# 1.07 Chondrites and Their Components

E. R. D. Scott and A. N. Krot

*University of Hawai'i at Manoa, Honolulu, HI, USA*

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1.07.1 INTRODUCTION

1.07.1.1 What Are Chondrites?

Chondrites are meteorites that provide the best clues to the origin of the solar system. They are the oldest known rocks—their components formed during the birth of the solar system ca. 4,567 Ma—and their abundances of non-volatile elements are close to those in the solar photosphere. Chondrites are broadly ultramafic in composition, consisting largely of iron, magnesium, silicon, and oxygen. The most abundant constituents of chondrites are chondrules, which are igneous particles that crystallized rapidly in minutes to hours. They are composed largely of olivine and pyroxene, commonly contain metallic Fe,Ni and are 0.01–10 mm in size. Some chondrules are rounded as they were once entirely molten but many are irregular in shape because they were only partly melted or because they accreted other particles as they solidified. Chondrites themselves were never molten. The definition of a chondrite has expanded recently with the discovery in Antarctica and the Sahara Desert of extraordinary meteorites with chondrules 10–100 μm in size, and chondrites so rich in metallic Fe,Ni that they were initially classified as iron meteorites with silicate inclusions. Thus, in meteoritics, as in other fields of planetary science, new discoveries sometimes require definitions to be modified.

Chondrites are so diverse in their mineralogical and textural characteristics that it is not possible to describe a typical chondrite. We show one with diversely textured chondrules including prominent, esthetically pleasing, rounded chondrules (Figure 1a), and another with more uniformly textured chondrules (Figure 1b). Owing to the high abundance of rounded or droplet chondrules in the so-called ordinary chondrites (Figure 1a), studies of the origin of chondrules have commonly been based on these chondrites.

Chondrites contain diverse proportions of three other components: refractory inclusions (0.01–10 vol.%), metallic Fe,Ni (<0.1–70%), and matrix material (1–80%). Refractory inclusions are tens of micrometers to centimeters in dimensions, lack volatile elements, and are the products of high-temperature processes including condensation, evaporation, and melting. Two types are recognized: calcium- and aluminum-rich inclusions or Ca–Al-rich inclusions (CAIs), and amoeboid olivine aggregates (AOAs). CAIs are composed of minerals such as spinel, melilite, hibonite, perovskite, and Al–Ti-diopside, which are absent in other chondritic components (see Chapter 1.08). Amoeboid olivine aggregates consist of fine-grained olivine, Fe,Ni metal, and a refractory component largely composed of aluminum-diopside, anorthite, spinel, and rare melilite. Grains of metallic Fe,Ni occur inside and outside the chondrules as grains up to a millimeter in size and, like the chondrules and refractory inclusions, formed at high temperatures. Matrix material is volatile-rich, and fine-grained (10 nm–5 μm) and forms rims on other components and fills the interstices between them. Chondrite matrices have diverse mineralogies: most are disequilibrium mixtures of hydrated and anhydrous silicates, oxides, metallic Fe–Ni, sulfides, and organic material and contain rare presolar grains.

1.07.1.2 Why Study Chondrites?

Goldschmidt, Suess, and Urey showed that chondrites provide the best estimates for the mean abundances of condensable elements in the solar system. These estimates were essential
for developing theories for the formation of elements in evolved stars (see Chapters 1.01 and 1.03). Presolar grains (see Chapter 1.02) provide additional clues to nucleosynthesis and the subsequent growth of circumstellar grains. Chondrules, metal grains, refractory inclusions, and matrix materials formed under very diverse conditions in the solar system and appear to offer insights into processes that occurred during the formation of the Sun and planets from a collapsing cloud of interstellar dust and gas. The rocks themselves provide clues to the geological processes including impact processes that affected asteroids over 4.5 Ga. Studies of chondrites help us to match chondrite groups with asteroid classes, to understand the origin and evolution of the asteroid belt, the nature of planetesimals that accreted into terrestrial planets, and the reason for the dearth of planetary material between Mars and Jupiter. Finally, chondrite studies help us to understand the physical and mineralogical structure of unmelted asteroids and to assess what should be done about rogue near-Earth objects that threaten Earth.

In this chapter, we focus on the insights that chondrites offer into the earliest stages in the formation of asteroids and planetesimals in the solar nebula—the protoplanetary disk of dust and gas that evolved into the planetary system. Other chapters review many other aspects of chondrite studies. Since the first edition of the Treatise on Geochemistry, there have been considerable advances in understanding the chronology of chondrule and CAI formation by reconciling data from short- and long-lived isotopes (see Kita et al., 2005 and Chapter 1.16), possible mechanisms responsible for the oxygen-isotopic anomalies in chondrites, and in the use of detailed isotopic measurements to distinguish and date nebula and parent body alteration effects. A surprise to many is the discovery that planetesimals already existed in the nebula when chondrules were forming, and that in some cases at least, chondrules may have formed from preexisting bodies (Kleine et al., 2005; Hevey and Sanders, 2006; Krot et al., 2005a). Comets too are not as pristine as once believed. Chondritic porous interplanetary dust particles (IDPs), like pristine chondrite matrices, contain abundant forsterite and enstatite grains that lack large isotopic anomalies, showing that most silicates in comets were thermally processed in the solar nebula (Messenger et al., 2003; Wooden et al., 2005).

1.07.1.3 Historical Views on Chondrite Origins

At the beginning of the space age in the 1960s, there were two views about the origin of chondrules and the variations in the concentrations of the most volatile elements in chondrites. Ringwood, Urey, and others invoked volcanism, impacts, and other planetary processes, whereas Wood, Larimer, and Anders invoked processes in the solar nebula (Wood, 1963; Larimer, 1967; Larimer and Anders, 1967). In the early 1970s, studies of CAIs by Grossman and others appeared to strongly favor an origin
for chondritic components as condensates from the solar nebula (Grossman and Larimer, 1974). However, this simple picture was disrupted by discoveries of ubiquitous isotopic anomalies in CAIs and the complexity of the mineralogical and isotopic record in chondritic components, which seemed inconsistent with the standard model of a hot, monotonically cooling solar nebula. In addition, astronomical evidence and theoretical studies suggested that the solar nebula was not hot enough to vaporize silicates where chondrules formed. The solar nebula was envisaged as a place where there were dynamic, energetic, dust-rich zones with constantly changing dust/gas ratios and fluctuating high temperatures. “Mineral material caught in this maelstrom went through multiple cycles of melting, evaporation, recondensation, crystalization, and aggregation” (Wood, 1988).

