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# Chemical, Mineralogical and Isotopic Properties of Chondrules: Clues to Their Origin

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**Abstract.** We review chemical, mineralogical and isotopic properties of chondrules that can be used to investigate chondrule origins. Although many interpretations of chondrule properties are hampered by the lack of sufficient data for the least-equilibrated chondrites, we can make general inferences about formation conditions. Chondrules exhibit considerable diversity in their bulk chemistries, oxygen isotope ratios, and oxidation states that are present both within and among individual chondrite groups. Chondrules formed by melting of solid precursors composed of aggregates that included a mixture of fine-grained or amorphous material (silicates, oxides, Fe,Ni-metal, sulfides, carbon) and larger silicate grains that were likely derived from previous generations of chondrules. Bulk compositions generally show varying abundances of (unfractionated) refractory lithophile elements (Ca, Al, Ti, rare earth elements), and varying degrees of fractionation of moderately volatile lithophile (Mn, Na, K) and siderophile (Fe, Ni, Co) elements. Bulk compositions were probably modified during chondrule-forming events by open system behavior. Most material in the chondrule forming region was heated at least twice. Diversity in chondrule precursors can be attributed to random aggregation of diverse mineral grains, as well as progressive changes in solid compositions with time and/or space in the solar nebula.

## 1. Introduction

Chondrules are the most abundant constituents of most chondritic meteorites. Chemical, mineralogical and isotopic properties of chondrules can provide constraints on the nature of the most abundant solid materials in the inner part of the protoplanetary disk as well as on the nature of the transient heating events that melted them. In addition to obvious textural diversity (Fig. 1), chondrules exhibit considerable chemical and isotopic diversity, which is present both within individual chondrite groups and among the various chondrite groups. Understanding the nature and extent of the variations in properties such as volatility-related elemental abundances, oxidation state, and oxygen isotope ratios may provide insights into the nature of the dust in chondrule-forming regions as well as the chondrule-forming process itself.

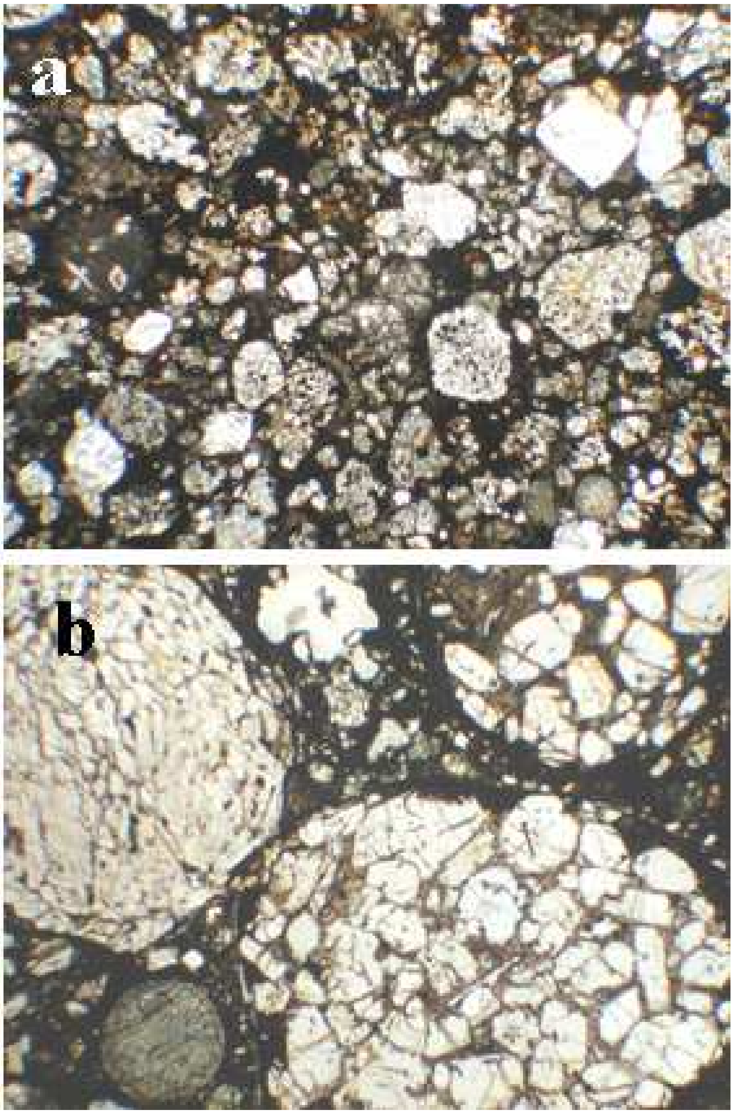

Figure 1. Textures of unequilibrated chondrites: a) Lancé, CO3.4, b) Ragland, L3.5. The width of both images is 3 mm. Within each chondrite, chondrules have diverse textures reflecting diversity in chemistry and oxidation state. Relative abundances of chondrules and matrix, and mean chondrule size, differ among chondrite groups.

Unfortunately, it is often not a trivial task to identify exactly what may be inferred from a given observation. A thorough understanding of the petrology of a chondrule is essential for an appropriate interpretation of a given data set. For example, a chondrule with a low bulk iron content might have been formed from a precursor with inherently low bulk iron, it may have physically lost iron metal during chondrule formation, or it may have lost Fe by evaporation. An additional complication is that some chondrule properties can be modified significantly by even the mildest forms of aqueous alteration (alteration by water) or thermal metamorphism (alteration by heat). It is essential to appreciate the effects that these processes may have on chondrule properties so that we can decipher the information relevant to the formation of chondrules.

In this chapter, we review the most important properties of chondrules that are essential to understanding their origins. Our approach is to examine the properties of chondrules that can be used to address several fundamental questions: What did chondrule precursors consist of? What was the initial redox state of chondrules? To what extent did chondrules interact with the surrounding gas before and during chondrule formation? How many times were chondrules heated? We preface this discussion with a brief review of essential terminology relating to chondrule petrology, and a summary of the characteristics of chondrules that have not been affected by secondary alteration.

Throughout this paper, we use a working definition of a chondrule as being an essentially ferromagnesian silicate object that shows evidence for at least partial melting as a free-floating droplet. Our focus is on the most abundant type of chondrules that are normally described as ferromagnesian, because the emphasis of this paper is the diversity of chondrule properties and differences between chondrite groups. We do not discuss aluminum-rich or silica-rich chondrules in detail. Aluminum-rich chondrules have been discussed recently by Russell et al. (2000), Krot & Keil (2002), Krot et al. (2001), Krot, Hutcheon, & Keil (2002a) and MacPherson & Huss (2005). Their relationship to both chondrules and refractory inclusions is discussed by Russell et al. (this volume). Hezel et al. (2003) discussed silica-rich chondrules in CH chondrites. Other objects that we do not consider here include metallic chondrules (e.g., Gooding & Keil 1981), amoeboid olivine inclusions (e.g., Grossman & Steele 1976) and refractory inclusions (MacPherson et al. this volume).

## 2. Chondrule Terminology

Several different classification schemes have been used to describe the wide chemical and textural variety of ferromagnesian chondrules. The details of these schemes have been summarized recently by Connolly & Desch (2004), Connolly (this volume) and Lauretta, Nagahara, & Alexander (2005) and do not need to be reiterated. The most essential textural terms for the purposes of this chapter are the following: A *barred* texture is one in which individual crystals, typically olivine, occur in sets of parallel, elongated bars or plates (Fig. 2a). In a *porphyritic* chondrule (Fig. 2b), individual mineral grains (typically olivine and pyroxene) have sides of more equal lengths in all dimensions. Individual grains are termed phenocrysts. A *radial* texture is one in which crystals (pyroxene in the vast majority of cases) appear to radiate from one or more points on the chondrule surface; these may be extremely fine-grained and grade into *cryptocrystalline* textures in which individual pyroxene crystals are submicrometer in size. The material that occurs between the mineral grains in a chondrule of any texture is termed the mesostasis: this may consist of glass and/or very fine-grained crystals (Fig. 2c) and represents the liquid that remained at the point when the chondrule became frozen as it cooled. Mesostasis in ferromagnesian chondrules has compositions from which the feldspar mineral, plagioclase, could crystallize, so it is commonly referred to as feldspathic.

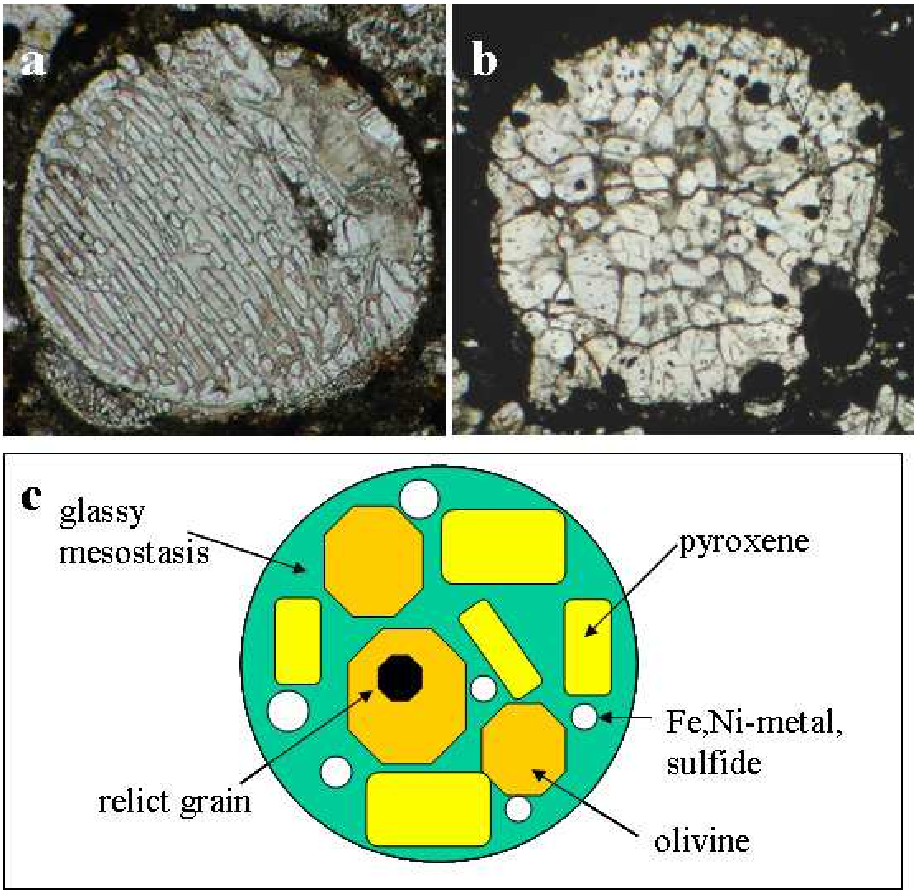

Figure 2. Chondrule textures and definitions of terms: a) Barred olivine texture, showing elongate, sub-parallel bars of olivine with clear glass between the bars. Chondrule is from the Lancé (CO3.4) chondrite; image is 0.4 mm across; b) Porphyritic texture. Chondrule is a low-FeO (type I) chondrule from the Semarkona (LL3.0) chondrite. White crystals are olivine and low-Ca pyroxene; rounded black areas are Fe,Ni-metal / sulfide assemblages; c) Schematic chondrule. Most olivine and pyroxene crystals grew from the molten chondrule as it cooled. "Relict" grains survived the transient heating event of chondrule formation. The term "mesostasis" refers to the interstitial material and represents the final liquid that was present when the chondrule froze as it cooled.

The most important minerals found in chondrules are summarized in Table 1. Olivine may have a composition with any ratio of Fe/Mg (this is referred to as a solid solution). The Mg end-member is forsterite (Fo), and the Fe end-member is fayalite (Fa). Olivine compositions are commonly given in terms of fayalite contents, where Fa (mole%) = Fe / (Fe+Mg). Pyroxene has a higher proportion of silica than olivine, and has three variable major elements: Fe, Mg and Ca. There are many different varieties of pyroxene that have varying amounts of calcium: most pyroxene in chondrules is low-Ca pyroxene. The Mg end-member is enstatite (En), the Fe end-member is ferrosilite (Fs) (Fs = Fe/(Fe+Mg+Ca)), and the Ca content is given as the wollastonite (Wo) content: Wo = Ca/(Fe+Mg+Ca). Elements such as Al and alkalis occur mainly in the mesostasis, whereas Ca may be partly in mesostasis, partly in pyroxene. Metal in chondrules is typically the low-Ni phase known as kamacite (typically 3-7 wt% Ni). The dominant sulfide mineral is troilite (stoichiometric FeS), except in chondrules from enstatite chondrites where sulfides of other elements also occur (e.g., Ca, Mn, Na, Cr, Mg). Aluminum-rich chondrules typically have phenocrysts of plagioclase and spinel as well as olivine and pyroxene. Plagioclase consists of a solid solution between the Ca end-member, anorthite (An) and the sodium end-member, albite (Ab).

