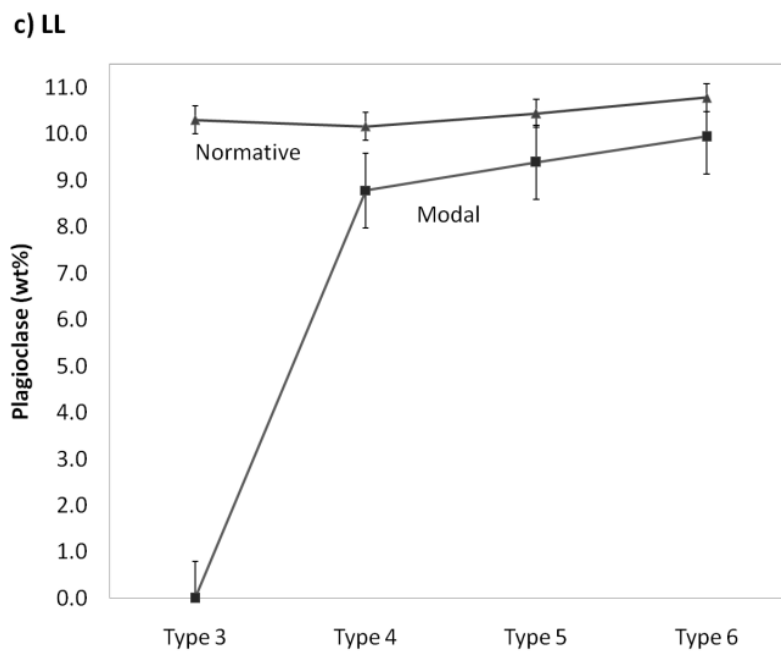


Figure 3.7. Continued.

PART IV

SPECTROSCOPIC CALIBRATIONS FOR ORDINARY CHONDRITES AND THEIR PARENT ASTEROIDS

This chapter is a reformatted version of a paper, by the same name, to be submitted to *Icarus* by Tasha L. Dunn, Harry Y. McSween Jr., Timothy J. McCoy, Jessica A. Sunshine and Thomas H. Burbine.

Dunn T.L., McSween H.Y. Jr., McCoy T.J., J.A. Sunshine, and T.H. Burbine. Spectroscopic Calibrations for Ordinary Chondrites and Their Parent Asteroids

ABSTRACT

Mineral compositions and abundances derived from visible/near-infrared (VISNIR) spectra are used to classify asteroids, identify meteorite parent bodies, and understand the structure of the asteroid belt. Using a suite of 48 equilibrated (types 4-6) ordinary (H, L, and LL) chondrites containing orthopyroxene, clinopyroxene, and olivine, we have derived new calibrations for determining mineralogy (ol/(ol+px) and cpx/(opx+cpx) ratios) from VISNIR spectra. Ol/(ol+px) calibrations produce mineral abundances that agree very well with measured data for all ordinary chondrites groups, and also appear to be valid for other meteorites with mineral abundances and chemistries similar to those of the ordinary chondrites. Calibrations for cpx/(opx+cpx) do not appear to be valid, based on low R^2 values, suggesting that it is not possible to establish the abundances of all mafic silicates from reflectance spectra using simple regressions. Ordinary chondrite spectral data from this study also indicate that FeO content may be the controlling factor in the spectral classification of the S(IV) asteroids, rather than mixing of olivine and low-Ca pyroxene, as the current classification would suggest.

1. INTRODUCTION

Visible/near-infrared spectra have been widely used to determine mafic mineral abundances and compositions of asteroids since the relationship between spectral properties (i.e. absorption features) and mineralogy in meteorites was first recognized (Adams 1974; Adams 1975; Burns et al. 1972; Cloutis 1985; Cloutis and Gaffey 1991). Most previous work examining the spectral properties of silicate minerals has focused on olivine and pyroxene, both

of which have diagnostic spectral properties in the VISNIR. Olivine and pyroxene are the two primary mineral components of ordinary chondrites, and are found extensively in many types of non-chondritic meteorites.

The primary diagnostic feature in olivine is a composite absorption feature at $\sim 1 \mu\text{m}$, which can be distinguished as three distinct absorption bands. This feature is attributed to electronic transitions of Fe^{2+} that occupies both the M1 and M2 crystallographic sites (Burns 1970). Pyroxenes have two absorption bands at $\sim 1 \mu\text{m}$ (Band I) and $\sim 2 \mu\text{m}$ (Band II), both of which are associated with crystal field transitions in Fe^{2+} , which preferentially occupies the M2 site (Clark 1957; Burns 1970). Orthopyroxenes, which are conventionally defined as having less than 11 mol% CaSiO_3 (wollastonite, or Wo) (Adams 1974), show a well-defined relationship between absorption band positions and composition, as both Band I and Band II positions increase with increasing ferrous iron content (Adams 1974; Burns et al. 1972; Cloutis 1985). There is also a correlation between composition and band positions in clinopyroxenes, although the relationship is complicated by the presence of calcium in addition to iron. In spectral type B clinopyroxenes ($< \text{Wo}_{50}$), there is a positive correlation between calcium content and Band I and II position, regardless of iron content (Cloutis and Gaffey 1991). However, there does not appear to be a systematic relationship between Band I or Band II position and Ca and Fe content in spectral type A clinopyroxenes ($> \text{Wo}_{50}$) (Cloutis and Gaffey 1991). In mixtures of orthopyroxene and clinopyroxene, spectral shape and band positions are dominated by the orthopyroxene component, as clinopyroxene only begins to affect the band positions at abundances $> 75 \text{ wt\%}$ (Cloutis and Gaffey 1991).

In addition to pyroxene composition, Bands I and II are also sensitive to the relative proportions of olivine and pyroxene. The ratio of the areas of these two bands (Band II/Band I)

(Cloutis et al. 1986) is commonly used to estimate olivine and pyroxene abundances in meteorites and asteroids. The band area ratio (BAR) can be expressed graphically (Gaffey et al. 1993) or as a linear regression function relating band area ratio to relative abundances of olivine and pyroxene (Cloutis et al. 1986). Cloutis et al. (1986) first recognized that the ratio of pyroxene to olivine + pyroxene ($px/(ol+px)$) was a linear function of the band area ratio in mixtures of olivine and orthopyroxene. They expressed this relationship as

$$BAR = 0.024 \times (px/(ol+px)) - 1.25. \quad (1)$$

While Cloutis et al. (1986) utilized this equation to derive BARs from mixtures of known mineral proportions, Gastineau-Lyons et al. (2002) applied this equation to deriving mineral abundances from BARs of asteroid spectra, recasting the Cloutis et al. (1996) calibration as

$$px/(ol+px) = 0.417 \times BAR + 0.052. \quad (2)$$

Because the Cloutis et al. (1986) regression is based on simple mixtures of olivine and orthopyroxene, the presence of more than one pyroxene (or other additional phases) could complicate spectral interpretations made using this calibration.

In an attempt to determine the mineralogy of the S-type asteroids, Burbine et al. (2003) used normative olivine, orthopyroxene, and clinopyroxene abundances of ordinary chondrites to derive a relationship between BAR and $ol/(ol+px)$. Burbine et al. (2003) expressed their equation as

$$ol/(ol+px) = -0.228 \times BAR + 0.768. \quad (3)$$

The Burbine et al. (2003) calibration yields ordinary chondrite $ol/(ol+px)$ ratios between 0.50 and 0.72, which fall within the same general range of $ol/(ol+px)$ ratios measured from normative mineral abundances of ordinary chondrites (McSween et al. 1991). There are systematic

differences, however, between ol/(ol+px) ratios calculated from spectra and ratios measured from normative mineral abundances.