Since the mid-1980s, much progress has been made in understanding chondrites, though the origin of their components has not been resolved. Discoveries of new kinds of carbonaceous chondrites have shown that the Allende meteorite, which is the most-studied chondrite, is not as pristine as once believed. Its components were modified in asteroids (e.g., Krot et al., 1995, 1998b) or the solar nebula (e.g., Palme and Fegley, 1990; Weisberg and Prinz, 1998). Detailed isotopic and chemical data for CAIs and chondrules from ion microprobe studies have been invaluable in understanding how and where chondritic components were altered, but have not yet resolved their origin. Most authors now accept that CAIs and most chondrules formed in some kind of solar nebula environment, and several promising models have been developed, but some workers argue that planetesimals were essential for the formation of chondrules (e.g., Sanders, 1996; Lugmair and Shukolyukov, 2001; Hsu et al., 2000). To meteoriticists like Wood, who argued in 1963 that chondrites were aggregates of solar nebular condensates, it has seemed that chondrite research has stagnated and that little progress has been made in developing plausible theories for the origins of chondrules, CAIs, and chondrites (Kerr, 2001). However, most find the excitement of studying presolar grains, solar nebula particles, and annual batches of new types of meteorites from Antarctica to be irresistible (Bischoff, 2001).

1.07.1.4 Chondrites and the Solar Nebula

Chondrites used to be considered as products of a “minimum” solar nebula (containing just enough material to make the planets) that accreted from components formed at a single nebula location. However, it now appears that chondritic components formed at various locations over a period of several million years during which the nebula mass would have decreased by an order of magnitude or more. Refractory inclusions probably formed close to the protosun at an early stage when the disk was most active and accretion rates onto the protosun were highest (Wood, 2000b, 2004). Chondrules probably formed over several million years in localized heating events near their accretion site with the youngest and oldest chondrules forming and accreting by different mechanisms (see Kita et al., 2005; Scott and Krot, 2005b; Krot et al., 2005a). However, some chondrules, such as CAIs, may have formed at the inner edge of the disk prior to injection into the asteroid belt by bipolar outflows (Liffman and Brown, 1996a, b; Shu et al., 1996, 2001). Alternatively, Alexander et al. (2001) have argued that CAIs and chondrules both formed in localized heating events in the asteroid belt.

Astronomical studies of star-forming regions have provided considerable insights into the early evolution and dynamic environment of the Sun and its protoplanetary disk and possible origins for components in chondrites and comets (Reipurth, 2005; Alexander, 2005). However, the 7° difference between the planetary and solar angular momentum vectors (Hutchison et al., 2001), the multiplicity of protostellar systems, and the discovery of numerous “hot Jupiters” around other stars provide additional reminders of the complexity of disk evolution.

1.07.2 CLASSIFICATION AND PARENT BODIES OF CHONDRITES

1.07.2.1 Chondrite Groups, Clans, and Parent Bodies

Many thousands of chondrites have been classified into 15 groups; about 15 other chondrites do not fit comfortably into these groups and are called ungrouped (Table 1). Thirteen of these groups comprise three classes: carbonaceous (CI, CM, CO, CV, CR, CH, CB, and CK), ordinary (H, L, and LL), and enstatite (EH and EL). The K and R chondrites do not belong to the three classes (see Chapter 1.05). Chondrites are also classified into petrologic types 1–6, which indicate the extent of asteroidal processing (see Table 2 of Chapter 1.05). Type 3 chondrites are the least metamorphosed and least altered; type 6 are the most metamorphosed. Type 1 chondrites, which lack chondrules, are composed almost entirely of
Table 1 Abundances of refractory inclusions, chondrules, metallic Fe,Ni, and matrix and other key properties of the chondrite groups.

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<th>Refract. lith./Mg rel. CI</th>
<th>CAI and AOA (vol.%)</th>
<th>Chondrule average diameter (mm)</th>
<th>Chondrules (vol.%)*</th>
<th>Metal (vol.%)*</th>
<th>Matrix (vol.%)*</th>
<th>Fall frequency (fall frequency)*</th>
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</table>

Sources: Scott et al. (1996); other data from Weisberg et al. (1996, 2001), Rubin (2000), Krot et al. (2002a), Kimura et al. (2002), and Bischoff et al. (1993).

*Mean ratio of refractory lithophiles relative to magnesium, normalized to CI chondrites.

*Includes chondrule fragments and silicates inferred to be fragments of chondrules.

*Includes matrix-rich clasts, which account for all matrix in CH and CB_b chondrites (Greshake et al., 2002).

*Fall frequencies based on 918 falls of differentiated meteorites and classified chondrites (Grady, 2000).
minerals that formed during aqueous alteration. Type 2 chondrites are partly altered.

Elemental ratios are commonly used for comparing chondrite compositions instead of concentrations, as some chondrites have excessive amounts of one component such as water or metallic Fe,Ni, for example, that dilute elements in other components. The elements silicon and magnesium are commonly used for normalizing lithophiles; nickel is used for comparing siderophile elements. CI chondrites, which have the highest concentrations of volatile elements, are used as the reference standard because they provide the best match for the composition of the solar photosphere, neglecting the incompletely condensed elements hydrogen, helium, carbon, nitrogen, oxygen, and the noble gases (see Chapter 1.03).

Ratios of refractory and moderately volatile lithophile (figure 3 in Chapter 1.05) or siderophile elements (Figure 2) provide the best criteria for classifying chondrites. On these plots, the range within each group is a small fraction of the total range shown by all chondrites. Each group has a unique chemical composition implying that its members formed in a separate location. The CB group, which is split into two subgroups with rather different properties, is an exception. Unfortunately, many newly discovered, unusual chondrites have not been chemically analyzed, so their classification and the compositional limits of newly discovered groups are not well defined. Two other properties are useful for classifying chondrites and understanding their compositional diversity and genetic relationships: bulk oxygen-isotopic compositions (see Chapter 1.06) and the distribution of iron among silicate, metal, and sulfide phases (figure 7 of Chapter 1.05). The latter requires classical methods of rock analysis (Jarosewich, 1990), which are no longer applied to chondrite. Many chondrite groups can also be distinguished by other parameters such as the sizes and proportions of their components and the minerals in their chondrules, CAIs, or other components. See Brearley and Jones (1998) (hereafter abbreviated B&J), for a detailed account of chondrite mineralogy.

The chemical, mineralogical, and isotopic properties of chondrites distinguish closely related groups, which constitute “clans.” For example, chondrules in the H, L, and LL groups are chemically and isotopically similar, though their average properties are different, and these three groups form a clan. Four other clans are recognized: the EH–EL, the CM–CO, the CV–CK, and the CR–CH–CB.