Table 1. Formulae of common minerals in chondrules.

| Mineral | Formula |
|---|---|
| Olivine | $(Fe,Mg)_2SiO_4$ |
| Pyroxene | $(Fe,Mg,Ca)_2Si_2O_6$ |
| Plagioclase (feldspar) | $CaAl_2Si_2O_8$ - $NaAlSi_3O_8$ |
| Spinel | $MgAl_2O_4$ |
| Chromite | $FeCr_2O_4$ |
| Troilite | FeS |
| Kamacite | Fe-Ni |

We adopt a simplified chemical classification scheme for chondrules: Type I refers to chondrules that have low Fe/(Fe+Mg) atomic ratios (<10%) in their olivine or low-Ca pyroxene; Type II refers to chondrules that have higher Fe/(Fe+Mg) atomic ratios (>10%) in their silicate minerals. Because we are restricting our discussion to primitive chondrites with minimal metamorphism, it is possible to apply this compositional distinction. Many chondrules provide textural clues to whether they are type I or type II, for example in the size and shape of their phenocrysts and the abundance of metallic Fe,Ni. Fe/(Fe+Mg) contents are dependent on the temperature at the time of crystallization, and can vary as a function of the bulk composition of the chondrule or the oxidation state, as discussed below. We note that the cutoff value of Fe/(Fe+Mg) = 10% is arbitrary: Grossman & Brearley (2005) showed that for olivine-rich chondrules, petrologic properties actually change at around $Fa_2$. But because chondrules with intermediate Fa contents are rare, the choice of the cutoff value is not very significant.

Many chondrules have rims of material that are distinct from the chondrule host. The two main types of rims have very different characters. *Fine-grained rims* consist of aggregates of (sub-) micrometer grains of FeO-rich, silicate minerals (predominantly olivine and pyroxene), Fe,Ni metal, and sulfides (Scott et al. 1988; Brearley 1996; Nuth et al. this volume). These rims are similar in character and composition to fine-grained chondrule matrix; however, in part because matrix material contains chondrule fragments, the mean grain size of chondrule rims is smaller than that of matrix material**.** Fine-grained chondrule rims probably formed from highly porous, low-temperature, FeO-rich dust in which the chondrule (after cooling from its final heating event) became embedded in the nebula. The porous dust most likely compacted around the chondrule to become a rim after accretion to the parent asteroid. Fine-grained rims are most abundant in carbonaceous chondrites, most notably the CM, CO and CV chondrites. Many fine-grained rims in OC and CR chondrites are metal-rich. Coarse-grained *igneous rims*, which are very common in the CV and CR chondrites (Rubin 1984; Krot & Wasson 1995, Krot et al. 2002b), consist of a layer of material that was heated and melted in an event that post-dated melting of the host chondrule. Although igneous rims are generally more FeO-rich than their host chondrules, their bulk compositions do not match those of fine-grained rims.

## 3. Primary Properties of Chondrules

It is only possible to use chemical, mineralogical and isotopic properties of chondrules to infer information about their origins if we can be sure that the properties we observe do not record subsequent events that modified the chondrules. We refer to primary properties of a chondrule as being characteristic of the chondrule at the time of solidification, immediately after the last high-temperature event that it experienced, and secondary properties as those that were produced after modification of the chondrule at a later time. Secondary processes include aqueous alteration, thermal metamorphism, and shock processes resulting from impacts, all of which likely took place on chondrite parent bodies, and reactions of solids with surrounding gas, which could be a nebular or parent-body process. Terrestrial weathering can also be a significant problem. All of these processes may obscure primary chemical properties of chondrules.

The degree to which chondrites have been altered by secondary processes is described by assigning each chondrite a *petrologic type* classification (Van Schmus & Wood 1967; Sears et al. 1980, Grossman & Brearley 2005). The least altered chondrites are classified as type 3.0, or type 3.00 in the ordinary chondrites which are the best studied in terms of their metamorphic histories. Increasing degrees of thermal metamorphism are described as types 3.1 (3.05 in ordinary chondrites) through 3.9, followed by types 4, 5, and 6. Increasing degrees of aqueous alteration are described as petrologic types 2 to 1, although some chondrites may be both aqueously altered and thermally metamorphosed, defying classification in this one-dimensional scheme. The degree of shock recorded by a chondrite is given as a shock stage classification, stage S1 through S6 (Stöffler et al. 1991). Even in type 3.05 or 3.1 chondrites, some redistribution of certain elements has taken place (most notably sulfur, chromium, and alkalis; Grossman & Brearley 2005).

In order to determine the primary properties of chondrules, we need to examine the least altered samples. Unfortunately, such chondrites are rare. The effects of secondary processing are apparent in many of the least-altered samples from each chondrite class, including all enstatite (E) chondrites, ordinary (O) and CO chondrites of petrologic type ≥3.00, all CM, CV, CK and R chondrites, and most CR chondrites. The best examples of primary chondrules are found in a small number of type 3.0 chondrites that include the LL3.00 ordinary chondrite, Semarkona, the CO3.0 chondrites, Y-81020, ALHA77307 and Colony, and the unique carbonaceous chondrites, Acfer 094 and LEW85332. (Division of low petrologic types into 3.xx was introduced by Grossman & Brearley (2005).) As we discuss below, the data available for these ideal chondrites are limited, and we need to resort to observations on chondrites that are not ideal to interpret primary chondrule characteristics. An essential future goal of chondrite studies is to determine these primary chondrule properties in the least-altered chondrites, so that primary chondrule properties can be understood without the complication and uncertainty of having to disentangle secondary effects.

In this paper, we do not discuss the CH or CB chondrite groups because at present it is unclear if they formed mainly by nebular or parent-body processes. The occurrence of chondrules and CAIs in CH chondrites, and the presence of metal grains with zoning that indicates a condensation origin, are consistent with formation of these chondrites in the nebula (e.g., Grossman, Rubin, & MacPherson 1988; Scott 1988; Weisberg, Prinz, & Nehru 1988; Meibom et al. 1999; Campbell & Humayun 2004). However, the very high metallic Fe content, the occurrence of numerous tiny cryptocrystalline chondrules, the low abundance of troilite, the lack of $^{26}$Mg excesses in some CAIs (Weber, Zinner, & Bischoff 1995), and the relatively young Pb-Pb ages of chondrules have caused some authors to invoke an asteroidal origin (e.g., Wasson & Kallemeyn 1990; Amelin & Krot 2005). Condensation of metal grains in $CB_a$ chondrites may have occurred in an impact plume (Campbell, Humayun, & Weisberg 2002). The presence of large barred olivine chondrules in CB chondrites, and the presence of $^{16}$O-enriched CAIs, have led some to believe that these rocks formed in the nebula (e.g., Krot et al. 2001), but others have suggested that they may have been formed by condensation in an impact plume on a chondritic asteroid (Rubin et al. 2003).

## 4. Processes that may Modify the Composition of a Chondrule during Chondrule Formation

When a chondrule is molten, it can behave as an open system with respect to the ambient gas. Before we examine the chemical composition of chondrule precursors, it is important to discuss several effects, summarized in Figure 3, that might have played a role in modifying chemical compositions during the chondrule-forming heating event. The importance of these processes is that the measured chemical composition of a chondrule may be significantly different from the composition of its precursor aggregate. If we want to understand the nature of the dust in the solar nebula, we need to understand the extent to which chondrules behaved as open systems at high temperature.

In an open system, chemical and isotopic fractionation and exchange with the gas may take place. The details of isotopic fractionation effects as a result of evaporation and gas/liquid condensation have been reviewed recently by Lauretta et al. (2005) and are discussed in this volume by Davis et al. and Nagahara & Ozawa. Chondrules, unlike CAIs (MacPherson et al. this volume), show very little evidence for mass-dependent isotopic fractionation in chondrules. Although mass-dependent fractionation effects for oxygen isotopes have not been demonstrated, barred olivine chondrules appear to record oxygen isotopic exchange with the surrounding gas during the time in which they were molten, as discussed below.

In a low-pressure environment, evaporation of volatile elements from the surface of a molten chondrule would almost certainly have taken place; significant loss of Na, K and S takes place in minutes in the laboratory (Yu, Hewins, & Zanda 1996; Yu et al. 2003). If primary Na and S can be shown to be present in chondrules, this may place constraints on the composition and partial pressure of the surrounding gas, and the duration of heating. It is also possible that major lithophile oxides such as FeO and $SiO_2$ could have been partially lost by evaporation during high-temperature processing of chondrule precursors. Trends in type-I chondrule compositions going from relatively FeO-, alkali- and $SiO_2$-rich type IB chondrules to the more reduced, alkali-poor, olivine-rich type IA chondrules have been explained by this sort of processing (e.g., Sears 1996).

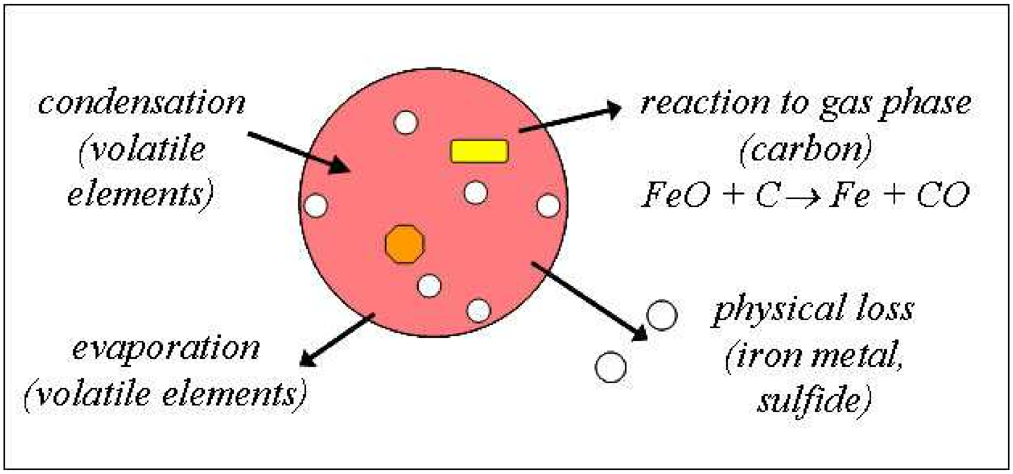

Figure 3. Open system behavior during chondrule formation. When the chondrule is molten, chemical and isotopic changes can take place as a result of interactions with the surrounding gas. These include evaporation and condensation of volatile elements, loss of carbon as CO gas, and physical loss of metal-sulfide beads.

Many (although by no means all) type I (low-FeO) chondrules have a texture that is dominantly porphyritic olivine in the center, with grains of low-Ca pyroxene forming a mantle at the edges. This texture may be caused by progressive condensation of silica, from the gas, on to the surface of the chondrule as it cools (Tissandier, Libourel, & Robert 2002). The presence of $SiO_2$-rich igneous rims around type I chondrules in CR chondrites (Krot et al. 2000) is consistent with this concept. Other putative evidence for condensation during cooling is the presence of concentration gradients for volatile elements in some chondrules (Matsunami et al. 1993; Libourel, Krot, & Tissandier 2003). Grossman et al. (2002) and Grossman & Alexander (2004) have argued that this effect is due to parent-body processing. Nevertheless, it remains a possibility that volatiles entered chondrule melts and diffused throughout the partially molten assemblage at high temperature, long before this low-temperature zoning was established, as the liquid exchanged with surrounding gas (Alexander & Grossman 2005). The presence of Na in Ca-rich pyroxene that crystallized from chondrule melts implies that at least some Na was present during the time that the chondrules were molten (e.g., Jones 1996a; Alexander & Grossman 2005).