In this paper, we revisit spectral calibrations for mineral abundances using a suite of 48 ordinary chondrites, for which quantitative determinations of actual orthopyroxene, clinopyroxene, and olivine abundances and compositions have been made (Dunn et al. 2008). New calibrations based on the ordinary chondrites should yield more accurate mineralogical interpretations of asteroid spectra.

2. ANALYTICAL METHODS

Reflectance spectra of 48 H, L, and LL ordinary chondrites were acquired using a bidirectional spectrometer at Brown University's Keck/NASA Reflectance Experiment Laboratory (RELAB). Spectra of 37 chondrite falls in this study were collected by Burbine et al. (2003), from powders originally prepared for bulk chemical analysis by E. Jarosewich as part of the Smithsonian Institution's Analyzed Meteorite Powder Collection. Small chips of the remaining 11 chondrites (RELAB IDs MT-HYM-075 through MT-HYM-085) were acquired from the Natural History Museum in London and from the Smithsonian Institution. These samples were ground with mortar and pestle to an approximate grain size of 100 μm , and the metal fraction of the samples was removed magnetically. This is consistent with sample preparation described in Burbine et al. (2003), for which only the silicate portion of each sample (<150 μm) was analyzed. Removing metal does not affect spectrally derived mineral abundances or compositions. Spectra for all 48 samples were collected over a range of 0.32 to 2.55 μm at a sampling interval of 0.01 μm . An incident angle of 30° and an emission angle of 0° were used during spectral analysis. Representative spectra of all H, L, and LL chondrites are shown in Figure 4.1. (All Figures and Tables are located in Appendix V). Band area ratios (BARs) were derived by

calculating the area underneath a tangent line connecting the peaks on either side of an absorption band, which yields an average uncertainty of 0.1. Band centers were determined by dividing out a linear continuum from the peak at 0.7 μm to the peak at 1.5 μm and then selecting the lowest point each band as the center. The uncertainty of band centers is typically between 0.02 and 0.04 μm . Classifications, grain sizes, and spectral BARs are listed in Table 4.1.

Mineral abundances of all 48 ordinary chondrites were determined using a whole-pattern XRD fitting procedure, as previously reported and described by Dunn et al. (2008). These data are expressed in weight proportions rather than volume proportions, to allow for easy comparison with normative and spectral abundances. Ol/(ol+px) ratios from this dataset are given in Table 4.2, along with the same ratios calculated from CIPW norms using the bulk chemical analyses of Jarosewich (1990). XRD-measured and normative cpx/(opx+cpx) ratios are given in Table 4.3. The average error associated with XRD-measured ol/(ol+px) ratios is 0.1, which is calculated using the uncertainty of the XRD technique. The average uncertainty for normative ratios is 0.01 (Burbine et al. 2003).

3. RESULTS

3.1. Olivine and Pyroxene Abundances

XRD-measured weight ratios of ol/(ol+px) vary slightly from those based on normative mineral abundances of McSween et al. (1991) (Table 4.2). XRD-measured ratios are systematically lower than normative weight ratios due to differences between measured and normative abundances of olivine and high-Ca pyroxene (Dunn et al. 2008). A thorough examination normative and XRD mineral abundances, along with a discussion of error associated with the XRD method, is presented by Dunn et al. (2008). We suggest that XRD-measured abundances are more representative of ordinary chondrite mineralogies, and

therefore use measured abundances of olivine and pyroxene to derive a new equation for determining ol/(ol+px) ratios from spectra. Linear regression of ol/(ol+px) modal ratios as a function of BARs is presented in Figure 4.2a. A least-squares fit of the data yields

$$\text{ol}/(\text{ol}+\text{px}) = -0.230 \times \text{BAR} + 0.726, \quad (4)$$

with an R^2 value of 0.672. Ol/(ol+px) ratios derived from reflectance spectra using equation (6) are presented in Table 4.2. The error associated with the calculated ol/(ol+px) ratios is the mean absolute difference between measured and spectrally derived values (± 0.03).

Our calibration is very similar to that of Burbine et al. (2003), although the Burbine calibration yields a much higher R^2 value (0.932). Burbine et al. (2003) based their calibration on normative ol(ol+px) ratios in 39 ordinary chondrites, one R chondrite (high olivine abundance), and one angrite (high pyroxene abundance). Only 19 of the same chondrites were used in both our study and the Burbine et al. (2003) study, but normative data are available for a total of 38 chondrites examined here. A regression of normative ol/(ol+px) ratios from these 38 chondrites as a function of BAR (Figure 4.2b) demonstrates that there is no appreciable difference between the R^2 values derived from XRD-measured ratios (0.672) and from normative ratios (0.632) for the samples in this study. The Burbine et al. (2003) regression may have a higher R^2 value because the trend is anchored by two outliers, an angrite and an R chondrite, which were not included in our calibration. Both calibrations yield ol/(ol+px) ratios that correlate well with measured and normative weight ratios. However, ol/(ol+px) ratios derived using our calibration correlate better with XRD-measured than ratios derived using the Burbine et al. (2003) calibration in 73% of the samples.

Our equation appears to be valid for other meteorites with mineralogies similar to those of the ordinary chondrites (e.g. alcapulcoites), but does not work well on samples dominated by

either olivine or pyroxene, such as R-chondrites, Angrites, and Eucrites. Our calibration yields an ol/(ol+px) ratio of 0.50 for Alcapulco, a primitive achondrite with a normative ol/(ol+px) ratio of 0.52. However, D'Orbigny, an angrite with a measured ol/(ol+px) ratio of 0.65, yields a spectrally derived ratio of 0.72. The spectrally derived ol/(ol+px) ratio of the R chondrite Rumuruti is 0.71, significantly lower than its normative ol/(ol+px) ratio of 0.94. We also derived ol/(ol+px) ratios for 11 eucrites, differentiated meteorites that contain two pyroxenes and no olivine. In the absence of olivine, the ol/(ol+px) ratio of the eucrites should be zero. Our calibration yields ol/ol+px ratios ranging from 0.12 to 0.46. This is not, however, significantly different from the Cloutis et al. (1986) calibration, which yields very similar values and only correctly measures the ol/(ol+px) ratios in 3 eucrites.

3.2. Low- and High-Ca Pyroxene Abundances

Gaffey et al. (2002) proposed that mafic silicate abundances can be constrained even further by considering the effect of high-Ca pyroxene on the Band II position, which they suggested is an almost linear function of the relative abundance of the two pyroxenes. Gaffey et al. (2002) derived ratios of high-Ca pyroxene to total pyroxene (cpx/(opx+cpx)) for average normative ordinary chondrite clinopyroxene abundances, but did not provide a calibration for this calculation. Using XRD-measured pyroxene abundances and Band II centers, we have derived an equation for establishing the ratio of high-Ca pyroxene to total pyroxene. A least-squares fit of the data (Figure 4.3a) yields

$$\text{cpx}/(\text{opx}+\text{cpx}) = 0.533 \times \text{Band II center} - 0.795, \quad (5)$$

with a very low R^2 value of 0.145. XRD-measured cpx/(opx+cpx) ratios, normative ratios, and ratios derived from reflectance spectra are presented in Table 4.3. The uncertainties for each method are the same those for stated previously. Although spectrally derived cpx/(cpx+opx)

ratios correspond well with measured ratios, the R^2 value indicates this correlation is poorly constrained. This relationship appears to be even less valid for normative cpx/(cpx+opx) ratios, which yield an R^2 value of only 0.072 (Figure 4.3b). These results indicate that there is no significant correlation between Band II position and relative pyroxene abundance. We conclude that Band II should not be used to derive pyroxene abundances from reflectance spectra.