Cosmic-ray exposure ages suggest that chondrites in many groups were exposed to space as meter-sized objects in a limited number of impacts (Chapter 1.13). For example, about one-third of the LL chondrites were exposed to cosmic rays 15 Ma and half the H chondrites have exposure ages of 7 Ma (Graf and Marti, 1994, 1995). Three or four large collisions appear to have generated two-thirds of all H chondrites (Wieler, 2002). Since all petrologic types are found in the 7 and 33 Ma peaks, it is possible that all H chondrites come from a single body. Some other groups show distinctive impact ages or shock properties, suggesting that they were involved in a single impact. For example, many L chondrites, which are strongly shocked, have radiometric ages of ~0.5 Ga (Bogard, 1995). These features suggest that each group comes from one, or possibly a few bodies.

We do not know for certain that two chondrite groups did not originate from a single body but it is rather unlikely (except possibly for the EH and EL chondrites). Evidence from meteorites, impact modeling of asteroid collisions, and asteroid density determinations suggests that all asteroids, except the few largest, were well fragmented and mixed by collisions before meteoroids were removed. Impacts also weld rock fragments from different locations into coherent rocks that reach Earth as meteorites. Thus, if CV and CO chondrites, for example, had formed in a single body, we might expect to find meteorites containing both types of material. Their absence makes it unlikely that one body ever contained both groups. Nevertheless, regolith breccias contain a few volume percent of foreign clasts showing that small amounts of material from different sources

Figure 2  Plot of Ga/Ni versus Ir/Ni showing bulk compositions of chondrites in nine groups. Each group is well resolved. The proportions of these siderophiles are not correlated with other chemical properties showing that the chemical variations in chondrites are complex. Reproduced by permission of Verlag der Zeitschrift für Naturforschung from Scott and Newsom (1989).
were mixed together. The close proximity of the orbits of an EL6 and an H5 chondrite, which might imply that they have a common parent (Spurny et al., 2003), appears to be coincidental (Pauls and Gladman, 2005).

Given the extraordinary diversity of chemical and mineralogical properties of the 15 chondrite groups and the rapid rate at which new groups are being identified (only nine were listed by Wasson, 1985), we should expect many more unusual types to be discovered. Our sampling of chondrites is also biased toward tough rocks that can survive the journey to Earth, and we cannot expect these to be representative samples. Thus, it is important to study components in all kinds of chondrites if we need to understand how they formed, not just those in the most common chondrite groups or those that are present in the largest falls, like Allende.

1.07.2.2 Ordinary Chondrites

Since ordinary chondrites account for ~ 80% of all meteorite falls (Table 1), it was once believed that their parent bodies were common in the main asteroid belt. However, spectral studies show that most asteroids are dark and featureless (C and related types), and most of the brighter S types are spectrally unlike ordinary chondrites. H group chondrites probably come from one or more S-type asteroids, possibly 6 Hebe (Burbine et al., 2002). Ordinary chondrites are probably rare in the main part of the asteroid belt (Meibom and Clark, 1999), though a significant fraction of the near-Earth asteroids including Eros are probably made of ordinary chondritic material (Binzel et al., 2002; Chapman, 2004). A few ordinary chondrites including Tieschitz (Figure 1a) do not fit comfortably into the H, L, and LL groups and may be derived from separate bodies.

1.07.2.3 Carbonaceous Chondrites

Some carbonaceous chondrites are rich in carbon (CI and CM chondrites have 1.5–6% carbon), but others are not. Carbonaceous chondrites are now defined on the basis of their refractory elemental abundances, which equal or exceed those in CI chondrites. Carbonaceous chondrites are derived from very diverse asteroids, which probably formed in very different locations. The parent bodies of CI and CM chondrites are highly altered, yet the parent bodies of CH and CB chondrites are less altered than all other chondrite bodies. Young et al. (1999) infer from oxygen-isotopic compositional data that CI, CM, and CV chondrites could have been derived from different zones in a single, aqueously altered body. However, bulk chemical differences between these groups indicate fractionation during nebular processes, not aqueous alteration (see below), and the components in CM and CV chondrites are quite different.

Most carbonaceous chondrites are thought to come from the low-albedo, C-type asteroids, which are the most abundant type between 2.7 and 3.4 AU (Bell et al., 1989), CM chondrites may be derived from an altered C-like asteroid called G-type (Burbine et al., 2002). The ungrouped C chondrite, Tagish Lake, has been linked with D asteroids, which appear to dominate the asteroid population beyond 4 AU (Jones et al., 1990; Hiroi et al., 2001). CB chondrites have only very minor amounts of phyllosilicates and may come from W-type asteroids (“wet-M” asteroids). Lodders and Osborne (1999) discuss the possibility that CM and CI chondrites could be derived from a small fraction of comets that evolve into near-Earth objects after losing volatiles. A small fraction of near-Earth asteroids are derived from Jupiter-family comets, and Lodders and Osborne (1999) suggest that they are supplying us with CI and CM chondrites. Gounelle et al. (2006) also favor a cometary origin for Orgueil meteorite based on its inferred orbit. However, Campins and Swindle (1998) argue that cometary meteorites, if they exist, probably resemble carbon-rich, unaltered chondrites without chondrules. The extremely fragile nature of chondritic porous IDPs, which are probably derived from comets (Rietmeijer, 1998, 2002; Chapter 1.26), suggests that larger cometary meteoroids would not survive atmospheric entry (Messenger et al., 2006).

Although most comets clearly accreted far beyond the asteroid belt, similarities between the matrices of the most primitive carbonaceous chondrites and the chondritic porous IDPs (Section 1.07.5.8) and the discovery that some C-type asteroids show cometary activity (Hsieh and Jewitt, 2006) have blurred the distinction between comets and asteroids.

1.07.2.4 Enstatite Chondrites

The genetic relationships among E chondrites are poorly understood, in part because of poor sampling but also because the cause of their chemical and mineralogical diversity is obscure. EH and EL chondrites may come from one (Kong et al., 1997) or two bodies (Keil, 1989). Although there are compositional discontinuities between the EH and EL groups (e.g., in gold and aluminum), Kong et al. concluded that elemental concentrations appear to vary
continuously through the sequence EH4, 5, EH3, EL3, and EL6. Oxygen-isotopic compositions of EH and EL chondrites show a large overlap, but do not resolve the issue (Newton et al., 2000). On the basis of their noble gas analyses, Patzer and Schultz (2002b) advanced an entirely different proposal that “EH3 and EL3 chondrites are derived from one body and EH4–6 and EL4–6 from a second.” They found that E3 and E4–6 chondrite types have different trapped noble gas components (called “Q-gases”), and inferred that this difference could not be attributed to asteroidal processing. In addition, about one-third of the E3 chondrites contain solar noble gases, which are absent among E4–6 chondrites. Unfortunately, the cosmic-ray exposure age data do not yet provide definitive constraints. The 60-odd E chondrites have a wide range of exposure ages, 0.07–70 Ma with broad peaks as their precision is ~20% (cf. 10% for ordinary chondrites) (Patzer and Schultz, 2002a; Okazaki et al., 2000). However, the data are not inconsistent with a single E chondrite body, as Kong et al. (1997) proposed.