Significant amounts of carbon may have been lost from chondrule precursors during heating events because carbon takes part in iron reduction reactions:

$FeO$ (in silicates) + C → $Fe^0$ (metal) + CO (gas),

and the reaction product, CO, is a gas that would escape from the system. Because chondrules contain little or no residual graphite, it is difficult to prove that this reaction occurred, and that carbon was actually present. Variable amounts of carbon have been measured in chondrule silicates (Hanon, Robert, & Chaussidon 1998; Varela & Métrich 2000). There is clear evidence for the reduction of FeO to Fe during chondrule formation in "dusty" relict olivine grains: these contain numerous small metal particles that precipitated from the olivine during a reduction process (Fig. 4: Nagahara 1981; Rambaldi & Wasson 1982; Jones & Danielson 1997; Leroux et al. 2003). In addition, observations that metal in chondrules has a lower Ni content than would be expected from a nebular condensate provide support for at least some chondrule metal being produced by reduction reactions (Rambaldi & Wasson 1984; Connolly, Huss, & Wasserburg 2001). Along with $H_2$ in nebular gas, carbon is a very plausible reducing agent, if it is present at an abundance of 4-6 wt% (Connolly et al. 1994; Hanon et al. 1998). Although the actual extent of carbon loss is impossible to determine quantitatively, it is likely that at least some carbon was present in chondrule precursors.

As a consequence of reduction processes such as those caused by carbon, iron metal is formed. Disproportionation of FeS during heating, accompanied by S loss may also produce metallic Fe in chondrules (Cohen & Hewins 2004). Metal may also be present among chondrule precursor assemblages. Liquid or solid metal droplets entrained in the silicate melt are able to migrate towards the boundaries of chondrules, especially if the chondrule is spinning. Metal droplets that end up at the surface of the chondrule may be physically lost from the chondrule (King 1983; Grossman & Wasson 1985). Reduction and subsequent iron loss might be responsible for significant depletions in iron observed in bulk chondrule compositions relative to chondrule precursors.

## 5. The Physical Nature of Chondrule Precursors

### 5.1. Sizes of Precursor Assemblages

Most chondrules are sub-millimeter in size. Typical chondrule masses are 0.05 and 0.40 mg for chondrule diameters of 300 and 600 micrometers, respectively. The distribution of chondrule sizes in each chondrite group is essentially log normal (Rubin 1989; Nelson & Rubin 2002; Rubin & Grossman 1987). About 90% of the chondrules in each group have a diameter within a factor of 2 of the mean group diameter,

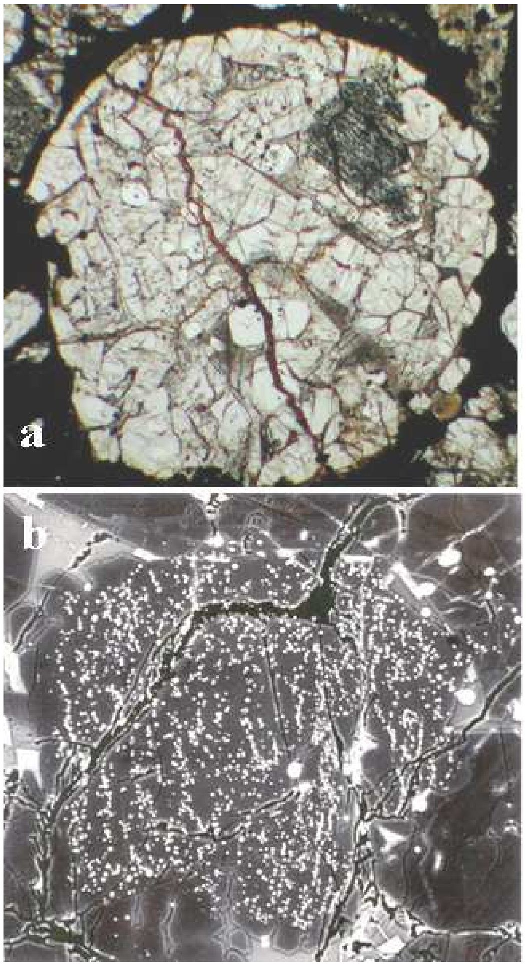

Figure 4. "Dusty" relict grains in chondrules provide evidence for in situ reduction of more FeO-rich silicates (olivine, pyroxene). a) Transmitted-light image of an FeO-poor porphyritic chondrule containing elongate grains of pyroxene, and clear olivine. The black grain at top right is a dusty olivine relict. (Image is 1 mm across) b) Back-scattered electron image of a dusty olivine grain showing numerous round blebs of white Fe-metal. (Image is 50 micrometers across) The metal precipitated from the olivine in a reduction process.

which may indicate that size sorting has occurred. Size sorting may have manifested itself in several different ways: chondrule precursor assemblages may have been physically sorted according to size, resulting in production of different sized chondrules in different locations or at different times; or, already-formed chondrules may have been sorted, either in the protoplanetary disk or on parent bodies due to regolith processes, resulting in the formation of chondrites with a variety of grain sizes. However, the observed size distributions may also be the direct result of the process by which chondrules or their precursors formed in the nebula. For example, the dynamics of the heating mechanism may have been capable only of producing chondrules from a limited size-fraction of precursor assemblages, with others either escaping melting or getting completely vaporized. Alternatively, precursor assemblages themselves may have only been able to form or accrete in a limited range of sizes. The fact that multiple size fractions of chondrules derived from a single parent population have never been found among chondrites argues strongly in favor of the latter type of explanation for the limited size range of chondrules.

## 5.2. Mineralogy of Precursors

Chondrule precursors probably consisted of fine-grained, ((sub-)micrometer) aggregates of silicates, metal, sulfide and other materials that are commonly termed dustballs (Fig. 5). Because these aggregates have melted, it is not possible to determine whether precursor silicates were crystalline or amorphous. Possible sources for this material include amorphous condensates (e.g., Nuth et al. this volume), or finely crystalline material similar to that of chondrite matrix. However, the present chemical composition of chondrite matrix is too iron-rich for it to be considered as direct chondrule precursor material (e.g., Brearley 1996). Experimental constraints on chondrule precursors are discussed by Hewins (this volume).

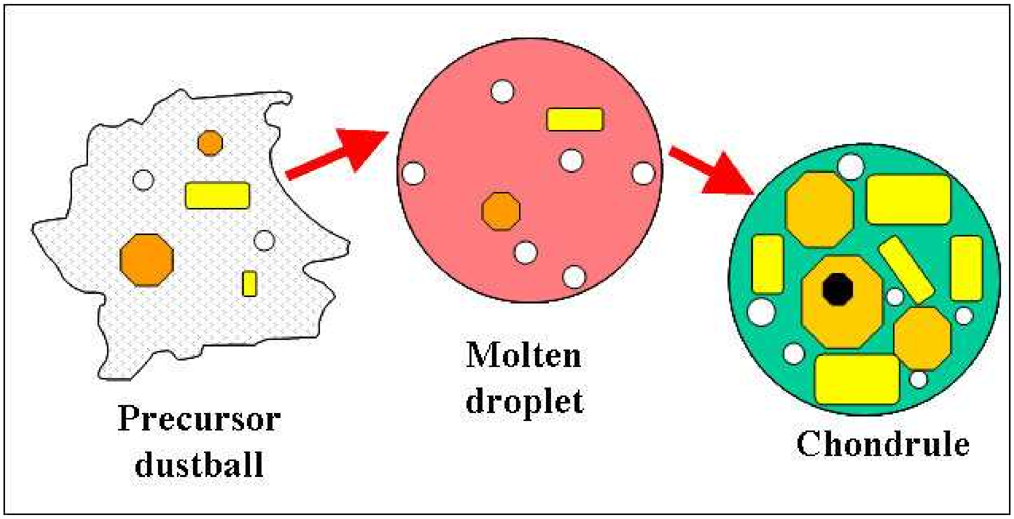

Figure 5. Formation of a chondrule. The precursor aggregate (dustball) includes fine-grained or amorphous silicate material, oxides, Fe,Ni-metal, sulfides, and carbon. Larger silicate grains in the precursor assemblage are mostly derived from previous generations of chondrules, and/or they could be condensate grains. When heating occurs, the chondrule melts. Fe-Ni-S droplets are immiscible in the silicate liquid. Larger silicate grains that were present in the precursor are partly dissolved, but are large enough to remain recognizable. As the chondrule cools, silicate grains (olivine, pyroxene) grow. The grains that survived melting ("relict grains") are incorporated into the melt-grown grains. Fe-Ni-S melts solidify to metal and sulfide phases.

Larger grains, up to several tens or even hundreds of micrometers in diameter, were also present in chondrule precursor assemblages. The evidence for this is that we observe “relict” grains in chondrules – grains that have chemical and isotopic compositions inconsistent with crystallization from the host chondrule melt. Relict grains must have been present in the precursor assemblage and survived the melting event, during which they did not completely dissolve. Most relict grains are olivine, apparently derived from previous generations of chondrules, and indicating that recycling occurred (Jones 1996b), although it is possible that some of them are gas-solid condensates (Steele 1986; Weinbruch, Palme, & Spettel 2000). Relict pyroxene grains are rare. Relict grains of metal may be present in chondrules, although this has not been confirmed. Relict calcium-aluminum inclusions and amoeboid olivine aggregates have also been found in a few chondrules, especially Al-rich ones (Misawa & Fujita 1994; Krot & Keil 2002; Krot et al. 2002a; Yurimoto & Wasson 2002), showing that, at least some of these more refractory materials were present in the precursor assemblages. Relict grains can provide constraints on the length of time that chondrules were held at high temperatures (or the temperature, if the time is known): relict grains of enstatite and forsterite can survive for only a few seconds in a chondrule melt at temperatures above 1557°C and 1900°C respectively (Greenwood & Hess 1996).

The existence of relict grains argues against the possibility that chondrule precursors were liquid droplets that condensed directly from a completely vaporized gas. Another argument against direct condensation of liquids is that relatively high dust enrichments and elevated gas pressures relative to the canonical solar nebula are required (e.g., Ebel & Grossman 2000); however, in order to retain volatile elements and avoid mass-fractionation from a chondrule melt, high pressures are needed at least locally in the chondrule-forming region. Also, in order to create a porphyritic texture, a population of submicroscopic crystal nuclei must be present in the chondrule melt. The most obvious source for these is the remnants of precursor dust grains although, as an alternative, external seeding may play a role (Connolly & Hewins 1995; Hewins et al. this volume).

## 6. Bulk Compositions of Chondrules and Their Precursors

It is clear from the above discussion that measured bulk chemical compositions of chondrules do not necessarily provide complete information about the chemical compositions of chondrule precursor materials, even in the most primitive chondrites where there is minimal secondary alteration. This must be borne in mind as we discuss the considerable chemical diversity that is exhibited within individual chondrite groups, and some essential differences in the distribution of bulk chemical compositions among chondrite groups. Unfortunately, to complicate matters further, there are relatively few suites of chondrule bulk chemical composition data available, and these are not all from the most primitive chondrites. We point out the pitfalls of the available data in the following discussion.

The best sets of data for bulk chemical compositions of chondrules are for the LL3.00 chondrite, Semarkona, and for the ungrouped type-3.0 carbonaceous chondrite, LEW85332. For other chondrite groups, the best data are compromised to varying extents by secondary processes. In order to be able to make comparisons between chondrules in different groups, we must include additional chondrites that have low petrologic subtypes (>3.0), including the oxidized CV3 chondrites, Allende and Mokoia, the CO3 chondrite, Ornans, and the EH3 chondrite, Qingzhen. The best data for H chondrite chondrules are from Sharps (H3.4) (Rubin & Pernicka 1989). Although other data exist for bulk compositions of chondrules, these suites of data are the only ones available that enable an overview of the diversity of chemical compositions within individual chondrites.