4. SPECTROSCOPIC CLASSIFICATION OF THE S(IV) ASTEROIDS

Our calibrations for deriving ol/(ol+px) ratios from reflectance spectra are best suited for samples with mineralogies consisting of olivine, orthopyroxene, and clinopyroxene. The majority of asteroids, with the exception of the M-type asteroids, are dominated by these mafic silicate minerals. Of the many asteroid classes, our calibrations are particularly well suited for the S-type asteroids. The S(IV) subgroup is thought to contain objects with mineralogies similar to the ordinary chondrites (Gaffey et al. 1993; Murchie and Pieters 1996), and the S(IV) asteroid 6 Hebe has been hypothesized to be the parent body of the H chondrites (Gaffey and Gilbert 1998). Figure 4.4 shows that the majority of our ordinary chondrites, along with two S(IV) asteroids, Eros and Itokawa, plot in the spectral region associated with S(IV) objects. Several ordinary chondrites, however, plot outside this field. The size of the L chondrite field, which is larger than the H and LL fields, may be due to impact shock on the L chondrite parent body. Shock effects on the mineralogies and chemistries of these ordinary chondrite samples are discussed in Dunn et al. (2008).

The current classification for S(IV) asteroids is based primarily on the suggestion that all ordinary chondrites form a mixing line between olivine and low-Ca pyroxene (as seen on Figure 4.4). However, examination of the ordinary chondrite spectral data from this study suggests that there is an alternative interpretation. The H, L, and LL chondrites appear to form linear

trends, in which BI center increases at a constant BAR. This may suggest that BI center is controlled almost entirely by the abundance of FeO in olivine and pyroxene, and can serve as a proxy for bulk FeO content. Because BAR is a measure of the abundances of olivine and pyroxene, it should also serve as a proxy for ol/(ol+px) ratios. If both of these proxies are valid, then the linear relationship between BAR and BI center should be reproducible using mol % Fa or mol % Fs (as a measure of FeO) and ol/(ol+px). Figures 4.5a and 4.5b show mol% Fa and mol% Fs, respectively, plotted as a function of ol/(ol+px) in the 48 chondrite samples analyzed in this study. In both cases, the FeO proxy (mol% Fa or Fs) increases with constant ol/(ol+px), suggesting that BI center is a function of FeO content.

Based on the linear relationship between BI center and BAR in ordinary chondrites, we have developed a new classification for S(IV) asteroids (Figure 4.6). It appears that, instead of the “boot”-shaped area previously associated with the S(IV) asteroids, which was based on mixing of olivine and pyroxene, this field is better described by an “L” shape, in which FeO contents in the ordinary chondrite groups increase linearly from the Hs to the LLs (Figure 4.6). The H, L, and LL ordinary chondrites occur as distinct clusters, although the H and L chondrite groups overlap slightly, allowing this diagram to be used to distinguish the three ordinary chondrite groups. Based on our interpretations, it seems unlikely that the spectra of all ordinary chondrites fall precisely on the olivine and low-Ca pyroxene mixing line, as the current classification for S(IV) asteroids would suggest, and it appears that the relationship between FeO content and silicate abundances may be a stronger factor in the spectral classification of the S(IV) asteroids.

5. SUMMARY

In this paper, we revisited spectral calibrations for mineral abundances using a suite of 48 ordinary chondrites, for which quantitative determinations of actual orthopyroxene, clinopyroxene, and olivine abundances and compositions have been made (Dunn et al. 2008). Reflectance spectra of these ordinary chondrites were acquired using a bidirectional spectrometer at Brown University's Keck/NASA Reflectance Experiment Laboratory, and band area ratio (BAR) and Band I center were determined using established techniques.

Our new spectral calibration for deriving ol/(ol+px) ratios from band area ratios, based on measured mineral abundances rather than calculated mineral norms, works extremely well for all ordinary chondrite groups, and also appears to be valid for other meteorites with mineralogies similar to those of the ordinary chondrites. However, the Cloutis et al. (1986) calibration is more accurate in samples dominated by olivine or a single pyroxene, such as the angrites and the eucrites. These calibrations are applicable to many types of asteroids, including S-type and R-type asteroids. They do not work as well on asteroids that are dominated by a single silicate phase. The linear relationship between Band II position and total pyroxene suggested by Gaffey et al. (2002) does not appear to be robust, based on low R^2 values. This would suggest that it may not be possible to establish the abundances of all mafic silicates from reflectance spectra using simple regressions.

Based on the ordinary chondrite spectral data from this study, we suggest that there is an alternative interpretation to the current spectra classification of ordinary chondrites and S(IV) asteroids. It appears that on a plot of Band I center versus Band I/II area ratio the S(IV) asteroids form a field with an "L" shape, in which FeO content the ordinary chondrite groups increases linearly from the Hs to the LLs. This suggests that the bulk FeO content may be the

controlling factor in the spectral classification of the S(IV) asteroids, rather than mixing of olivine and low-Ca pyroxene as the current classification would suggest.

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Appendix V

Table 4.1. Meteorite spectra measured in this study

Meteorite	Type	RELAB ID ^a	Grain Size	Band I (μm)	Band II (μm)	BAR
Bernares (a)	LL4	MT-HYM-083	<150 μm	0.996	1.984	0.58
Greenwell Springs	LL4	TB-TJM-075	<150 μm	0.974	1.959	0.53
Hamlet	LL4	MT-HYM-075	<150 μm	0.969	1.974	0.61
Witsand Farm	LL4	MT-HYM-076	<150 μm	0.991	2.001	0.53
Aldsworth	LL5	MT-HYM-077	<150 μm	0.966	1.960	0.61
Alta'ameem	LL5	MT-HYM-078	<150 μm	0.972	1.952	0.46
Olivenza	LL5	MT-HYM-085	<150 μm	0.997	1.969	0.42
Paragould	LL5	MT-HYM-079	<150 μm	0.975	1.968	0.40
Tuxtuac	LL5	MT-HYM-080	<150 μm	0.946	1.950	0.55
Bandong	LL6	TB-TJM-067	<150 μm	0.991	1.987	0.29
Cherokee Spring	LL6	TB-TJM-075	<150 μm	0.968	1.940	0.40
Karatu	LL6	TB-TJM-077	<75 μm	0.995	1.992	0.32
Saint-Severin	LL6	TB-TJM-145	<150 μm	0.990	1.881	0.28
Attarra	L4	TB-TJM-065	<150 μm	0.936	1.927	0.78
Bald Mountain	L4	TB-TJM-102	<150 μm	0.917	2.001	1.09
Rio Negro	L4	TB-TJM-081	<150 μm	0.942	1.932	0.96
Rupota	L4	TB-TJM-121	<150 μm	0.943	1.951	0.58
Ausson	L5	MT-HYM-084	<150 μm	0.942	1.918	1.09
Blackwell	L5	MT-HYM-081	<150 μm	0.935	1.953	0.55
Cilimus	L5	MT-HYM-082	<150 μm	0.932	1.925	0.54
Guibga	L5	TB-TJM-134	<150 μm	0.946	1.943	0.63
Mabwe-Khoywa	L5	TB-TJM-107	<150 μm	0.935	1.944	0.79
Malakal	L5	TB-TJM-109	<150 μm	0.943	1.977	0.81
Messina	L5	TB-TJM-099	<150 μm	0.953	1.960	0.67
Apt	L6	TB-TJM-064	<150 μm	0.942	1.940	0.51
Aumale	L6	TB-TJM-101	<150 μm	0.940	1.946	0.70
Karkh	L6	TB-TJM-137	<150 μm	0.944	1.930	0.39
Kunashak	L6	TB-TJM-139	<150 μm	0.953	1.942	0.53
Kyushu	L6	TB-TJM-140	<150 μm	0.949	1.933	0.54
New Concord	L6	TB-TJM-130	<150 μm	0.940	1.928	0.64
Farmville	H4	TB-TJM-128	<150 μm	0.923	1.928	0.91
Forest Vale	H4	TB-TJM-093	<75 μm	0.932	1.934	0.79
Kabo	H4	TB-TJM-136	<150 μm	0.926	1.934	0.91
Marilia	H4	TB-TJM-078	<150 μm	0.922	1.945	0.92
São Jose do Rio Preto	H4	TB-TJM-082	<150 μm	0.921	1.901	0.92
Allegan	H5	TB-TJM-104	nm	0.924	1.897	1.03
Ehole	H5	TB-TJM-074	<150 μm	0.926	1.945	1.04
Itapicuru-Mirim	H5	TB-TJM-097	<150 μm	0.927	1.922	0.83
Lost City	H5	TB-TJM-129	<150 μm	0.926	1.936	0.97
Primbram	H5	TB-TJM-143	<150 μm	0.928	1.906	0.79
Schenectady	H5	TB-TJM-083	<150 μm	0.922	1.913	0.80
Uberaba	H5	TB-TJM-085	<150 μm	0.933	1.943	0.89
Andura	H6	TB-TJM-088	<75 μm	0.917	1.929	0.91
Bustura	H6	TB-TJM-069	<150 μm	0.919	1.918	0.78
Canon City	H6	TB-TJM-131	<150 μm	0.937	1.932	0.78
Chiang Khan	H6	TB-TJM-132	<150 μm	0.930	1.920	0.85
Guarena	H6	TB-TJM-094	<150 μm	0.923	1.916	0.74
Ipiranga	H6	TB-TJM-135	<150 μm	0.927	1.921	0.83