1.07.3 BULK COMPOSITION OF CHONDRITES

1.07.3.1 Cosmochemical Classification of Elements

The chemical fractionations observed among chondrites and the compositions of many chondritic components are best understood in terms of quenched equilibrium between phases in a nebula of solar composition (Palme, 2001; Chapters 1.03 and 1.15). The equilibrium model assumes that minerals condensed from, or equilibrated with, a homogeneous solar nebula at diverse temperatures. Isotopic variations among chondrites and their components show that this assumption is not correct and detailed petrologic studies have identified relatively few chondritic components that resemble equilibrium nebular products. Nevertheless, the equilibrium model is invaluable for understanding the chemical composition of chondrites and their components as the solar nebular signature is etched deeply into their chemistry and mineralogy.

In a cooling nebula at a pressure of 10⁻³ atm, calcium, aluminum, and titanium condense as oxides in the temperature range 1,800–1,450 K along with refractory trace elements like the rare earth elements (REEs) and platinum group metals (figure 2 of Chapter 1.15). Between 1,450 and 1,350 K, magnesium and silicon condense as forsterite and enstatite and iron condenses as metallic Fe,Ni along with cobalt. Between 1,250 and 650 K, the highly volatile elements like the halogens and inert gases condense. The division of the elements into refractories (1,800–1,450 K), major elements (1,350–1,250 K), moderately volatile elements (1,250–650 K), and highly volatile elements (<650 K) is the key to understanding the chemical variations among chondrites and their components. Note that only three phases condense entirely from the gas phase—Al₂O₃, Mg₂SiO₄, and Fe,Ni—all other minerals form by reaction between solids and gas.

At 10⁻³ atm, FeO concentrations in silicates are minimal above 650 K and all condensed phases are solid. If the total pressure increases, condensation temperatures rise, but the sequence in which minerals condense does not change significantly except that silicate melts become stable at pressures above ~10⁻² atm. If condensation occurs in systems that have been enriched in dust relative to gas, FeO concentrations in silicates become appreciable at high temperatures (up to ~1,100 K for 10³-fold dust enrichments), and liquids are also stabilized (Wood and Hashimoto, 1993; Ebel and Grossman, 2000). Pressures and temperatures at the midplane of the nebula vary considerably as the solar nebula evolves, decreasing as the accretion rate falls (Wood, 2000a; Woolum and Cassen, 1999). Additional insights into chondrite properties can be gained from fractional condensation models in which condensates are continually sequestered (Petaev and Wood, 2000).

1.07.3.2 Chemical Compositions of Chondrites

A large number of chondrites have been analyzed with instrumental and radiochemical neutron activation analysis using ~250–350 mg samples of chondrites (Kallemeyn and Wasson, 1981; Wasson and Kallemeyn, 1988; Kallemeyn et al., 1991, 1994, 1996). Samples of this size can also be analyzed for many elements with comparable accuracy using X-ray fluorescence analysis (Wolf and Palme, 2001). Mean compositions of chondrite groups are given by Lodders and Fegley (1998).

Chemical variations among chondrites are commonly attributed to the accretion of different proportions of five components: the refractory component, magnesium silicates, metallic Fe,Ni, moderately volatile elements, and highly volatile elements (see chapters in
In addition, variations in oxygen fugacity are invoked to explain the diverse distribution of iron among metallic and silicate phases (figure 7 of Chapter 1.05). In general, chemical fractionation patterns are simple: refractory elements, for example, are uniformly enriched relative to CI chondrites in carbonaceous chondrites by factors of 1.0–1.4, whereas they are depleted in ordinary and enstatite chondrites by factors of 0.8–0.95 (Figure 3). Moderately volatile elements decrease in abundance with decreasing condensation temperature. (Note that enstatite chondrites do not follow these rules as closely as the other groups.) Although the chemical fractionation patterns for most groups of chondrites are known (Wasson and Kallemeyn, 1988), their origins have proved to be surprisingly elusive. In particular, the relative importance of localized processes that made chondrules and CAIs and nebula-wide thermal gradients is controversial (see Cassen, 2001a):

1. **Refractory elements.** All the elements that condense above 1,450 K are precisely those found in CAIs, and there is some correlation between the bulk concentrations of refractory elements and refractory inclusions (Table 1). This suggests that the fractionation of refractory elements among chondrites is simply caused by addition or loss of CAIs. However, this is incorrect as the proportion of the refractory elements that is present in CAIs is generally small, except for CVs, where it approaches ~50%. Chondrules, which are much more abundant and have approximately CI-like levels of refractories relative to silicon, account for most of the refractory elements in chondrites. Note that the depletions of refractory elements in E and O chondrites require that their chondrules formed from a condensate that was depleted in refractories.

2. **Magnesium silicates.** Forsterite and enstatite, which are the major minerals in chondrules, form in the temperature range 1,450–1,350 K, the latter by reaction between forsterite and gaseous SiO. Thus, equilibrium condensation can produce a range of molar enstatite/forsterite ratios of 0–1.2 (figure 2 of Chapter 1.15), provided that the condensates are sequestered from the gas over a range of temperatures. To reach the composition of E chondrites, which are almost pure enstatite, would require removal of forsterite condensate. A correlation between the Mg/Si and refractory/Si ratios of the chondrite groups suggests that refractories were partly associated with forsterite (Larimer and Wasson, 1988).

3. **Metallic Fe,Ni.** which condenses over the same temperature range as the magnesium silicates, is closely associated with them in chondrules. At $10^{-7}$ atm, Fe,Ni condenses at slightly lower temperatures than forsterite, but above $10^{-4}$ atm there is a reversal. Some

---

**Figure 3** Mean abundances of lithophile elements normalized to CI chondrites and silicon arranged in order of increasing volatility in seven chondrite groups. Refractories (elements condensing above V) are uniformly enriched in CO, CM, and CV chondrites and depleted in H, L, and EH chondrites. Moderately volatile elements, which condense below magnesium and silicon, are all depleted relative to CI chondrites. These fractionations are related in poorly understood ways to the formation of CAIs and chondrules. Reproduced by permission of The Royal Society from Wasson and Kallemeyn (1988).
groups such as the CV3 chondrites did not suffer metal/silicate fractionation (figure 2 of Chapter 1.15), but the EH–EL, H–L–LL, and CR–CH–CB clans clearly did. Fe/Si ratios are \( \sim (2-5) \times 10^2 \) in CR chondrites because metal was enriched relative to silicate; EL, L, and LL chondrites were depleted in metallic Fe,Ni.