Figures 6a and 6b illustrate the diversity of chondrule compositions for lithophile elements in Semarkona, using data from Jones & Scott (1989) and Jones (1990, 1994, 1996a). These data were measured using broad-beam electron microprobe

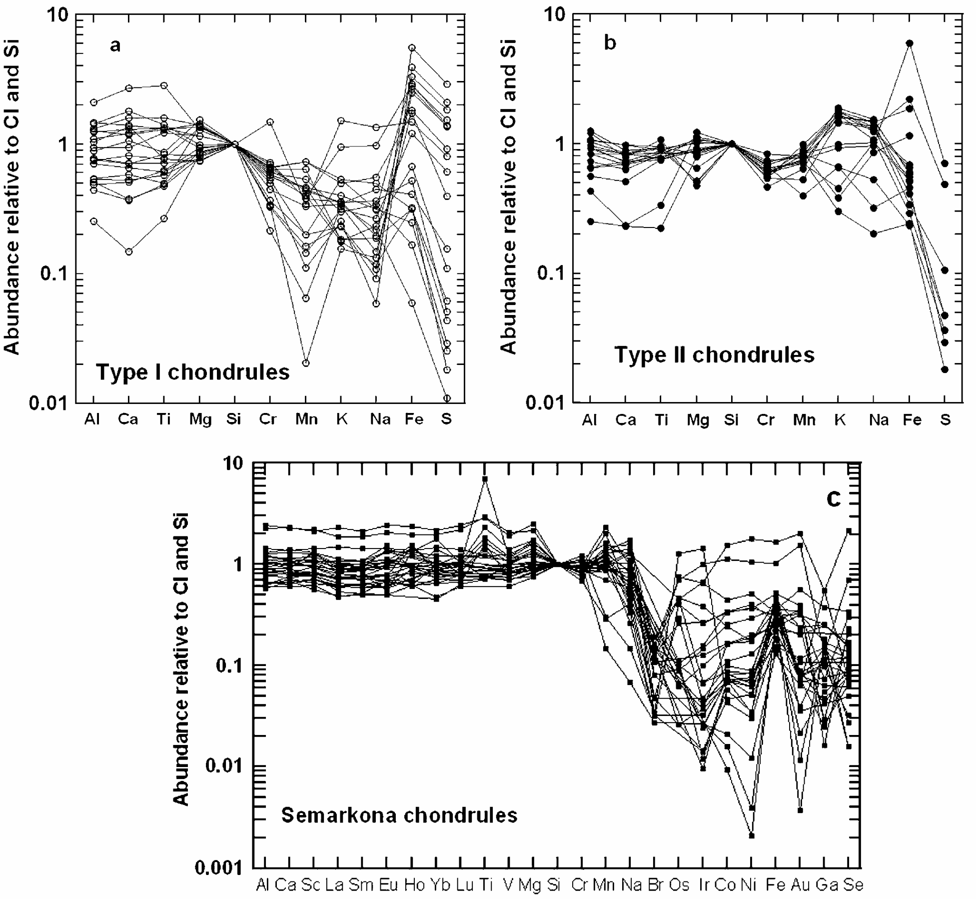

Figure 6. Variation in chemical composition between chondrules in Semarkona (LL3.00). Elemental abundances are plotted relative to silicon and to CI chondrite abundances. Elements on the ordinate are arranged in order of increasing volatility. a), b) Data obtained by electron microprobe analysis (Jones & Scott 1989; Jones 1990, 1994, 1996b, c). Data obtained by instrumental neutron activation analysis (Grossman & Wasson 1983, 1985).

analysis (EPMA) on polished thin sections. The disadvantage of this technique is that it only measures the composition of one random section through each chondrule, which may not be representative of the proportions of different phases throughout the chondrule. Also, only elements present in abundances greater than ~0.05 wt% are measured. The Semarkona data are somewhat selective in that they are taken from studies that were limited to chondrules with specific textural properties, mostly porphyritic. The most important points to observe in this plot are: 1) in most individual chondrules, refractory element abundances (Al, Ca, Ti) are not fractionated relative to one another (i.e. their abundance patterns are flat), and Mg is only minimally fractionated from the refractories; 2) there is about an order of magnitude range in the abundance of refractory elements relative to Si in individual chondrules; 3) there is more than an order of magnitude range in the abundance of volatile elements (K and Na) relative to Si in individual chondrules; 4) type II (FeO-rich) chondrules are generally more volatile-rich and refractory-poor than type I (FeO-poor) chondrules.

These basic observations apply to more complete bulk chemical analyses of Semarkona chondrules (Fig. 6c) obtained by instrumental neutron activation analysis (INAA) (Grossman & Wasson 1983, 1985). INAA has the advantage of measuring the abundance of a broader suite of elements, including trace elements in low (ppb level) abundances. One disadvantage of INAA is that silicon is not measured. INAA also introduces a selection effect because, typically, only larger and less friable chondrules are disaggregated from a chondrite for analysis. Since size can be correlated with chemical composition (e.g., in ordinary chondrites, FeO-poor chondrules are significantly smaller than FeO-rich chondrules), this can introduce bias.

INAA data for Semarkona chondrules show that there are Ni-rich and Ni-poor varieties, each group having a distinctive siderophile-element pattern (Grossman & Wasson 1985). In Ni-rich chondrules, element abundances vary as relatively smooth functions of volatility, i.e., these chondrules are enriched in refractory siderophiles relative to whole-rock values and increasingly depleted in common and volatile siderophiles. The Ni-poor chondrules have appreciably less metal than the Ni-rich chondrules and have more irregularly shaped siderophile-element patterns. These patterns may have resulted in part from the occurrence of siderophile elements in chondrule silicates (which have a pronounced effect in metallic-Fe-Ni-poor samples). However, these low-siderophile samples are also susceptible to contamination by adhering matrix and rim material.

INAA data for bulk chondrules in the CO3 chondrite, Ornans, were obtained by Rubin & Wasson (1988). Because Ornans is classified as subtype 3.4, it is likely that the Fe contents of chondrules, especially the most abundant FeO-poor chondrules, are significantly higher than primary compositions, and that elements such as Na and K have been redistributed during metamorphism. Refractory lithophiles, with the possible exception of Ca, were probably fairly immobile during metamorphism of Ornans chondrules, and these show similar trends to those observed in Semarkona, i.e. flat patterns and a wide range of abundances relative to CI chondrite and Si.

Because Si can be lost by evaporation during chondrule formation or gained by condensation while chondrules are molten, some of the variability in the abundance of refractory elements in chondrules from ordinary and CO chondrites may be caused by changes in the normalizing element, Si; precursors could conceivably have had refractory/Si ratios equal to those in CI chondrites. Likewise, because volatiles and metal may be lost from precursor assemblages during melting, it is plausible that precursor assemblages had solar ratios of these elements as well. These possibilities are discussed below. It is certain, however, that chondrule precursors for these chondrites did not have large interelement fractionations among refractories.

In EH3 Qingzhen, Grossman et al. (1985) found that many chondrules have relatively flat refractory lithophile abundance patterns indicating that the precursors of these chondrules were probably silicates that were not heated sufficiently to cause evaporation of non-volatile phases. These refractory lithophile elements include Ca and rare-earths which are present to a significant degree in the chondrules in the sulfide oldhamite (CaS). This implies that sulfidation of silicates occurred before chondrule formation, and was a property of the precursor assemblages. Although the siderophile abundances vary significantly in the chondrules due to different abundances of metallic Fe-Ni, there is little fractionation between volatile and refractory siderophile elements (e.g., Au and Ir, respectively). This is also consistent with a low degree of evaporation during chondrule formation. An unusual feature of the Qingzhen chondrules is their high (CI-level) abundances of halogens (Br and Cl). In fact, chondrule mesostases contain several weight percent Cl. In view of the alteration of mesostases in ordinary and CO chondrites (Grossman et al. 2000), it seems likely that the high halogen concentrations in Qingzhen chondrules could also have resulted from parent-body alteration processes.

Bulk chemical analyses of chondrules in LEW85332 have been determined by Wasson, Kallemeyn, & Rubin (2000). Two groups of chondrules were identified: Low-FeO chondrules have unfractionated refractory lithophile elements, depletions in volatile lithophile elements, and volatility-controlled depletions in siderophile elements. High-FeO chondrules have essentially unfractionated refractory lithophiles, high abundances of volatile lithophiles, and fractionated siderophiles with a significant depletion in refractory Ir and a high abundance of Fe relative to other siderophiles.

Major element compositions of chondrules from different chondrite groups are compared in Figures 7-9. Data in these plots include the INAA data discussed above, EPMA data for Semarkona discussed above, and EPMA data for chondrules in type 3 enstatite chondrites (Schneider et al. 2002), CO3 chondrites Kainsaz and Ornans (McSween 1977; unpublished data) and the reduced CV chondrite, Vigarano (McSween 1977; unpublished data). Silicon abundances for the Grossman & Wasson (1983) Semarkona INAA data are calculated rather than measured values. Additional INAA data for Semarkona in Figure 8 are from Huang et al. (1996) and Huang & Sears (1997). Silicon abundances for the Ornans INAA data (Rubin & Wasson 1988) and the Qingzhen INAA data (Grossman et al. 1985) were obtained from complementary EPMA analyses on polished sections of each separated chondrule.

Figures 7-9 illustrate the themes that we emphasize throughout this paper: chondrules within each chondrite group show a great diversity of chemical compositions; and there is significant diversity among the chondrite groups. In most cases, compositions obtained by INAA and EPMA are consistent, although there are some discrepancies, discussed below.

Iron, magnesium, silicon and oxygen account for >85% of the mass of most chondrules. Not surprisingly, most chondrule compositions plot between the olivine

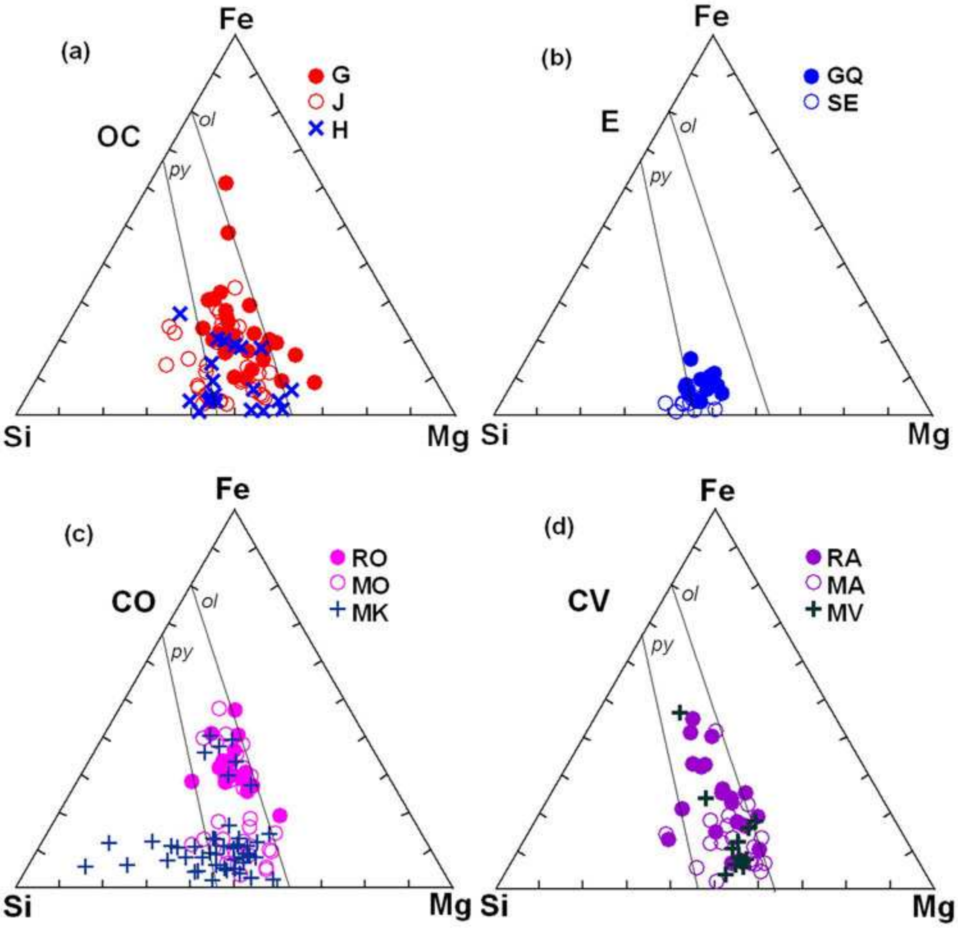

Figure 7. Relative abundances of Fe, Si and Mg in chondrules from unequilibrated chondrites. Filled symbols are INAA data; open symbols are EPMA data. Ol and Py are tie lines showing the compositions of olivine and pyroxene. a) Ordinary chondrites: all chondrules are from Semarkona (LL3.00). G: Grossman & Wasson (1993, 1995); J: Jones & Scott (1989), Jones (1990, 1994, 1996b); H: Huang et al. (1996), Huang & Sears (1997). b) Enstatite chondrites. Chondrules from Qingzhen, GQ: Grossman et al. (1985). Other type 3 E chondrites, SE: Schneider et al. (2002). c) CO chondrites. Chondrules from Ornans (CO3.4), RO: Rubin & Wasson (1988), MO: McSween (1977; unpublished data). Chondrules from Kainsaz (CO3.1), MK: McSween (1977; unpublished data). d) CV3 chondrites. Chondrules from Allende, RA: Rubin & Wasson (1987); MA: McSween (1977; unpublished data). Chondrules from Vigarano, MV: McSween (1977; unpublished data).

and pyroxene tie-lines on Fe-Mg-Si ternary plots (Fig. 7). Chondrules in Semarkona (Fig. 7a) show a continuous spread of Fe contents, mostly up to Fe/(Fe+Mg+Si) = 0.3, and cover a range of Si abundances consistent with the observation that chondrules in ordinary chondrites include porphyritic olivine- and pyroxene-rich types as well as a range of FeO contents (e.g., Brearley & Jones 1998).