^aSpectra are available on the RELAB database at <http://www.planetary.brown.edu/relabdata/>

Table 4.2. Ol/(ol+px) ratios derived from XRD, normative, and spectral data

Meteorite	Type	ol/(ol+px) (XRD)	ol/(ol+px) (norm) ^a	ol/ol+px (spectra) ^b
Bernares (a)	LL4	0.58	nm	0.59
Greenwell Springs	LL4	0.64	0.66	0.60
Hamlet	LL4	0.62	nm	0.59
Witsand Farm	LL4	0.65	nm	0.61
Aldsworth	LL5	0.65	nm	0.59
Alat'ameen	LL5	0.62	nm	0.62
Olivenza	LL5	0.64	0.67	0.63
Paragould	LL5	0.65	nm	0.63
Tuxtuac	LL5	0.63	nm	0.60
Bandong	LL6	0.66	0.73	0.66
Cherokee Spring	LL6	0.67	0.68	0.63
Karatu	LL6	0.69	0.72	0.65
Saint-Severin	LL6	0.65	0.70	0.66
Attarra	L4	0.56	0.62	0.55
Bald Mountain	L4	0.55	0.56	0.48
Rio Negro	L4	0.55	0.59	0.51
Rupota	L4	0.57	0.58	0.59
Ausson	L5	0.55	0.64	0.48
Blackwell	L5	0.56	nm	0.60
Cilimus	L5	0.58	nm	0.60
Guibga	L5	0.58	0.60	0.58
Mabwe-Khoywa	L5	0.58	0.60	0.54
Malakal	L5	0.57	0.60	0.54
Messina	L5	0.57	0.60	0.57
Apt	L6	0.56	0.67	0.61
Aumale	L6	0.59	0.60	0.57
Karkh	L6	0.59	0.65	0.64
Kunashak	L6	0.60	0.63	0.60
Kyushu	L6	0.61	0.61	0.60
New Concord	L6	0.60	0.64	0.58
Farmville	H4	0.46	0.51	0.52
Forest Vale	H4	0.48	0.57	0.54
Kabo	H4	0.46	0.51	0.52
Marilia	H4	0.46	0.49	0.51
São Jose do Rio Preto	H4	0.46	0.54	0.50
Allegan	H5	0.47	0.48	0.50
Ehole	H5	0.51	0.55	0.50
Itapicuru-Mirim	H5	0.53	0.50	0.54
Lost City	H5	0.49	0.54	0.50
Primbram	H5	0.49	0.51	0.54
Schenectady	H4	0.54	0.59	0.54
Uberaba	H5	0.51	0.56	0.52
Andura	H6	0.53	0.60	0.52
Bustura	H6	0.51	0.53	0.55
Canon City	H6	0.54	0.53	0.53
Chiang Khan	H6	0.53	0.53	0.55
Guarena	H6	0.60	0.54	0.56
Ipiranga	H6	0.52	0.53	0.54

^aFrom McSween et al. (1991); nm indicates that a norm has not been calculated^bErrors are 0.1 for XRD-measured ratios, 0.01 for normative ratios, and ± 0.03 for spectral ratio

Table 4.3. XRD-measured, normative, and spectral cpx/(opx+cpx) ratios

Meteorite	Type	cpx/(opx+cpx) XRD	cpx(opx+cpx) norm	cpx/(opx+cpx) spectra
Bernares (a)	LL4	0.29	n.m.	0.26
Greenwell Springs	LL4	0.23	0.21	0.25
Hamlet	LL4	0.24	n.m.	0.26
Witsand Farm	LL4	0.25	n.m.	0.27
Aldsworth	LL5	0.24	n.m.	0.25
Alat'ameen	LL5	0.25	n.m.	0.25
Olivenza	LL5	0.24	0.18	0.25
Paragould	LL5	0.25	n.m.	0.25
Tuxtuac	LL5	0.26	n.m.	0.24
Bandong	LL6	0.29	0.23	0.26
Cherokee Spring	LL6	0.26	0.22	0.24
Karatu	LL6	0.32	0.24	0.27
Saint-Severin	LL6	0.27	0.22	0.21
Attarra	L4	0.34	0.25	0.23
Bald Mountain	L4	0.25	0.15	0.27
Rio Negro	L4	0.25	0.15	0.23
Rupota	L4	0.25	0.16	0.24
Ausson	L5	0.22	0.17	0.23
Blackwell	L5	0.27	n.m.	0.25
Cilimus	L5	0.21	n.m.	0.23
Guibga	L5	0.27	0.16	0.24
Mabwe-Khoywa	L5	0.20	0.16	0.24
Malakal	L5	0.26	0.18	0.26
Messina	L5	0.26	0.15	0.25
Apt	L6	0.27	0.20	0.24
Aumale	L6	0.27	0.17	0.24
Karkh	L6	0.26	0.15	0.23
Kunashak	L6	0.26	0.16	0.24
Kyushu	L6	0.29	0.17	0.24
New Concord	L6	0.29	0.19	0.23
Farmville	H4	0.21	0.12	0.23
Forest Vale	H4	0.22	0.15	0.24
Kabo	H4	0.20	0.12	0.24
Marilia	H4	0.19	0.11	0.24
São Jose do Rio Preto	H4	0.24	0.13	0.22
Allegan	H5	0.21	0.13	0.22
Ehole	H5	0.21	0.15	0.24
Itapicuru-Mirim	H5	0.21	0.12	0.23
Lost City	H5	0.23	0.14	0.24
Primbram	H5	0.23	0.14	0.22
Schenectady	H4	0.20	0.14	0.22
Uberaba	H5	0.25	0.14	0.24
Andura	H6	0.16	0.22	0.23
Bustura	H6	0.18	0.17	0.23
Canon City	H6	0.20	0.15	0.23
Chiang Khan	H6	0.20	0.13	0.23
Guarena	H6	0.18	0.13	0.23
Ipiranga	H6	0.20	0.15	0.23

^aNormative ol/(ol+px) ratios are from abundances in McSween et al. (1991); nm indicates a sample for which norms have not been calculated. Errors are the same as Table 4.2.