4. Moderately volatile elements. The gradual depletion of moderately volatiles with decreasing condensation temperature can be attributed to loss of fine volatile-rich dust (Wasson and Kallemeyn, 1988), incomplete condensation due to isolation of condensed phases (Palme et al., 1988; Cassen, 2001b), or to evaporation prior to or during chondrule formation (see, e.g., Young, 2000; Lugmair and Shukolyukov, 2001; see also Chapter 1.15).

5. Highly volatile elements may have failed to accrete from the nebula because of high ambient temperatures during accretion or inefficient accretion of volatile-rich dust, or they may simply have been lost during asteroidal metamorphism.

1.07.3.3 Isotopic Compositions of Chondrites

Major and minor planetary bodies are essentially uniform isotopically (e.g., Palme, 2001). The great majority of elements are isotopically uniform to within 0.01%. The exceptions are found for oxygen (discussed below), effects due to short-lived isotopes (Chapter 1.16), slightly larger effects (per mil or less) due to anomalies in \( ^{54}\text{Cr} \) and \( ^{50}\text{Ti} \) in chondrites and their components (e.g., Podosek et al., 1997; Niemeyer, 1988), and isotopically anomalous components in chondrites: interstellar grains, certain rare CAIs called FUN inclusions (containing fractionated and unidentified nuclear isotopic effects) and some hibonite inclusions (see Chapter 1.08). The isotopic anomalies in interstellar grains are orders of magnitude larger than those in refractory grains in chondrites and the latter probably reflect incomplete homogenization of the former (e.g., Ott, 1993, 2001). Depending on one’s viewpoint, the isotopic anomalies provide evidence that vaporization of presolar materials was limited (Taylor, 2001) or that isotopic homogenization was remarkably complete (Palme, 2001).

1.07.3.4 Oxygen-Isotopic Compositions

The discovery of large and ubiquitous oxygen-isotopic anomalies in refractory inclusions in carbonaceous chondrites and smaller anomalies in chondrules transformed the study of chondrites (see Clayton, 1993; Chapter 1.06). It galvanized the search for presolar grains, provided another way to classify meteorites, and offered numerous constraints on the origin of chondrites and their constituents and subsequent asteroidal processing. In particular, the oxygen-isotopic anomalies appeared to eliminate the conviction that the meteorites and inner planets were derived from a hot, gaseous, and homogeneous nebula (e.g., Begemann, 1980). However, the origin of the oxygen anomalies remains a mystery, presolar grains were not discovered by searching for the source of the anomalous oxygen (Ott, 1993), and the oxygen anomalies are now known to be associated with nebular condensates, as well as evaporative residues (see Scott and Krot, 2001; Krot et al., 2002b). The recent introduction of ion and laser microprobe techniques has produced an explosion of new oxygen-isotopic analyses of minerals in CAIs and chondrules, which have been especially valuable in distinguishing asteroidal and nebula processes (e.g., Choi et al., 1998; Yurimoto et al., 1998; Yurimoto and Wasson, 2002).

Differences between the bulk compositions of chondrites, planets and asteroids can be attributed to accretion from different batches of CAIs, chondrules and other components, which are spread along \( ^{16}\text{O} \) variation lines on the standard three-isotope plot. The preservation of oxygen-isotopic anomalies shows that there were numerous oxygen reservoirs for the manufacture of chondrules and CAIs that were quite separate. The source of the anomalies has been attributed to nucleosynthetic differences between batches of presolar materials (Wasson, 2000), mass-independent partitioning among oxygen-bearing molecules in the nebular gas (Thiemens, 1999), and photochemical self-shielding of CO at the inner edge of the solar nebula (Clayton, 2002), in the presolar molecular cloud (Yurimoto and Kuramoto, 2002), or in the surface of the nebula (Lyons and Young, 2005). Whatever the source, the \( ^{16}\text{O} \) variations in CAIs and chondrules imply that the anomalies can be understood in terms of mixing of \( ^{16}\text{O} \)-rich and \( ^{16}\text{O} \)-poor components in the solar nebula. The anomalies could have been preserved by enriching \( ^{16}\text{O} \)-rich dust relative to gas prior to vaporization (Cassen, 2001b; Scott and Krot, 2001). However, in the self-shielding model, the \( ^{16}\text{O} \)-poor component was anomalously heavy ice and the nebula was initially \( ^{16}\text{O} \)-rich, like the protosun. Luck et al. (2003) inferred that \( ^{16}\text{O} \) excesses were correlated with \( ^{63}\text{Cu} \)-isotopic anomalies, but the reason for this is not clear. It is hoped that the NASA Genesis mission will determine the oxygen-isotopic composition of the
solar wind and establish the origin of the oxygen anomalies (Wiens et al., 1999; Clayton, 2002).

1.07.4 METAMORPHISM, ALTERATION, AND IMPACT PROCESSING

All chondrites were modified in some way by geological processes in asteroids operating over 4.5 Gyr. If we want to understand how the components in chondrites were formed, we must understand how chondritic materials were modified in asteroids. Three processes affected chondrites: aqueous and hydrothermal alteration, thermal metamorphism, and impacts.

The most important heat source for the alteration and metamorphism of chondrites was heat from the decay of $^{26}\text{Al}$, and to a much lesser extent, $^{60}\text{Fe}$ (Chapter 1.16). If chondrites came from the first generation of planetesimals that formed, one could exclude $^{26}\text{Al}$ as a heat source for melting planetesimals (Kunihiro et al., 2004a). However, $^{182}\text{Hf} - ^{182}\text{W}$ dating and thermal modeling show that an earlier generation of bodies accreted $<0.5$ Myr after CAIs formed and melted due to the short-lived radioisotopes forming cores that are the sources of most iron meteorites (Kleine et al., 2005; Bizzarro et al., 2005; Scherstén et al., 2006). Evidence that $^{26}\text{Al}$ was adequately mixed in the solar nebula comes from the consistent chronology provided by $^{26}\text{Al} - ^{26}\text{Mg}$ and Pb–Pb dating (Zinner and Göpel, 2002; Kita et al., 2005).

Impacts also provide kinetic energy but for asteroids smaller than a few hundred kilometers in size, they are not an effective heat source for global metamorphism (Keil et al., 1997). For alternative views, see Rubin (1995, 2005), who favors heating by asteroidal impacts, and Kurat (1988), who argues for nebular heating processes. Electrical induction heating of asteroids by plasma outflow from the protosun is not currently favored (see Scott et al., 1989). Arguments against the concept of hot accretion without radiometric heating (Hutchison et al., 1979) were given by Haack et al. (1992) and Rubin and Brearley (1996).

Alteration and metamorphism used to be considered as separate processes: the former affecting carbonaceous bodies and the latter operating on enstatite and ordinary chondrites. However, it is now clear that fluids of some kind were present during thermal processing of virtually all chondrite classes.