Chondrules in E chondrites (Fig. 7b) cluster around the pyroxene tie-line, with very low total Fe contents. This is consistent with the mineralogy of enstatite chondrite chondrules, which are dominated by extremely FeO-poor enstatite.

In CO chondrites (Fig. 7c), there appears to be a hiatus in bulk compositions between an Fe-poor and an Fe-rich group of chondrules. INAA data (Rubin & Wasson 1988) almost exclusively sample the Fe-rich group. Chondrules in Ornans are likely to be enriched in Fe relative to primary compositions because it is petrologic subtype 3.4. Kainsaz, petrologic subtype 3.2 (Grossman & Brearley 2005), is more likely to preserve primary Fe-Mg-Si abundances. The distribution of bulk Fe contents in Kainsaz is more heavily weighted towards the Fe-poor group. The population of Kainsaz chondrules with high Si contents (more Si-rich than the pyroxene tie-line) consists of radial pyroxene chondrules. Silicon-rich chondrules certainly exist in ordinary chondrites, but were not included in the data sets that we have accessed.

Chondrules in CV chondrites (Fig. 7d) show less variation in Si than those in O and CO chondrites: they cluster closer to the olivine tie-line than the pyroxene tie-line. This is consistent with the observation that there are fewer pyroxene-rich chondrules in CV chondrites than in ordinary chondrites (Rubin 1984). Data for Allende show a fairly uniform distribution in Fe, whereas Vigarano chondrules tend to cluster around more Mg-rich compositions. Many chondrules in Allende have been affected by secondary processes including Fe-Mg redistribution during mild metamorphism, anhydrous alteration of chondrule mesostasis to form nepheline and sodalite (Ikeda & Kimura 1995), and oxidation of metal to form magnetite; these processes probably altered the bulk composition data. The Vigarano data probably provide a more accurate picture of primary compositions in CV chondrules, although Vigarano is a breccia and has also been metamorphosed to at least type 3.2 (Guimon et al. 1995**;** Grossman & Brearley 2005). Considering the Vigarano data alone, there is a possible hiatus between an Fe-rich group and an Fe-poor group, similar to that in Kainsaz (Fig. 7c). These observations are consistent with the fact that in carbonaceous chondrites, olivine in (type II) FeO-rich porphyritic olivine chondrules are commonly significantly more FeO-rich than those in ordinary chondrites (mean Fa contents > ~30 mole % in C chondrites vs ~15 mole % in O chondrites (e.g., Brearley & Jones 1998).

In order to include more comprehensive data based on INAA, it is necessary to plot element variations independent of Si. Figure 8 shows Fe and Mg abundances of chondrules in a variety of chondrites, relative to the CI chondrite composition. Trends are similar to those described for Figure 7. The Huang et al. (1996) and Huang & Sears (1997) INAA data for Semarkona are consistently lower in Mg than most other analyses of Semarkona chondrules. The difference can probably be attributed to an analytical artifact. Chondrule compositions in LEW85332 are different from other groups in that they define a fairly restricted area of the Fe-Mg diagram, mainly due to the lack of low-Fe analyses.

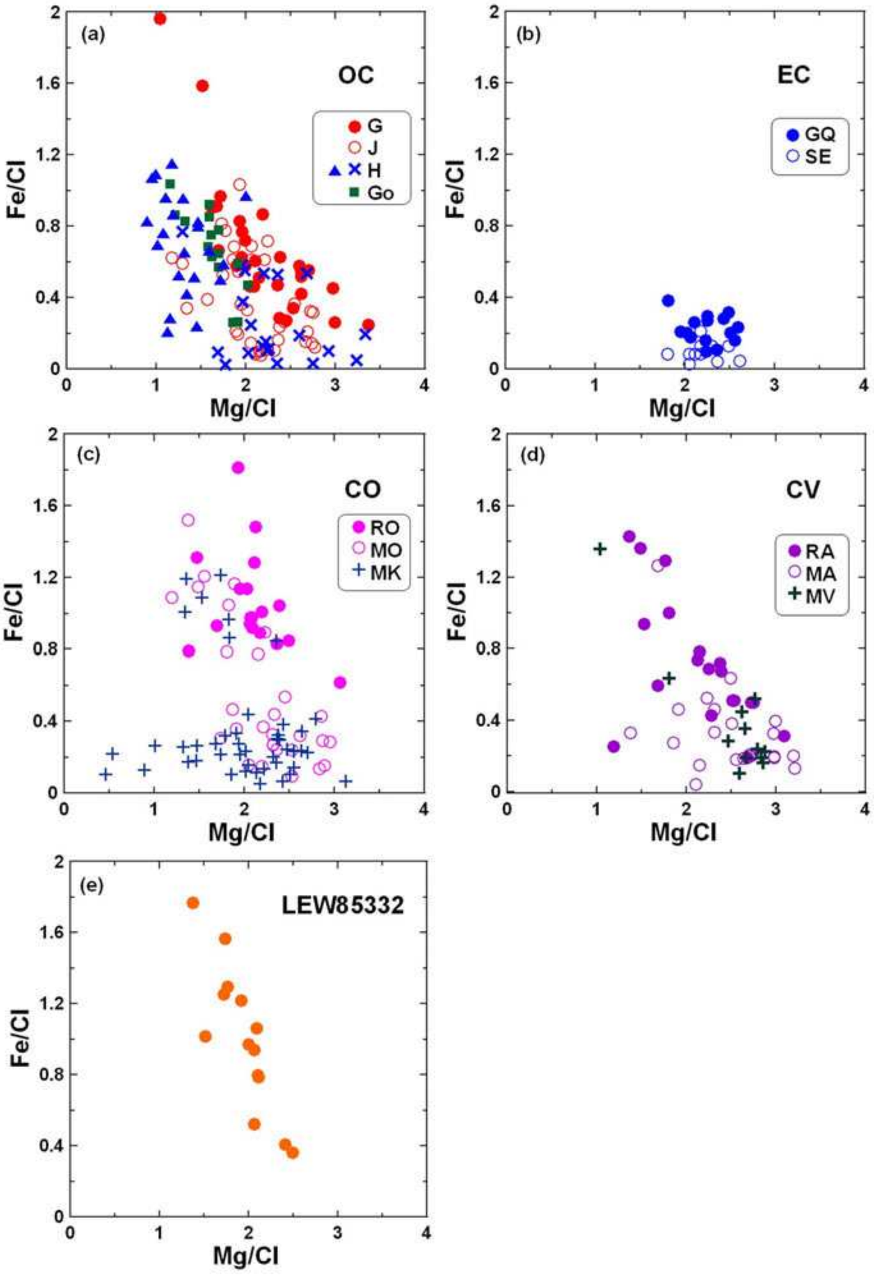

Figure 8. Relative abundances of Fe and Mg in chondrules from unequilibrated chondrites. Filled symbols are INAA data; open symbols are EPMA data. Symbols and data sources are as given for Figure 7. Additional data are: a) Semarkona, H includes INAA data from Huang et al. (1996), Huang & Sears (1997); Go: Gooding & Keil (1981). e) LEW85332: Wasson et al. (2000).

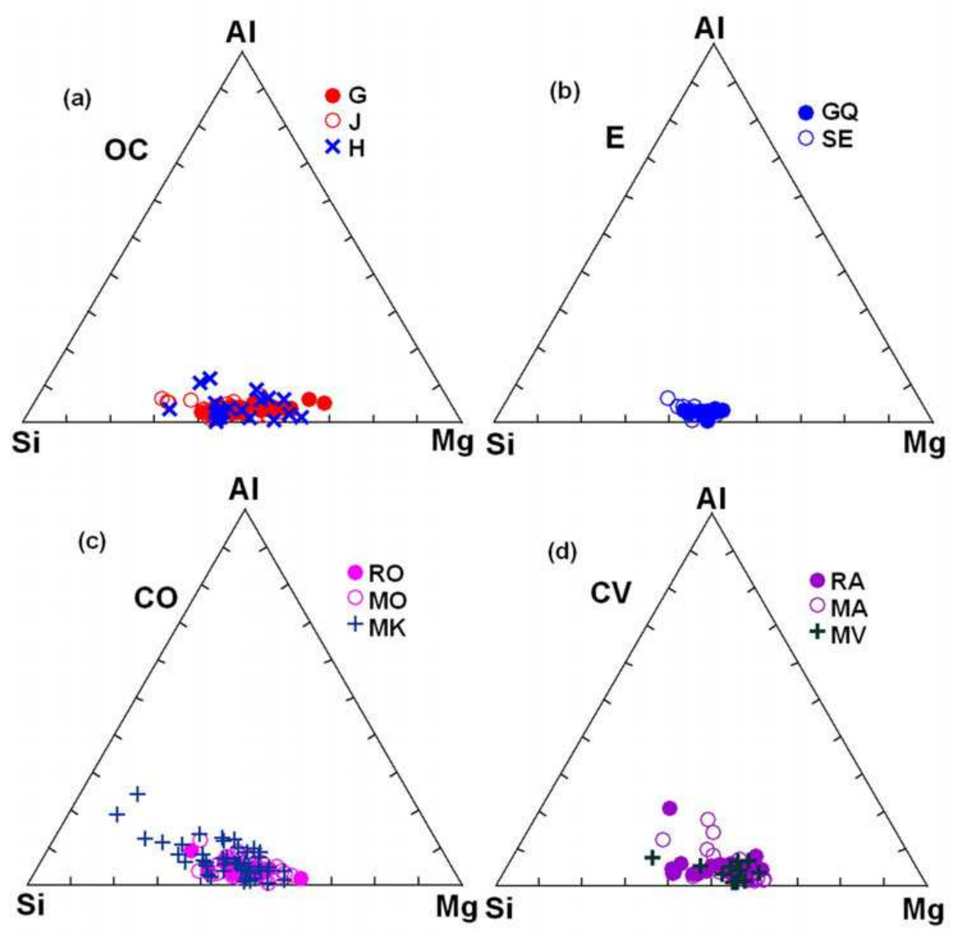

Figure 9. Relative abundances of Al, Si and Mg in chondrules from unequilibrated chondrites. Symbols and data sources are given in Figure 7.

Figure 9 shows the relationship of Al to the major lithophile elements Mg and Si for the same suite of chondrules shown in Figure 7. Since refractory lithophile elements are rarely fractionated relative to each other (Fig. 6), Al can be treated as a proxy for refractory elements. Al contents of chondrules are unlikely to be strongly affected by mild degrees of metamorphism such as those that have altered Ornans and Allende. Most chondrules in all chondrite types have low refractory element contents, and chondrules in the different chondrite groups are not generally distinguished on this plot. The trend towards high Al contents at low Mg/Si ratios in the CO chondrules, that is partly caused by the presence of Si-rich, Al-rich radial pyroxene chondrules in Kainsaz, is not observed in ordinary chondrites, which span a similar range of Mg/Si; indeed, radial pyroxene chondrules in Semarkona are Si-rich and quite Al-poor (Grossman & Wasson 1983). The Allende data of Rubin & Wasson (1987) include one Al-rich chondrule. The most aluminum-rich chondrule composition given by MacPherson & Huss (2005) has Al/(Al+Mg+Si) = 0.4.