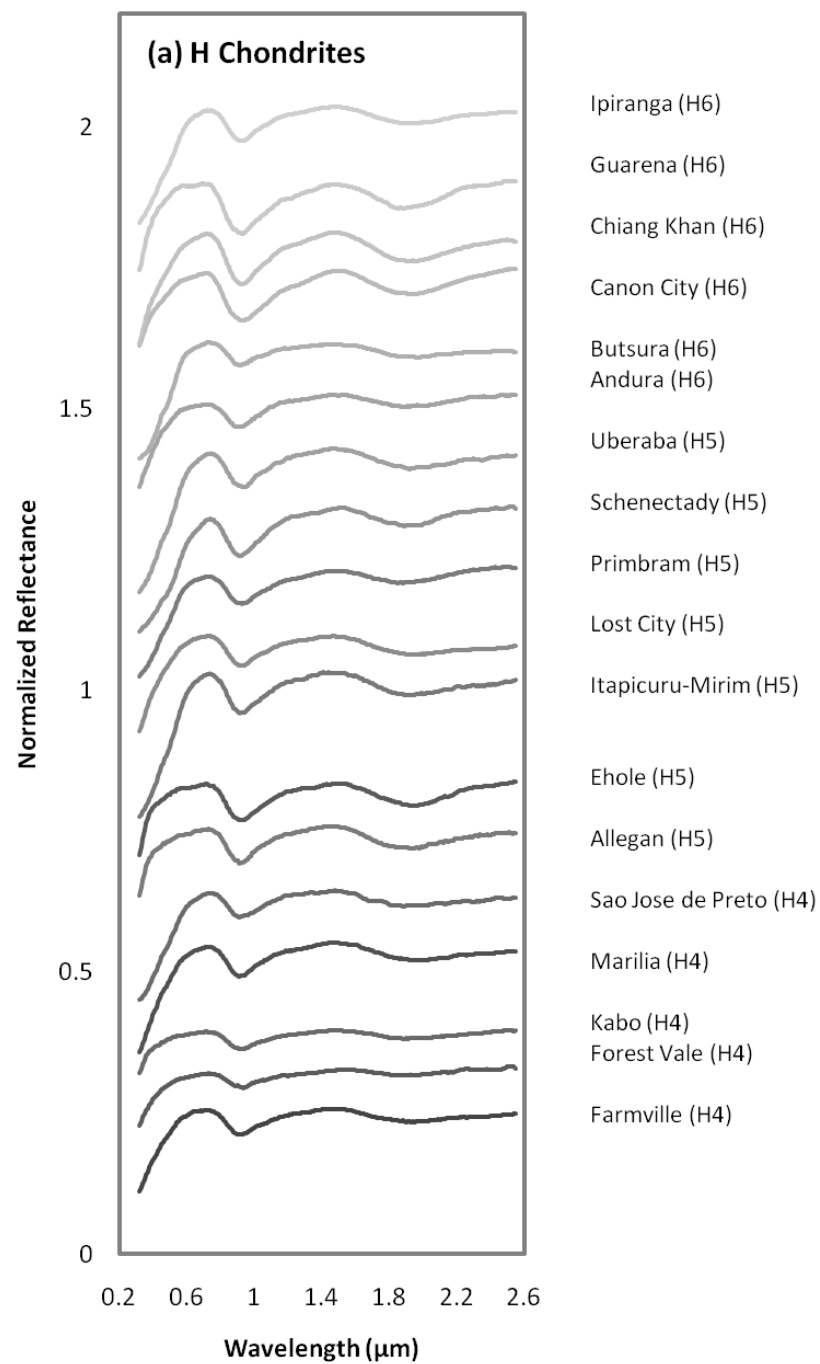


Figure 4.1. Reflectance spectra of all (a) H, (b), L, and (c) LL chondrites analyzed in this study. Band I is located at $\sim 1 \mu\text{m}$, and Band II is located at $\sim 2 \mu\text{m}$.

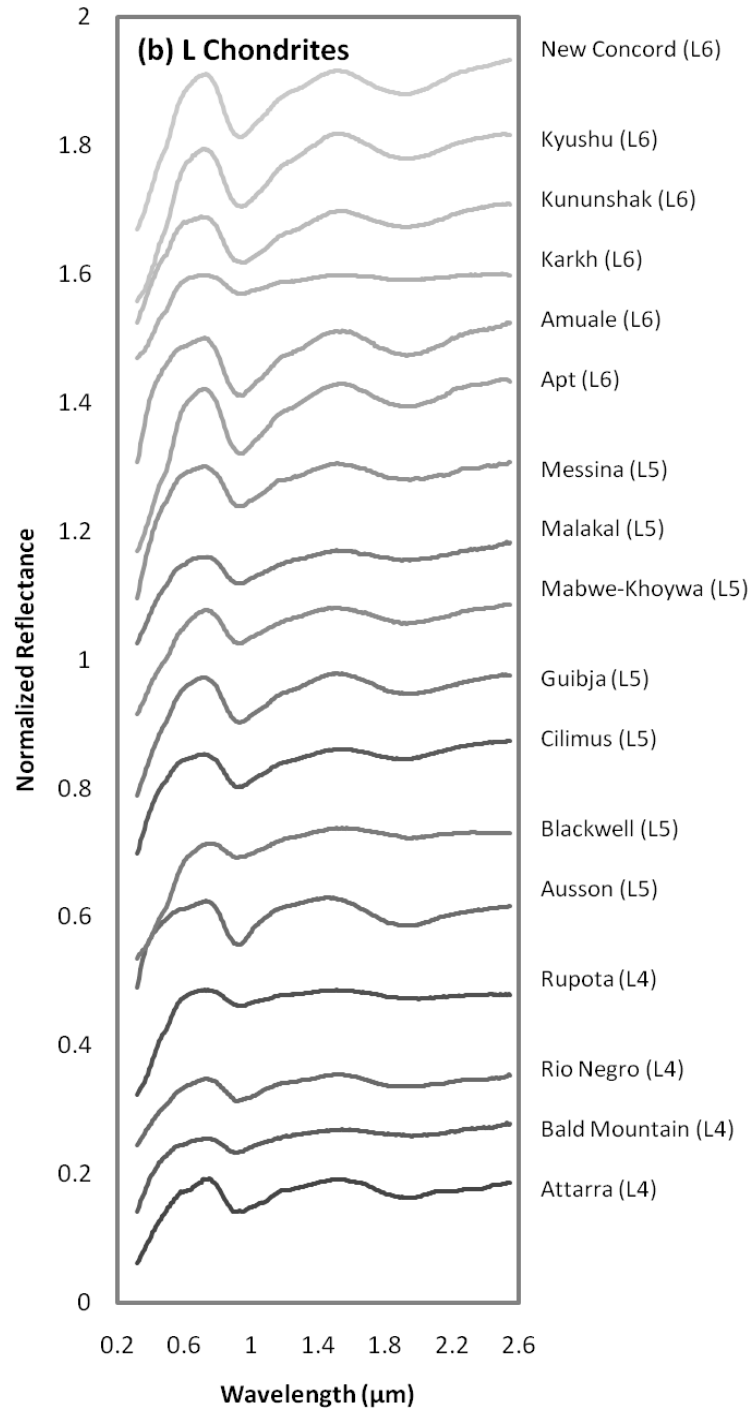


Figure 4.1. Continued.