1.07.4.1 Petrologic Types

Chondrites are classified into petrologic (or petrographic) types 1–6 to provide a guide to the extent and nature of asteroidal processing. This classification scheme, which has been invaluable (Anders and Kerridge, 1988), nevertheless provides only a very rough guide as our ideas about asteroidal processes have changed significantly since the scheme was first established, and because one number cannot summarize all the effects of complex asteroidal processing. As a result, the classification is not rigorous and may be ambiguous or even misleading.

The original division of chondrites by Van Schmus and Wood (1967) into six petrologic types was based on two underlying assumptions that are now known to be incorrect: (1) that type 1 chondrites are the least altered chondrites that best represent the mineralogy of the original materials that accreted into asteroids, and (2) that types 2–6 represent increasing degrees of thermal metamorphism of material that mineralogically resembled type 1 chondrites. Although CI1 chondrites are “chemically” most pristine as they are compositionally similar to the solar composition, almost all of their “minerals” formed during aqueous alteration. Type 3 chondrites are closest mineralogically to the original materials that accreted into asteroids (McSween, 1979).

An additional problem with the division into six petrologic types is that it ignores the role played by impacts in modifying and mixing chondritic material. Many chondrites are breccias of materials with diverse alteration or metamorphic histories. Thus the petrologic type may provide no information about the metamorphic history of the whole chondrite, only an approximate guide to the history of most constituents.

The criteria used for assigning petrologic types were first given by Van Schmus and Wood (1967) and have not changed significantly since (table 3 of Chapter 1.05). Table 2 shows the numbers of classified chondrites in petrologic types 1–6 within each group. The unrepresented cells in Table 2 may reflect poor sampling (e.g., in the poorly represented K group). However in many cases, it is likely that the missing types were volumetrically insignificant. It is very unlikely, for example, that the ordinary chondrite parent bodies ever contained significant amounts of type 1 and 2 material.

1.07.4.1.1 Type 1 and 2 chondrites

There is much ambiguity about the classification of type 1 and 2 chondrites that are not clearly associated with the major groups, CI and CM. Different workers favor different criteria, so that type 1, for example, may mean a
Chondrites and Their Components

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Numbers of classified chondrites in petrologic types 1–6 by group.</th>
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<tr>
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<td>1</td>
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<tr>
<td>Carbonaceous</td>
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<td>CI</td>
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<td>CK</td>
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| Ordinarya |
| H        | 187     | 1,371   | 3,319   | 1,784   | 6,661   |
| L        | 316     | 415     | 1,220   | 4,053   | 6,004   |
| LL       | 71      | 64      | 419     | 406     | 960     |

| Enstatite |
| EH       | 18      | 9       | 6       | 2       | 35      |
| EL       | 8       | 0       | 2       | 19      | 29      |

| Other    |
| K        | 2       |         |         |         | 2       |
| R        | 3       | 2       |         |         | 14      |

|         | 9 R3–6  |

Sources: Based largely on lists in Grady (2000) with additional data from Krot et al. (2002a) for CR, CH, and CB and Kalleneyn et al. (1996) and Boscholff (2000) for R chondrites. A small number of chondrites that are classified as intermediate types (e.g., 3–4 and 4–5) and mixed breccias (e.g., types 3–5) were omitted except for the R chondrites, which are mostly breccias of type 3–5 or 3–6 material.

*Numbers of H, L, and LL chondrites are italicized as they have not been corrected for probable pairings: the number of individual meteorites is probably ~2–4 times smaller than the number of specimens.

1.07.4.1.2 Type 3 chondrites

Type 3 chondrites show very diverse mineralogies and in several groups they have been subdivided. CO3, H3, L3, and LL3 chondrites, which are divided into subtypes 3.0–3.9, show correlated variations in mineralogy and concentrations of carbon and highly volatile elements that can largely be attributed to metamorphism. Subtypes were first defined for ordinary chondrites based largely on their thermoluminescence sensitivity, which is a measure of plagioclase growth in chondrule mesostases (Sears and Hasan, 1987; Sears et al., 1991, 1995a). Many other properties vary systematically with progressive metamorphism and have been used to assign subtypes, for example, chemical changes in chondrule olivines (Figure 4), the chemical homogenization of olivines, FeO/(FeO + MgO) ratios in matrices (Huss et al., 1981), loss of trapped noble gases and loss of carbon (Sears and Hasan, 1987), chromium levels in metallic Fe,Ni grains (Scott and Jones, 1990), and growth of ferroan olivine in amoeboid–olivine aggregates (Chizmadia et al., 2002). Especially in low-subtype chondrites, there is evidence that hydrothermal fluids promoted chemical equilibration and alteration in chondrule mesostases (B&J, 1998; Tomeoka and Itoh, 2004), CAIs (Russell et al., 1998), and matrices (Section 1.07.5.7). With increasing metamorphism, fluids were lost from the parent bodies. For CV3 chondrites, the effects of metamorphic alteration are more complex: subtypes based on thermoluminescence sensitivities appear to be
chondrites that were tainted by their asteroidal environ-
ment. Among the most pristine are the CBb3 and CB2 chondrites, subtypes 3.0 and 3.1 have been divided into subtypes using these parameters or many others (e.g., Sears and Hasan, 1987). Reproduced by permission of Elsevier from Scott et al. (1994).

Although type 3 chondrites are the least altered and metamorphosed chondrites, only a few of them are now thought to be relatively pristine samples, and all of these have components that were tainted by their asteroidal environment. Among the most pristine are the CB3 and CH3 chondrites, Viggarano and Leoville (CV3), ALHA77307 (CO3.0), Semarkona (LL3.0), Kakangari (K3), and two ungrouped carbonaceous chondrites, Acfer 094 and Adelaide. To aid in identifying the least metamorphosed chondrites, subtypes 3.0 and 3.1 have been divided into 3.0 to 3.15 on the basis of Cr2O concentrations in chondrule olivines that contain > 2 wt.% FeO (Grossman and Brearley, 2005). These data confirm that Acfer 094 and ALHA77307 are among the least metamorphosed chondrites. Chondrules in type 3 chondrites in the ordinary, K, CO, and CV groups were probably heated to around 400–600°C for > 10^6 years, as they contain kamacite and taenite that equilibrated at these temperatures (Keil, 2000). However, the CH3 and CB3 chondrites contain martensite that has not exsolved to kamacite and taenite and has retained chemical zoning patterns that were established prior to accretion (Meibom et al., 1999, 2000; Krot et al., 2002c). Electron microscopic studies of the metal show that CH3 chondrites were not heated above 300°C for more than a year and probably experienced much lower peak temperatures (Reisener et al., 2000).