It is essential to understand the limitations of data sets used for examining chondrule bulk compositions. We have attempted to summarize the best and most consistent data available for a variety of chondrite types, but unfortunately there is no single data set that can provide a complete overview. The most important conclusions that can be drawn from the data are: (1) refractory lithophile elements are generally unfractionated relative to each other; (2) abundances of refractory lithophile and volatile lithophile elements are extremely variable in chondrules; (3) siderophile elements commonly exhibit volatility-related abundance trends; (4) there are chemical differences in chondrules from different chondrite groups. Some variations in Fe, Si and volatile elements may be attributable to open-system behavior during the chondrule melting event. The challenge is to assess what part of the variation in bulk compositions can be attributed to differences in composition of chondrule precursor materials, and how precursor compositions changed during high-temperature processing.

## 7. Oxidation State of Chondrules

Chondrules show a range of oxidation states: within an individual chondrite, chondrules range from being reduced to relatively oxidized. While this is generally understood by most petrologists, based on the mineralogy and, hence, the observed oxidation state of iron, there are few quantitative determinations of the oxygen fugacity recorded by individual chondrules. Basically, iron can be present as metal ($Fe^0$), as $Fe^{2+}$ in silicate minerals such as olivine and pyroxene and in sulfide such as troilite, and/or as $Fe^{3+}$ (along with $Fe^{2+}$) in magnetite ($Fe_3O_4$).

Type I, FeO-poor chondrules are reduced. They contain abundant Fe,Ni metal and have low (<10 mole %) Fa and Fs contents in olivine and pyroxene, respectively. Metal grains in the most-reduced type I chondrules contain small but significant amounts of P, Si and Cr (Zanda et al. 1994; Rambaldi & Wasson 1981; Kong & Palme 1999; Lauretta & Buseck 2003) which indicates formation under reducing conditions. Calculated oxygen fugacities ($fO_2$) for type I chondrules, based on chemical equilibria between metal and silicates, are between $10^{-11}$ and $10^{-12}$ bars at 1600˚C (Zanda et al. 1994; Lauretta, Buseck, & Zega 2001). For comparison, the $fO_2$ of the iron-wüstite (IW) buffer curve at the same temperature is significantly higher, $\sim 10^{-8}$ bars. [This curve separates the fields wherein metallic iron and wüstite (FeO) are stable.]

Type II, FeO-rich chondrules record much more oxidizing conditions. They contain only minor Fe,Ni metal and their silicate minerals are considerably more FeO-rich, with abundant $Cr_2O_3$ and $P_2O_5$ components. In ordinary chondrites, mean Fa contents of olivine in type II PO chondrules are ~15 mole%. In carbonaceous chondrites, much higher Fa contents, up to 75 mole%, are observed. Typical Fa contents of olivine from type II chondrules in CO and CV chondrites are ~30 mole%. Experiments that reproduced type II chondrule compositions and textures in OC chondrules (e.g., Lofgren 1989) were carried out at 0.5 log units below the IW buffer. To our knowledge, there are no quantitative estimates of the oxygen fugacity for type II chondrules in CO chondrites, although measurements of the oxidation state of Cr in olivine suggest that type II chondrules in CO chondrites are considerably more oxidized than type II chondrules in OC (Sutton, Bajt, & Jones 1996).

The CV chondrites consist of two subgroups, the oxidized and reduced subgroups ($CV_{ox}$ and $CV_{red}$). In chondrites of the $CV_{ox}$ group, metal in chondrules has been oxidized to magnetite. Because Fe oxidizes more readily than Ni, most remaining metal in $CV_{ox}$ chondrites is Ni-rich. Various scenarios for producing the relatively oxidizing environment necessary to form magnetite have been proposed (e.g., Krot, Scott, & Zolensky 1995; Brearley & Jones 1998), most of which agree that magnetite is a secondary mineral produced by oxidation of Fe,Ni metal.

In enstatite chondrites, most chondrules are type I and extremely reduced. Rare FeO-rich pyroxene has compositions that range up to $Fs_{35}$ (Lusby, Scott, & Keil 1987; Kimura et al. 2003). Relict grains containing abundant particles of Fe metal are fairly common in these chondrules, indicating that oxidized materials were present among precursors.

Redox state may have been determined by the condensation temperature of precursor materials, by the ambient $fO_2$ of the gas in the chondrule-forming region (before or during chondrule formation), or by the abundance in the precursor assemblage of reducing agents such as C. In order to understand the information that chondrules can potentially provide about the redox state of their formation environment, we need to examine the evidence that indicates where redox states were established: did either reduction or oxidation affect chondrule precursors, and/or did either oxidation or reduction take place during chondrule-forming events?

The condensation sequence predicts that solid material condensing from the nebular gas would become more oxidized as the system cools: early, high-temperature, condensates are dominated by Fe metal and MgO-rich silicates, whereas lower-temperature condensates would include FeO-rich silicates. As discussed below, there is some evidence that FeO-rich chondrules are younger than FeO-poor chondrules: this could be considered to be consistent with a progressive change in oxidation state of chondrule precursors with time. Evidence that contradicts such a simple scenario is provided by a suite of type-I chondrules described by Hewins et al. (1997). They found that type I chondrules in Semarkona span an extremely wide range of grain sizes, down to slightly melted objects with crystal sizes of only a few micrometers. Fine-grained type I chondrules are rich in volatiles, including S (in the form of FeS). The precursors of these chondrules clearly represented a low-temperature assemblage that was quite poor in FeO.

Although we cannot readily determine whether carbon was an effective reducing agent, because it would be lost as CO gas during the redox process, it is very likely to have been present in chondrule precursors, as discussed above. Reduction of dusty relict grains very likely took place during chondrule formation, but it is less clear whether the reduced state of type I chondrules in general was established during chondrule formation, or in the precursor assemblage.

## 8. Oxygen Isotopic Compositions of Chondrules and Their Precursors

As was seen in bulk compositional data, oxygen isotopic compositions of chondrules shows great diversity both within and among the various chondrite groups. Chondrules from each of the main chondrite classes occupy distinct regions on the oxygen three-isotope plot (Fig. 10). Chondrules from O chondrites, E chondrites and C chondrites generally lie in a sequence of decreasing $\delta^{17}$O, consistent with the same trend for bulk chondrites. However, chondrules in the unique C chondrite, LEW85332, lie on an array that is distinct from those of other C chondrite chondrules (CV, CK, and CR groups).

In Figure 10, we have included data only for chondrites in which primitive oxygen isotope ratios are likely to have been preserved. Clayton et al. (1976) and Clayton, Onuma, & Mayeda (1991) argue that even though oxygen isotopic equilibrium between major minerals is established in type 5 and 6 chondrites, the scale of equilibrium is generally submillimeter. Bulk chondrules in type 3 chondrites are likely to have preserved their initial oxygen isotope signatures in their primary silicate minerals because diffusion rates of oxygen in these minerals are typically very low compared with diffusion rates of cations. Low-temperature aqueous alteration might change the isotopic composition of OC chondrules by increasing $\delta^{18}$O relative to $\delta^{17}$O (Clayton et al. 1991), and this may have a significant but small effect in some chondrules from Semarkona and Bishunpur, as these two meteorites have undergone some aqueous alteration (Hutchison, Alexander, & Barber 1987; Alexander, Barber, & Hutchison 1989). Because there are only seven oxygen isotope measurements of bulk chondrules from ordinary chondrites of very low petrologic subtype (3.0, 3.1) (Clayton et al. 1991), we include data for Chainpur (LL3.4) chondrules in Figure 10 (Clayton et al. 1991; Bridges et al. 1998). The E chondrite data included in Figure 10 are all for Qingzhen (EH3: Clayton & Mayeda 1985), one of the least equilibrated enstatite chondrites.

Of the carbonaceous chondrites, the CV chondrite group has been studied most extensively (Clayton et al. 1983; Rubin et al. 1990; Jones et al. 2004a): these data are shown separately in Figure 10b which has an expanded scale. The CV chondrule data are from the Allende and Mokoia chondrites, which are both oxidized CV chondrites. Oxygen isotopic compositions of chondrules from these chondrites might have been altered from their primary compositions during the reaction in which metal was oxidized to magnetite, or when chondrule mesostasis was replaced by secondary minerals. The CR chondrites, Al Rais and Renazzo, are both petrologic type 2, and have been affected by aqueous alteration, again causing significant changes to the mineralogy of chondrule mesostasis. Ningqiang, an anomalous CK chondrite, is petrologic type 3, and has properties that are probably equivalent to subtype 3.6 (e.g., no glass in chondrule mesostasis). LEW85332 is a primitive type 3 chondrite, but it is highly weathered, and it is possible that oxygen isotope ratios in chondrules in this chondrite could have shifted slightly towards more $^{18}$O-rich values during Antarctic weathering (Wasson et al. 2000). We need to bear these caveats in mind when we discuss the meaning of trends on the oxygen isotope diagram.

As was discussed above for the bulk compositions of chondrules, oxygen isotopes can be modified at various stages of chondrule evolution: the assemblage of precursor grains defines an initial isotopic composition, and the individual isotopic signatures of some precursor grains may be preserved in relict grains after chondrules solidify; oxygen isotopes can be fractionated by evaporation or changed by condensation; hot chondrules can exchange oxygen with surrounding gas; and, chondrules can be altered by secondary processes after solidification. Given this complexity, there has been a variety of interpretations of the oxygen isotope data for chondrules. In the oxygen three-isotope diagram (Fig. 10), a line of slope 0.5 (such as the terrestrial

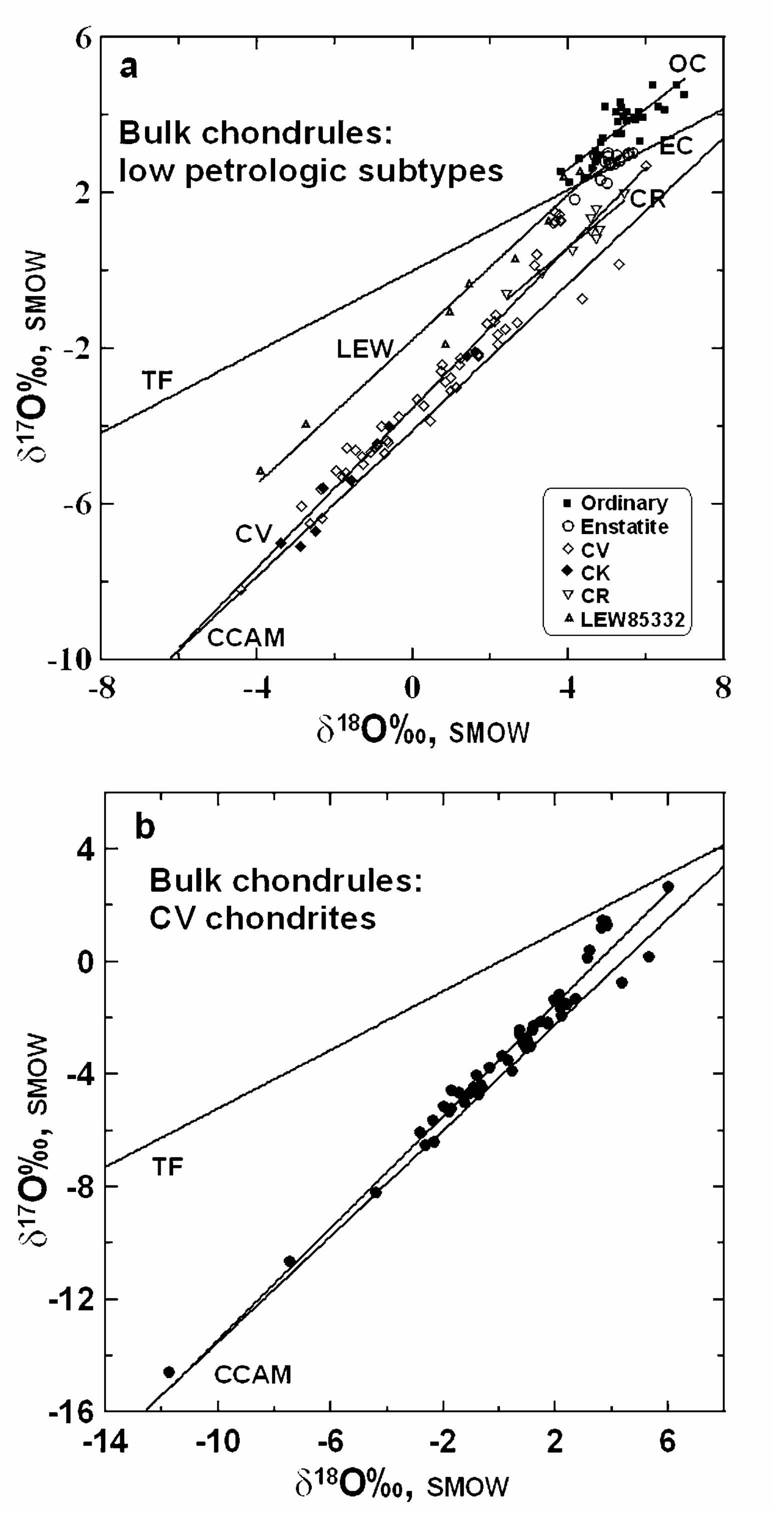
a
Bulk chondrules:
low petrologic subtypes
OC
EC
CR
LEW
TF
CV
CCAM
■ Ordinary
○ Enstatite
◇ CV
◆ CK
▽ CR
▲ LEW85332
6
2
-2
-6
-10
-8
-4
0
4
8
δ¹⁷O‰, SMOW
δ¹⁸O‰, SMOW
b
Bulk chondrules:
CV chondrites
TF
CCAM
4
0
-4
-8
-12
-16
-14
-10
-6
-2
2
6
δ¹⁷O‰, SMOW
δ¹⁸O‰, SMOW