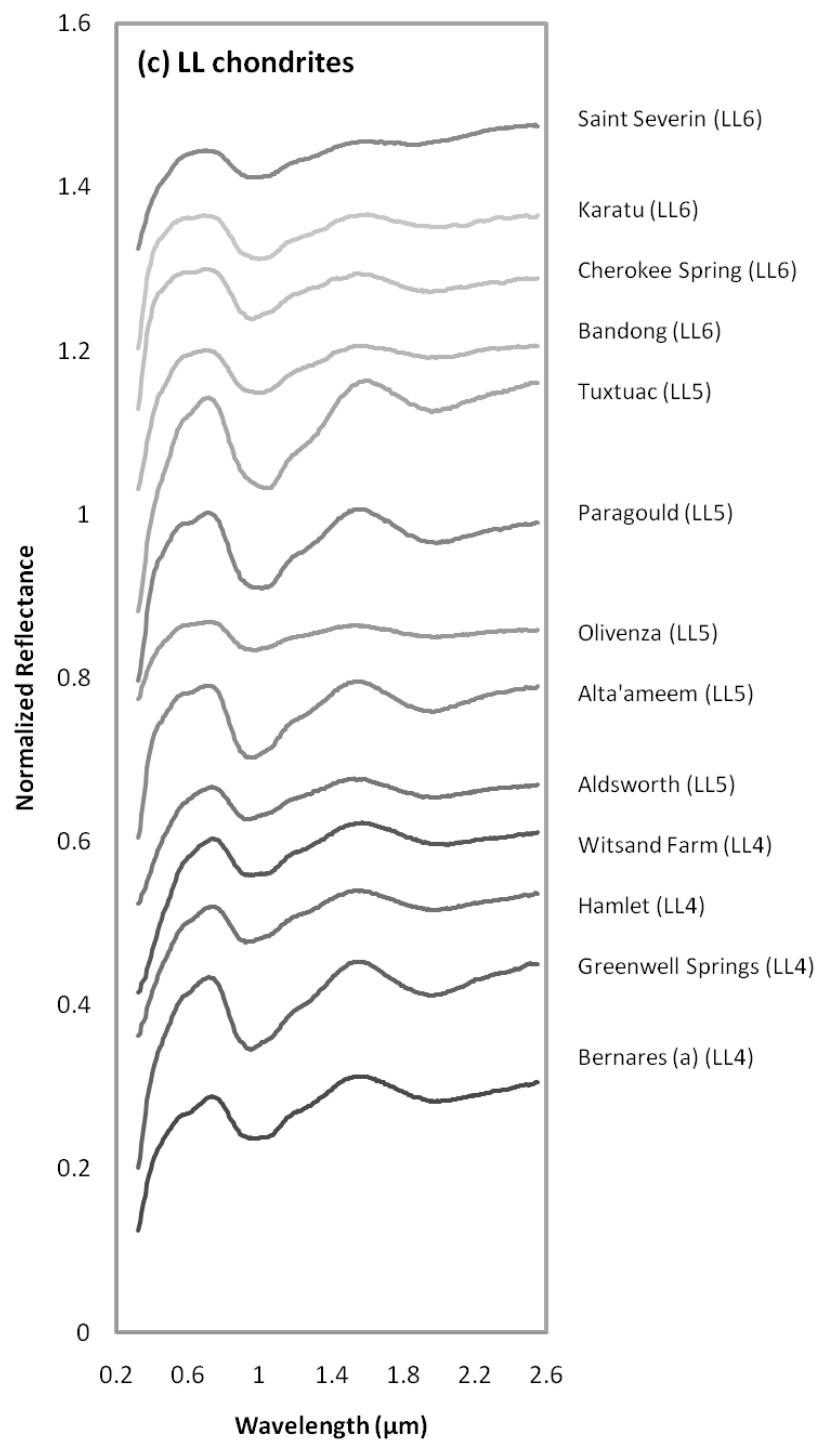


Figure 4.1. Continued.