1.07.4.1.3 Type 4–6 chondrites

Type 4–6 ordinary chondrites, which are also called equilibrated chondrites, are thought to represent an isochemical, metamorphic sequence: types 4 and 5 were heated to 500–800°C and type 6 to 800–1,000°C (see Keil, 2000). However, Wlotzka (2005) found similar olivine/Cr-spinel temperatures of 700–800°C for type 4–6 ordinary chondrites and suggests that these temperatures correspond to peak metamorphism. The most noticeable metamorphic effects are due to grain coarsening and growth of feldspar, chromite, and phosphate grains. Some type 4–6 chondrites are not simple metamorphic rocks: they are fragmental or regolith breccias of rock fragments that were metamorphosed prior to assembly (Rubin, 1990). In these cases, the petrologic type may only be a measure of the metamorphic history of most material in the rock. In addition, Rubin (2002, 2003, 2004) infers that practically all type 5 and 6 ordinary chondrites were shocked and later annealed and that many experienced multiple episodes of shock and impact-induced annealing. Within each group of ordinary chondrites, there are small but systematic increases in the FeO concentrations of olivines and pyroxenes with increasing petrologic. These are probably due to oxidation of metal by traces of water vapor during metamorphism (McSween and Labotka, 1993). Fluid inclusions are present in halite in two H chondrite regolith breccias and may have been derived from asteroidal fluids or icy projectiles (see Rubin et al., 2002).

The criteria for classifying types 4–6 were based solely on the properties of H, L, and LL types 3–6 chondrites and most cannot be used for asteroidally processed carbonaceous and enstatite chondrites. For these chondrites, the type is based almost entirely on the degree to which the chondrules are delineated. If the chondrules have been obscured by recrystallization during prolonged heating, the petrologic type is a good measure of the metamorphic history. However, for the EH4–6 and EL4–6 chondrites, evidence for simple thermal metamorphism is lacking. Rapid cooling rates recorded by sulfides and numerous examples of impact heating suggest that impact processing may have been more important for enstatite chondrites than heating by decay of ^26Al (Zhang et al., 1996; Rubin et al., 1997; Lin and Kimura, 1998). R chondrites experienced ubiquitous brecciation and although some have
been classified as R4 (or R3), all are probably breccias of type 3–5 or 3–6 material (Bischoff, 2000).

### 1.07.4.2 Thermal History and Modeling

To understand geological processes on chondritic bodies and to estimate their sizes we need to investigate the thermal history of unshocked or only lightly shocked samples. The simplest metamorphosed chondrites are the ordinary chondrites, for which there are three kinds of constraints: (1) mineral equilibration temperatures (e.g., McSween and Patchen, 1989); (2) radiometric ages that date cooling below isotopic closure in minerals using isotope systems such as $^{207}\text{Pb} -^{206}\text{Pb}$, $^{40}\text{K} -^{39}\text{Ar}$, and $^{87}\text{Rb} -^{87}\text{Sr}$ (e.g., Trieloff et al., 2003); and (3) cooling-rate determinations based on annealing of $^{39}$Ar fission tracks (Lipschutz et al., 1989) and metallographic cooling rates (Taylor et al., 1987). The cooling rates determined by the metallographic technique, which are mostly $1 - 10^7 ^{\circ} \text{C}\text{Myr}^{-1}$ in the temperature range of 400–500 $^{\circ}$C, are compatible with cooling rates in the range 100–500 $^{\circ}$C determined by the fission track technique. A third technique based on Fe–Mg ordering in orthopyroxene gives cooling rates in the range 340–480 $^{\circ}$C that are systematically higher by several orders of magnitude (Folco et al., 1997), probably because metamorphism was insufficient to reequilibrate the ordering imposed during chondrule formation (Artioli and Davoli, 1994). Cooling rates can also be estimated from radiometric age data for mineral grains that closed isotopically at different temperatures (Bogard, 1995; Ganguly and Tirone, 2001; Amelin et al., 2005).

Metamorphic ages of ordinary chondrites from Pb–Pb ages of phosphates in seven H4–6 chondrites range from 4.50 to 4.56 Ga (Göpel et al., 1994), while their Ar–Ar ages range from 4.45 to 4.53 Ga (Trieloff et al., 2003). The two H4 chondrites, which have metallographic cooling ages of $10^7 ^{\circ} \text{C}\text{Myr}^{-1}$, have the oldest ages while the H6 chondrites with cooling rates of $\sim 10^7 ^{\circ} \text{C}\text{Myr}^{-1}$ have younger ages. The negative correlation between age and metamorphic type for these seven chondrites is compatible with an onion-shell model in which burial depth correlates with petrologic type. However, Pb–Pb ages for two ordinary type 3 chondrites are significantly younger than the phosphate ages for the H6 chondrites and are not readily reconciled with this model (Göpel et al., 1994), and the selected H4 chondrites may not be representative (Wlotzka, 2005). Metallographic cooling rates for larger numbers of unshocked, ordinary chondrites show no correlation between cooling rate and petrologic type (Taylor et al., 1987) suggesting that if the petrologic types were once arranged sequentially in layers, the bodies must have been catastrophically fragmented and reassembled by impacts during cooling from peak metamorphic temperatures (Grimm, 1985). Regolith breccias show extreme variations in the cooling rates of their metal grains from 1 to $10^3 ^{\circ} \text{C}\text{Myr}^{-1}$ implying that the ordinary chondrite bodies were scrambled after metamorphism so that material from all depths could be combined together (Williams et al., 1999).

Estimates of the sizes of the ordinary chondrite parent bodies can be derived from thermal models as the timescale for cooling is controlled by conduction for dry asteroids >10–20 km in size (McSween et al., 2002). However, the thermal conductivity is very sensitive to the porosity, which can be reduced by sintering and increased by impacts. Layers of regolith <1 km thick can drastically reduce the cooling rate of asteroids and increase near-surface thermal gradients (Haack et al., 1990). Akridge et al. (1998) argue that H chondrites are derived from depths of <10 km from a 100 km radius asteroid and that material at greater depths has not been sampled. However, Bennett and McSween (1996) infer complete sampling of bodies with radii of $\sim 80–95$ km for the H and L chondrite parent bodies.

For volatile-rich carbonaceous chondrites like CI and CM chondrites, constraints on thermal histories are derived from carbonate ages and oxygen-isotopic data. The former indicate that alteration began soon after CAI formation and lasted $\sim 20$ Myr (Endress et al., 1996; Brearley et al., 2001). Oxygen-isotopic compositions of carbonates provide model-dependent temperatures under 50 $^{\circ}$C (see McSween et al., 2002). Modeling metamorphism of wet asteroids requires more complex models to track fluid flow, chemical and mineralogical changes during metamorphism, and exothermic serpentinitization reactions (e.g., Wilson et al., 1999; Cohen and Coker, 2000; Young, 2001; Young et al., 2003). McSween et al. (2002) suggest that thermal buffering by ice and water prevented high-temperature metamorphism in carbonaceous chondrite bodies. However, some CV and CK chondrites were clearly heated above 500 $^{\circ}$C.