Figure 10. Oxygen isotope ratios of bulk chondrules in chondrites of low petrologic subtype. The plot shows that there is considerable isotopic diversity among chondrules within a given group, and that there is diversity among chondrite groups. Ordinary chondrites: Semarkona (LL3.0), Krymka (LL3.1), Bishunpur (LL3.1) and Chainpur (LL3.4) (Clayton et al. 1991); Chainpur (Bridges et al., 1998). Enstatite chondrites: Qingzhen (EH3) (Clayton & Mayeda 1985); CV chondrites: Allende (CV3) (Clayton et al. 1983; Rubin et al. 1990), Mokoia (Jones et al. 2004a); CK chondrites: Ningqiang (anomalous CK3) (Mayeda et al. 1988); CR chondrites: Renazzo (CR2) and Al Rais (CR2) (Weisberg et al. 1993); Unique C chondrite LEW85332 (type 3.0-3.1) (Prinz et al. 1993; Wasson et al. 2000). Slopes of best-fit lines through the data for individual chondrite groups are: OC = 0.77, EC = 0.68, CV = 0.99, CR = 0.84, LEW = 0.93. A best-fit line through the data for CV chondrules and Ningqiang (CK-an) combined has a slope of 1.00. TF is the terrestrial fractionation line; CCAM is the carbonaceous chondrite anhydrous mineral line, defined by CAIs in CV chondrites.

fractionation line, TF) results from well-understood mass-dependent fractionation processes such as might be caused by fractionation during evaporation. Lines with other slopes indicate the contribution of mass-independent fractionation processes, such as have been proposed by Thiemens (1996) and in various self-shielding models (e.g., Clayton 2002; Yurimoto & Kuramoto 2004; Lyons & Young 2003: see Kuramoto & Yurimoto, this volume), the products of which lie along lines of slope 1. In unaltered chondrule populations, deviations from slope-0.5 lines can only be caused by formation from precursors that had this property, or by modification of the precursor isotopic composition through interactions with surrounding gas while the chondrule is hot.

The line defined by CV chondrite chondrules, on which chondrules from Ningqiang (CK) and CR chondrites also lie, has a slope of 0.99, and thus is controlled by mass-independent fractionation. The CV chondrule line has a slightly steeper slope than the CCAM line (slope 0.94) defined by CAIs in CV chondrites.

Lines of exactly slope 1 are not observed for chondrules in other chondrite groups, although all groups define trends with slopes above 0.5. The slope for LEW85332 is 0.93. The low petrologic type OC chondrules lie on a line of slope 0.77, and EC chondrules lie on a line of slope 0.68. These shallower slopes indicate that the oxygen isotopic compositions are controlled by mixing of independent isotopic reservoirs. In contrast, CAIs from the same groups all have similar, $^{16}$O-rich, isotopic compositions (McKeegan et al. 1998).

One possible explanation for oxygen isotopic compositions of chondrules is that chondrules in each chondrite group are defined by a separate solid reservoir that interacted with a common gas reservoir (e.g., Clayton et al. 1993). The CV chondrites may also be controlled by such a mixing line rather than by mass-independent fractionation. Differences in solid reservoirs among the chondrite groups are generally considered to result from stochastic isotopic variations among precursor materials, i.e., there is no apparent process controlling the isotopic composition of the separate solid reservoirs.

Several observations show that, in general, FeO-rich and barred olivine chondrules in carbonaceous chondrites are more $\delta^{18}$O-rich than FeO-poor chondrules in the same chondrite. This is true for chondrules in CV chondrites (Clayton et al. 1983;

McSween 1985; Jones et al. 2004a), and LEW85332 (Wasson et al. 2000), as well as for isolated mineral grains in CI chondrites (Leshin, Rubin, & McKeegan 1997). FeO-rich igneous rims on Allende chondrules also have higher $\delta^{18}O$ than their more FeO-poor, host chondrules (Rubin et al. 1990). Clayton et al. (1983) suggested that this effect is related to the degree of melting: FeO-rich and barred chondrules are likely to have undergone the most extensive exchange with nebular gas during the time they were molten. These observations lead to the inference that the gas was at the $\delta^{16}O$-poor end of the CV chondrule array. For OC chondrules, a correlation between $\delta^{18}O$ and chondrule size observed in Dhajala (H3.8) led Clayton et al. (1986) to propose that the solid precursor lies at the upper end of the OC chondrule mixing line, although Clayton et al. (1991) inferred the reverse. In contrast, Bridges et al. (1998) observed that in Chainpur chondrules, $\delta^{18}O$ decreases with increasing chondrule size.

Earlier interpretations suggested that a common gas reservoir lay close to the TF line, at around $\delta^{18}O = +4$ ‰ (Clayton et al. 1983). This was based on the observation that Allende chondrules (as well as O and E chondrite chondrules) appeared to trend towards this value. However, the Allende chondrules that define this trend (mostly FeO-rich, BO chondrules) are likely to have been perturbed by secondary processes (Young et al. 2002, Jones, Leshin, & Guan 2004b). Jones et al. (2004b) suggested that, if chondrules from all groups have interacted with a common gas reservoir, that reservoir is more likely to have a composition around $\delta^{18}O = +15$ ‰.

In general, oxygen isotope analyses of individual mineral grains in chondrules from the different chondrite groups are consistent with the trends shown by bulk chondrules. Significant oxygen isotopic diversity is observed within individual chondrules. Some of the diversity is a difference between phenocryst phases and mesostasis, for example in barred olivine chondrules from Allende where it can be attributed to secondary alteration of mesostasis (Young et al. 2002). In other examples, gas-melt exchange during chondrule formation has been proposed to explain isotopic diversity within individual chondrules (Russell et al., 2000; Maruyama & Yurimoto 2003; Jones et al. 2004a). Fine-grained porphyritic chondrules in Mokoia and Allende contain olivine grains that are extremely heterogeneous in oxygen isotope compositions and show spreads of $\delta^{18}O$ up to 50‰ along the CV chondrule line in a single chondrule (Jones et al. 2004a, b). This heterogeneity may be caused by the presence of $^{16}O$-rich relict grains, or interaction with the ambient gas when the chondrule was molten.

In Al-rich chondrules in ordinary chondrites, individual mineral grains spread along an array that is an extension of the OC array, below the TF line (Russell et al. 2000). There are currently insufficient data for individual mineral grains in OC chondrules to evaluate the oxygen isotopic variation within ferromagnesian chondrules, although Sears et al. (1998) and Saxton, Lyon, & Turner (1998) showed that oxygen isotope ratios of some olivine grains in Semarkona and Julesburg (L3.7) fall below the TF line.

Overall, the current interpretation of oxygen isotope data for chondrules suggests: 1) that there were isotopic differences among chondrule precursors in different chondrite groups, and 2) that chondrules preserve evidence for isotopic interaction with the ambient gas while they were molten. The ambient gas may have been common to all chondrite groups. However, the data currently available are generally inadequate to address these relationships in much detail, largely because measurements have not been made on chondrules from the appropriate primitive chondrites of low petrologic subtype.

## 9. Origin of the Variation in Chondrule Properties

There are several possible reasons for the diversity in physical, chemical and isotopic properties of chondrules. It has been proposed that much of the diversity can be attributed to changes that took place during chondrule heating events (open system behavior). Alternatively, diversity in all the properties discussed could be attributed to differences inherent in the individual chondrule precursor assemblages. Differences among precursors or in the extent to which chondrules behaved as open systems could vary with time and/or space. Random recycling of previous generations of chondrule materials could contribute significantly to precursor heterogeneity.

Variable degrees of reduction and subsequent iron loss, along with evaporation of volatile elements, including Si, has been proposed to account for the range of chondrule compositions, as well as sizes and oxidation states (Jones 1990; Sears et al. 1996; Connolly, et al. 2001). Iron loss takes place when Fe-metal beads are physically removed from the chondrule. This process would result in various degrees of refractory lithophile element enrichments in the residual chondrules, probably correlated with degree of reduction and volatile content. However, volatilization alone cannot account for all of the chemical and isotopic information for chondrules. The kinetics of chemical and isotopic evaporation and condensation during chondrule formation are reviewed at some length by Lauretta et al. (2005). The lack of isotopic fractionation in chondrules, for example in S, Mg and Si isotopes, means that isotopic reequilibration was significant during cooling. Chondrules likely lost moderately volatile elements by evaporation when they were molten, but then lithophile elements recondensed onto cooling chondrules to various degrees, and siderophile elements condensed as new phases that became incorporated into chondrule rims and matrix.

Much of the diversity we have discussed could be explained by having heterogeneous precursor assemblages that consisted of a random aggregate of fine-grained material incorporating FeO-rich and FeO-poor silicates, and varying amounts of carbon. Alexander (1994, 1996) proposed that chondrule recycling played an important role in producing the variation in bulk compositions. Because the refractory lithophile elements (Ca, Al, Ti, rare earth elements) are largely fractionated into the melt in a typical ferromagnesian chondrule, they become concentrated in chondrule glass. Hence, variable amounts of chondrule glass fragments in chondrule precursors would lead to varying refractory lithophile element abundances. Since we know that there was a certain amount of recycling in the chondrule-forming region (see next section), it is not unreasonable to consider that aggregates of grains within a given region of space varied in composition because of random sampling of a diverse population of materials. Clayton (1993) argued that the relatively tight cluster of oxygen isotopes for ordinary chondrite chondrules compared with CV chondrite chondrules reflects multiple reheating and an approach to equilibration with the nebular gas. However, if OC chondrules represented a greater degree of recycling than CC chondrules, we would predict that CC chondrites should show a smaller spread in refractory lithophile elements than OC chondrules, and this is not observed (Fig. 9).

Further evidence for a diversity of precursor compositions comes from agglomeratic olivine chondrules, which are characterized by fine-grained, compositionally heterogeneous assemblages of olivine, pyroxene, feldspathic glass, and minor chromite, metal and sulfide (Dodd 1971; Rubin 1984, Weisberg & Prinz 1996; Hewins et al. 1997). These objects are likely to be the best preserved candidates for chondrule precursors, although they have been heated to temperatures at which sintering took place, without significant melting.

The differences in physical, chemical and isotopic properties among the chondrite groups are hard to reconcile with a model in which all chondrules are derived from a common source material. Clearly, there were differences in the batches of chondrules that ended up in the different chondrite parent bodies. Chemical and isotopic differences between the O, C and E chondrite classes are sufficiently distinct as to make it necessary to have at least three different reservoirs of chondrules. Because these different chondrite classes, and probably the groups within them, appear to be derived from separate parent bodies, and because there is a compositional zonation in the asteroid belt, it seems that spatial heterogeneity could have played a part in producing the diversity of chondrule compositions. It is difficult to quantify this further based on the available data.