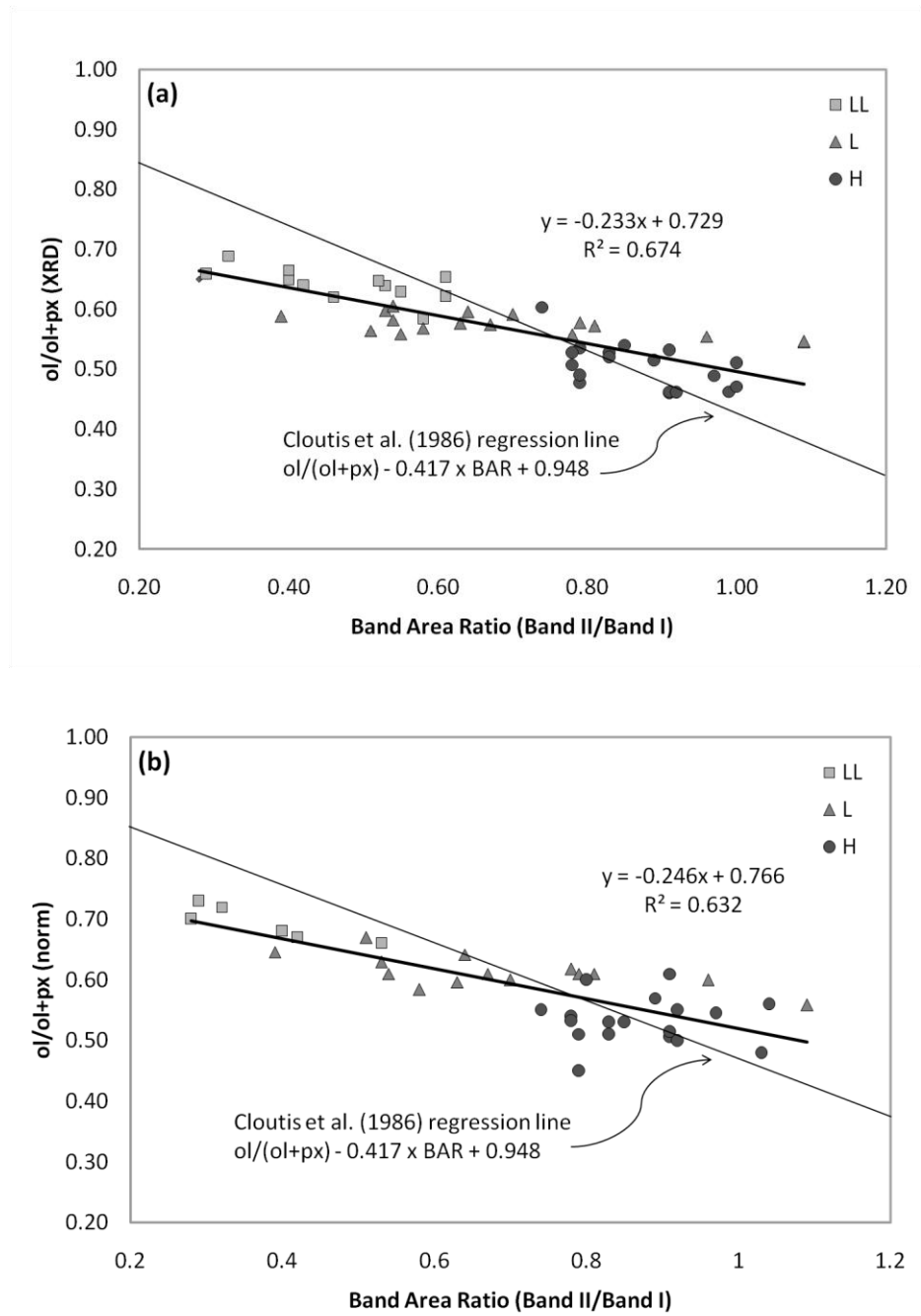


Figure 4.2. Band area ratios versus (a) XRD-measured ol/(ol+px) ratios and (b) normative ol/(ol+px) ratios for the ordinary chondrites in this study. Linear regression of our data is indicated by solid black lines. The bolded black lines are from Cloutis et al. (1986). Error bars are not shown for clarity. Uncertainties are stated in Table 4.2.

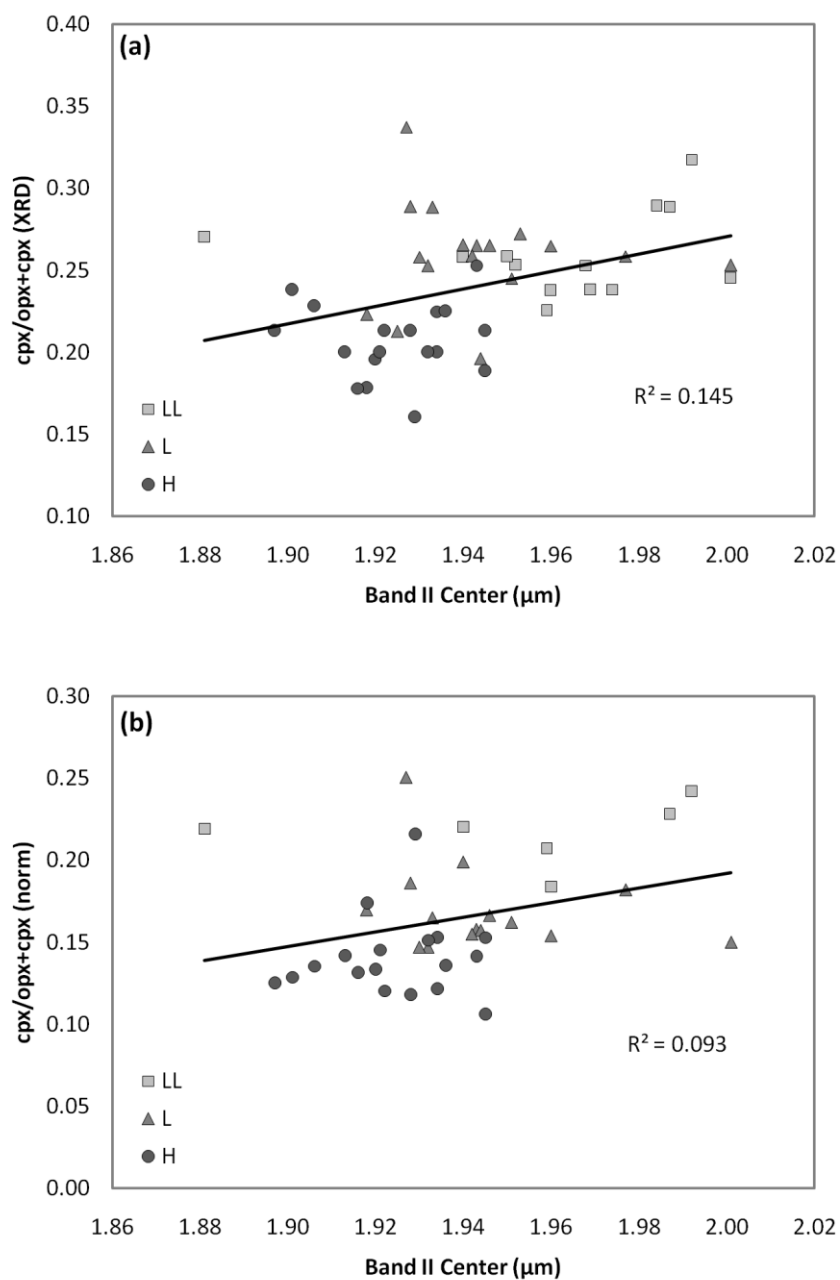


Figure 4.3. Band area ratios versus (a) XRD-measured cpx/(opx+cpx) ratios and (b) normative cpx/(opx+cpx) ratios for the ordinary chondrites in this study. Linear regression of our data is indicated by a solid black line. Uncertainties are stated in Table 4.3.

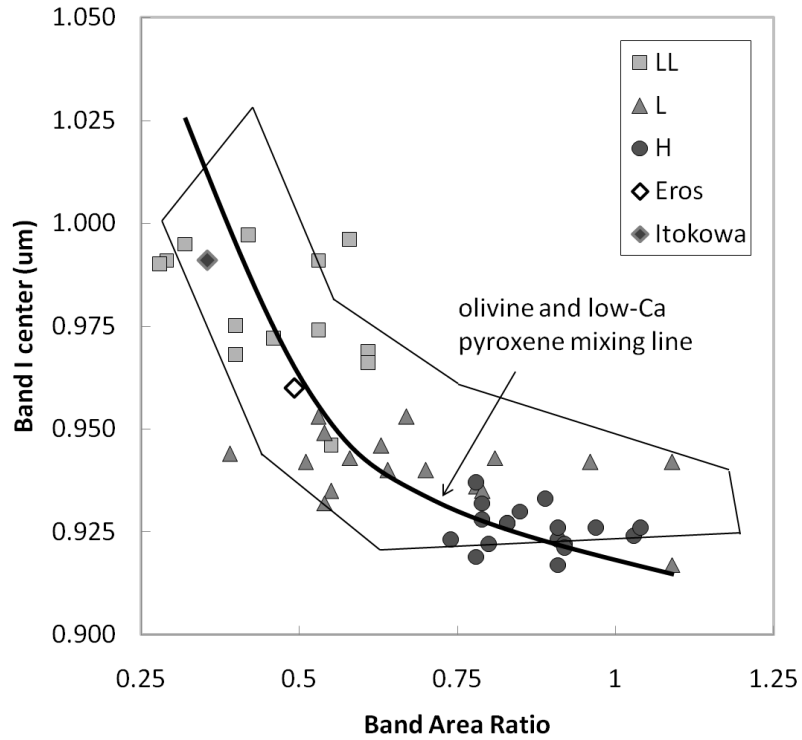


Figure 4.4. Current classification for S(IV)-type asteroids modified from Gaffey et al. (1993) and Gaffey and Gilbert (1998). The solid line represents a simple mixing line between olivine and low-Ca pyroxene (Gaffey et al. 1993). Spectral characteristics of 48 ordinary chondrites measured in this study, along with S(IV)-type asteroids Eros and Itokawa, are plotted on the diagram. Errors are the same as those shown in Figure 4.6.