At least part of the diversity of chondrule compositions has been interpreted as a chemical evolution with time. As the nebula cooled it evolved chemically, and condensing silicates would have become progressively more Si-rich and ultimately more Fe-rich. Arguments for this evolution include the fact that igneous rims on CV chondrules are more FeO-rich than their chondrule hosts (Rubin 1984). This evolution is accompanied by a change in oxygen isotopic composition towards heavier oxygen isotope ratios. Chondrule ages determined using the $^{26}$Al chronometer also argue for an evolution towards more Si-rich and Fe-rich compositions with time (Kita et al. this volume). In OC chondrites, chondrule ages correlate with bulk Si/Mg and abundances of volatiles (Mostefaoui et al. 2002; Tachibana et al. 2003), and in CO chondrites, FeO-rich chondrules are younger than type I chondrules (Kunihiro et al. 2004). Age differences are significant, up to 1 My. However, other petrologic observations, such as evidence from relict grains, argue that these trends were not universally true: FeO-rich relict grains (e.g., dusty relict olivine) are observed in low-FeO chondrules, and vice versa (Jones 1996b). This indicates that at least some FeO-rich chondrules formed and disaggregated before some FeO-poor chondrules, and argues against a uniform evolution towards more FeO-rich, more oxidized and more $^{16}$O-depleted compositions with time throughout the nebula.

The overall picture of chondrule precursor information that emerges is that there was a great diversity in bulk chemical and oxygen isotopic compositions of precursor aggregates. A given region of the solar nebula must have contained chondrule precursor aggregates with a wide range of compositions. Chondrule precursor heterogeneity occurred on a scale that allowed for different chondrule assemblages among chondrite groups, suggesting that accretion into parent bodies unique to each chondrite group occurred quite promptly after chondrule formation events. A unified picture of chondrule formation must reconcile the different observations that we have discussed. For example, if there was an overall chemical evolution with time, was this also accompanied by an evolution in oxygen isotope ratios? Did regions of the nebula corresponding to the different chondrite groups evolve separately? If so, how did they remain discrete over the extended time periods inferred from $^{26}$Al ages? If oxidation state was set by reduction reactions with carbon, does this provide indirect information about the speciation of C in precursor assemblages, which would have been present in the earlier formed chondrules, and absent in later generations? At present, we do not have sufficient information to answer such questions, but the field of chondrule research is beginning to address global nebula models that incorporate these different types of observations.

## 10. How Many Times were Chondrules Heated?

An important constraint for chondrule heating models is the number of heating and cooling events that chondrules experienced. The number of times a chondrule was heated can be inferred from several lines of petrologic evidence. There is widespread evidence for multiple heating events, especially in porphyritic chondrules. In many cases, it is clear that an initial generation of chondrules was formed, fragmented by collisions, and the fragments were incorporated into a new chondrule assemblage prior to the second heating event (or, alternatively, that new and compositionally different material was added to existing chondrules, which were then remelted). In these cases, evidence for reheating is incontrovertible. Examples of such processes include relict grains, igneous rims and (arguably) enveloping compound chondrules. More than 25% of OC chondrules and more than 50% of CV chondrules contain direct evidence for this type of process (Rubin & Krot 1996). Textural relationships between the objects described are illustrated in Figure 11.

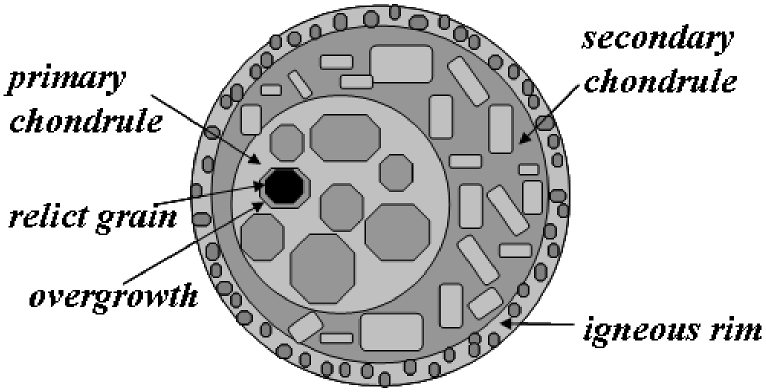

Figure 11. Schematic diagram showing different kinds of evidence for multiple melting episodes in chondrules.

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In other cases, where there is no evidence for recycling, the interpretation of textures is more difficult. A heating event does not necessarily melt a chondrule completely. If a chondrule is heated to a peak temperature well below its liquidus, partial melting of components with the lowest melting temperatures occurs. This typically includes the glassy mesostasis, metal and sulfide grains, pyroxene, and some fraction of the olivine. A chondrule may be reheated to the point of partial melting more than once without a significant change in overall texture if phenocryst phases do not significantly melt. In this case, evidence for reheating relies on interpretations of more subtle, and sometimes ambiguous, textural and compositional features, such as zoning in phenocrysts.

*Relict grains* are mineral grains or fragments within chondrules that survived the final chondrule melting event (Fig. 2). There are two main varieties of relict olivine grains: (1) Approximately 10-20% of low-FeO porphyritic olivine chondrules contain olivine phenocrysts that appear dusty when viewed microscopically in transmitted light (Fig. 3). The "dust" consists of low-Ni, metallic Fe blebs that formed by reduction of FeO from the olivine grain during chondrule heating (Nagahara 1981; Rambaldi 1981; Rambaldi & Wasson 1982). These olivine grains were appreciably richer in FeO than the grains that crystallized from the chondrule melt during the final heating event (e.g., Jones & Danielson 1997), and were probably reduced during the chondrule heating event, as discussed above. (2) Depending on the chondrite group, up to 90% of high-FeO porphyritic olivine chondrules contain small olivine grains with low-FeO compositions that are far out of equilibrium with the FeO-rich grains that crystallized from the host chondrule melt (Steele 1989; Jones 1990, 1992; Wasson & Rubin 2003; Kunihiro et al. 2004). The low-FeO grains tend to survive the melting event because they have a higher melting temperature than other components in the chondrule precursor. Both types of relict olivine grains are most likely derived from previous generations of chondrules (Jones 1996b), although some grains may be condensates (e.g., Steele 1986; Weinbruch et al. 2000). Hence, fragmentation and recycling of chondrules were common in the chondrule-forming region.

Laboratory crystallization experiments have shown that porphyritic textures can be produced only by incomplete melting because individual grains need to be seeded by a crystallization nucleus (e.g., Lofgren 1989, 1996; Lofgren & Russell 1986; Connolly & Hewins 1995). Nuclei may be submicroscopic, so in the plane of a thin section, it is unlikely that the nucleus of a phenocryst will be identifiable. Crystallization nuclei are not generally referred to as relict grains, although they do represent remnants of solid precursor grains. Connolly & Hewins (1995) have also shown that external seeding may take place by infalling dust, in which case the infalling dust grains are technically relict grains.

*Igneous rims* around chondrules consist of ~5-10-µm-size grains of olivine, pyroxene, plagioclase feldspar (or feldspathic glass), sulfide and metal. They occur as 10-1000-µm-thick spherical shells surrounding ~10% of the chondrules in ordinary chondrites and ~50% of those in CV carbonaceous chondrites (Rubin 1984). The rims appear to have undergone ~20-80% melting (Krot & Wasson 1995); many contain spheroidal metal blebs that solidified from molten metal droplets. Igneous rims could have formed by melting finer-grained (presumably dusty, highly porous) material which had enveloped the host chondrule in the nebula. This would indicate that the host chondrule experienced at least two heating events. Alternatively, it has been shown experimentally that igneous rims can be produced without a second heating event, when fine-grained dust impinges on a (molten) chondrule analog (Yu et al. 1998).

*Enveloping compound chondrules* are conjoined chondrules which have a contact arc exceeding 180° (Wasson et al. 1995). In many cases, the small "primary" chondrule is totally enclosed within the "secondary"; i.e., the latter forms a quasi-spherical shell around the former. There are two possible mechanisms for forming enveloping compound chondrules. (1) A small solidified chondrule collides inelastically with a larger molten or semi-molten droplet (e.g., Lux, Keil, & Taylor 1981; Kracher, Scott, & Keil 1984). (2) A small solidified chondrule becomes embedded in finer-grained, relatively porous material (e.g., Wasson 1993). When the assemblage is heated, the finer-grained material melts preferentially and forms a shell around the unmelted primary. This mechanism differs only in degree (i.e., higher temperatures, greater extent of melting) from the one responsible for the formation of igneous chondrule rims. If this latter mechanism is the dominant mechanism for forming enveloping compound chondrules, such objects provide further evidence for at least two heating events.

Evidence for reheating based on *chemical zoning* in phenocrysts is currently being discussed in some depth. Rubin (1989), Wasson & Rubin (2003) and Wasson (2004) argue that many of the large (>150 μm) phenocrysts in Type II, FeO-rich porphyritic olivine chondrules are relict grains in the sense that they did not crystallize in the last heating event that the chondrule experienced. Their arguments are based on the fact that FeO-rich overgrowths on FeO-poor relicts in these chondrules are very thin (~5-μm-thick). Wasson and Rubin argue that, if these rims are typical of the width of material that grew during cooling following the final chondrule melting event, it is not possible that the entire volume of 150-μm-wide olivine grains could have crystallized at the same time. Thus, the large grains are mostly relicts and the porphyritic chondrules that contain them must have been melted more than once, perhaps many times. This interpretation has been used by Wasson and coworkers to argue for multiple chondrule heating events, each with rapid cooling rates $>10^5$ K/hr.

The alternative explanation for the observation of thin rims on FeO-poor relicts in these chondrules is that the relict grain was continuing to be resorbed into the melt during the cooling interval, and that the overgrowth did not begin to grow until the final stages of olivine growth (Connolly & Jones 2005; Hewins et al. this volume). Thin rims on relict grains in the presence of larger, melt-grown phenocrysts are easily grown in experiments with single-stage cooling histories (Lofgren & Le 2000; Hewins & Fox 2004). In addition, zoning profiles across large olivine phenocrysts in these chondrules can be modeled closely by closed-system fractional crystallization in a single continuous cooling event (Jones 1990), which argues against the suggestion that these grains represent multiple stages of growth.

A second line of petrologic evidence that has been interpreted in different ways is observations of multiple, thin (1-2-μm) zoning bands ("oscillatory" zoning) in low-Ca pyroxene and olivine grains (Watanabe, Kitamura, & Morimoto 1986; Lusby et al. 1987; Noguchi 1989; Steele 1995; Jones 1996a; Wasson & Rubin 2003). Watanabe et al. (1986) argued that the zoning resulted from fluctuating redox conditions in the gas surrounding the chondrule. Jones (1996a) argued that the zoning is "oscillatory" zoning, resulting from disequilibrium growth at the crystal / melt interface during single-stage cooling of the chondrule. Wasson et al. (2003) argue that these grains preserve a record of multiple melting/crystallization events.

Rubin & Wasson (2005) argued that fine-grained (20-μm), multi-lobate, porphyritic chondrules common in CO3 chondrites provide evidence for multiple heating. The lobes of these objects are rounded, indicating that they are not fragments. A numerical analysis implies that if these grossly non-spherical objects had been completely molten, they would have collapsed into spheres within a millisecond. This is far too short a time to grow 20-μm-size grains. Thus, the final melting event experienced by these chondrules must have been followed by only very minor crystallization. The non-spherical chondrules must therefore have been melted more than once, and probably formed from remelted chondrule fragments.

In summary, although there is currently some disagreement about the interpretation of zoning features, it is clear that many chondrules record multiple heating events. It is safe to say that many, if not most, chondrules experienced a minimum of two melting or partial melting episodes. Although rare examples of three heating episodes have been described (Rubin 1984), most chondrules only retain a record of two heating events (with recycling occurring between the two events). Arguments for multiple heating events based on phenocryst zoning can be taken to infer that porphyritic chondrules suffered up to ten heating events, but this interpretation is controversial.

## 11. Summary

We have reviewed a variety of chondrule properties that provide information about chondrule precursors and formation conditions. It is clear that it is difficult to make simple statements about the physical, chemical and isotopic nature of chondrule precursors. One problem is that there is a lack of data from chondrules in the least-equilibrated chondrites. However, even in cases where we are fairly confident that chondrule properties are primary, we recognize that the transient heating events that formed chondrules may have perturbed the system, so that we must take into consideration the fact that observed chondrule properties are not necessarily those of their precursors. Despite these complications, it is clear that chondrules show a great diversity in their primary chemical compositions, oxidation states, oxygen-isotope compositions and physical properties both within and among chondrite groups. Some of this diversity may be attributable to temporal evolution of solid material in the nebula, and some to spatial heterogeneities. It is also likely that heterogeneities existed among precursor aggregates due to random sampling of a diverse population of solid materials in the chondrule-forming region.

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