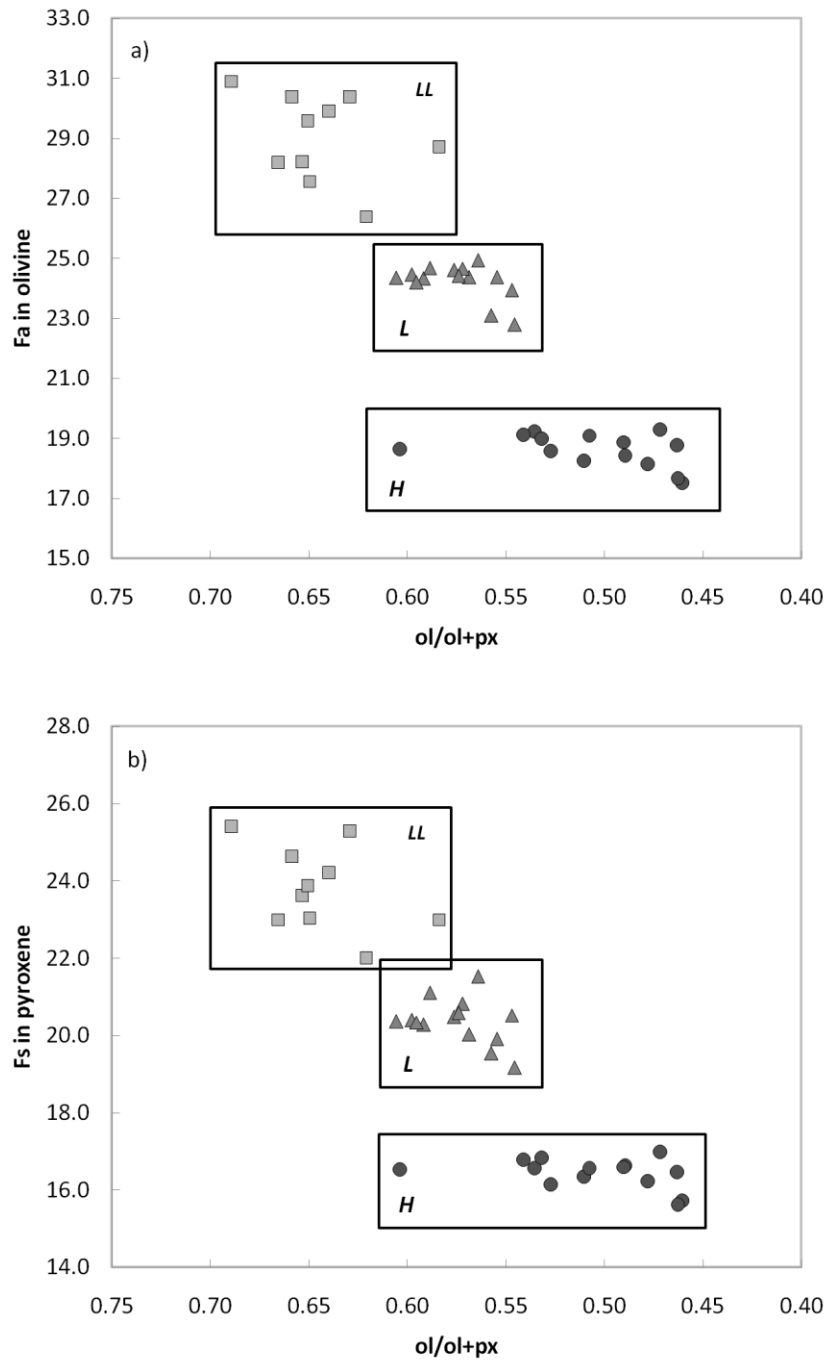


Figure 4.5. $Ol/(ol+px)$ plotted as a function of (a) Fa content in olivine and (b) Fs content in low-Ca pyroxene. $Ol/(ol+px)$ serves as a proxy for BAR, and Fa or Fs serves as a proxy for BI center.

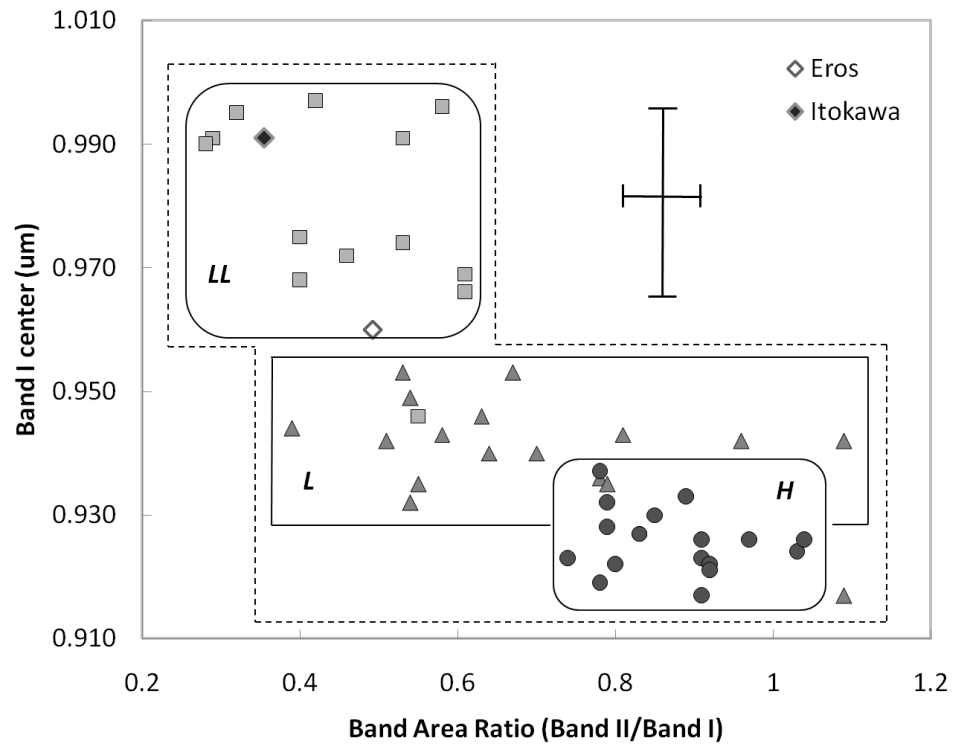


Figure 4.6. New classification for S(IV) asteroids based on spectral data from H, L, and LL chondrites measured in this study. S(IV) asteroids Eros and Itokawa are also plotted; both plot in the spectral range associated with the LL chondrites. Representative error bars for ordinary chondrites are shown.

VITA

Tasha Dunn was born in Atlanta, Georgia, on February 25th, 1978. She grew up on the south of Atlanta in an area some would call the ghetto, but Tasha called home. As a young child Tasha developed a strong interest in space exploration and decided to focus her studies in math and science, with hopes of one day becoming an astronaut. This dream was dashed, however, by her less than mediocre eyesight. In 1996, Tasha graduated at the top of her class from Forest Park High School and began college the following fall at Tulane University in New Orleans. Tasha graduated from Tulane with a Bachelor's of Science degree in Geology in May of 2000, with little accolade. After college, Tasha moved back to Georgia, land of peanuts and peaches, and worked as a staff geologist and project manager at Consultech Environmental, Inc for three years. Tasha spent much of this time in parts of South Carolina that are not often visited by outsiders. Tasha entered graduate school at the University of Tennessee in the fall of 2003, defended her master's thesis in August of 2005, and immediately began working on her PhD. Tasha's research took her to exciting place such as London, where she learned that fire doors are everywhere and Big Red chewing gum is not. After finishing her Ph.D., Tasha and her two cats, Hugo and Albite, will move on to bigger and better things, or at least better paying things. And, yes, Tasha named her cat Albite after the mineral.