### 1.07.4.3 Impact Processing of Chondritic Asteroids

Impacts fragmented, mixed, modified, melted, devolutilized, and lithified chondritic material. Asteroids were impacted throughout their history: when they accreted, during alteration and
metamorphism, and during the 4.5 Ga after their parent bodies were heated. For reviews of impact processing of ordinary chondrites, see Stöffler et al. (1991); carbonaceous chondrites, Scott et al. (1992); and enstatite chondrites, Rubin et al. (1997). Experimental studies of impact metamorphism of ordinary chondrites were made by Schmitt (2000) and Langenhorst et al. (2002), CV chondrites by Nakamura et al. (2000), and CM chondrites by Tomeoka et al. (1999). Meteorite evidence for impact processing of chondritic and other asteroids was reviewed by Keil et al. (1994) and Scott (2002). High-pressure minerals in shock veins in chondrites also provide clues to mineral stability at depth in the Earth (Stöffler, 1997).

Advocates for impact heating of chondrites point to Portales Valley, a breccia of H6 clasts embedded in a matrix of once-molten metallic Fe,Ni, which cooled slowly to form a Widmanstätten pattern (Rubin et al., 2001). Gaffey and Gilbert (1998) suggest that molten metal on the H parent body was derived from impact-formed melt sheets or residues of metal-rich projectiles and that the IIE irons were also derived from this melt (see section 1.12.2.5). However, the origin of Portales Valley and the link with IIE irons remain obscure as asteroids are thought to be too small for impacts to generate melt sheets (Keil et al., 1997), and Portales Valley may have been heated radiogenically prior to the impact (Ruzicka et al., 2005).

1.07.5 CHONDritic COMPONENTS

Below we review the geochemical properties and possible origins of chondritic components focusing on what appear to be primary features in the least altered type 2–3 chondrites. The rich diversity of chondritic components even in unaltered chondrites and the vast differences between chondrite groups are key features of chondrites. Several comprehensive reviews of chondrites and their components have been published since Kerridge and Matthews (1988). These include a comprehensive review of chondrite mineralogy (B&J, 1998), edited books on chondrules (Hewins et al., 1996), chondrites (Krot et al., 2005c), and constraints on early solar system processes (Lauretta and McSween, 2006), and several reviews on chondrules (Hewins, 1997; Rubin, 2000; Jones et al., 2000a; Zanda, 2004; Connolly and Desch, 2004) and CAIs (Ireland and Fegley, 2000; Chapter 1.08).

First we review CAIs and their forsterite-rich accretionary rims, then amoeboid olivine inclusions and aluminum-rich chondrules, which are intermediate in composition between CAIs and chondrules, and finally matrix, which is a complex mixture of many ingredients. Although chondrules are volumetrically more important, we start with CAIs as these formed first and their origins are better constrained by chemical and isotopic data. Chemical and isotopic variations in chondrules are much more modest than those in CAIs but there are enough related features and components with intermediate compositions to suggest that chondrules cannot be understood in isolation from CAIs and other components.

1.07.5.1 Calcium- and Aluminum-Rich Inclusions

There are two types of refractory inclusions: calcium- and aluminum-rich inclusions (this section) and amoeboid olivine aggregates (Section 1.07.5.3). Since the mineralogy, chemistry, and isotope chemistry of refractory inclusions were reviewed by MacPherson et al. (1988), many new analyses have been made of CAIs in CV, CM, CO, CR, CH, CB, ordinary, and enstatite chondrites that provide important constraints on physicochemical conditions, time, and place of CAI formation. CAIs are addressed in detail in Chapter 1.08, the role of condensation and evaporation in their formation in Chapter 1.15, and their clues to early solar system chronology in Chapter 1.16.

CAIs are the oldest objects in chondrites excluding presolar grains (Amelin et al., 2002) and probably formed during the most energetic phase of protosolar disk evolution (e.g., Ireland and Fegley, 2000; Wood, 2000b, 2004). They are composed of the minerals corundum, hibonite, grossite, perovskite, melilite, spinel, Al–Ti-diopside, anorthite, and forsterite, which are predicted to condense from a cooling gas of solar composition at temperatures >1,200–1,300 K and total pressure of 10^5 bar (e.g., Ireland and Fegley, 2000; Ebet and Grossman, 2000). Some CAIs are thought to be condensates because they have irregular shapes, fluffy textures, and minerals that match the sequence of mineral formation (Figure 5), and trace-element chemistry (e.g., Simon et al., 2002). The strongest argument in favor of condensation origin of some CAIs comes from their group II REE pattern, which is a highly fractionated pattern with much lower abundances of the heavy REEs Gd–Er and Lu, exhibited by ~30% of all CAIs (Palme and Boynton, 1993; Ireland and Fegley, 2000). This volatility-controlled pattern requires the prior removal of the ultrarefractory elements. However, the preservation of large isotopic anomalies (e.g., ^48Ca, ^50Ti) in platy hibonites
PLACs in CM chondrites and their lack of $^{26}$Al, plus mass fractionation effects and smaller nuclear anomalies in FUN inclusions (see Chapter 1.08), favor evaporation as the predominant process for other CAIs. CAIs may represent mixtures of solar nebula condensates and refractory residue materials formed by evaporating material of presolar origin (Ireland and Fegley, 2000).

Because of the diversity of CAIs, there is no universal classification scheme for all groups. The best studied CAIs from CV chondrites are divided into type A (melilite–spinel-rich), type B (composed of pyroxene, melilite, spinel, ± plagioclase), forsterite-bearing type B, type C (melilite-poor, pyroxene–plagioclase-rich), and fine-grained spinel-rich (e.g., MacPherson et al., 1988). Type A CAIs are subdivided into fluffy and compact subtypes. In other chondrite groups, CAIs are typically classified according to their modal mineralogy (e.g., corundum-, grossite-, and hibonite-rich). In CV chondrites, most coarse-grained CAIs were probably once molten. However, in other chondrite groups, CAIs were probably not molten, though definitive compositional data for comparison with melt–solid distribution coefficients are typically not available.

1.07.5.1.1 Comparison of CAIs from different chondrite groups

A comparison of CAIs from carbonaceous, ordinary and enstatite groups (Table 3) shows that most inclusion types can be found in many chondrite groups, and that the most common varieties of CAIs are spinel-, pyroxene-, and melilite-rich (e.g., Lin et al., 2006). However, the relative proportions of CAI types and their mean sizes, which are correlated with chondrule size (May et al., 1999), differ among the chondrite groups. For example, type B CAIs are almost exclusively found in CV chondrites; PLACs occur mostly in CM chondrites; grossite-rich, hibonite-rich, and aluminum-diopside spherules are common only in CH chondrites; CAIs in enstatite chondrites are rich in spinel and, in many cases, hibonite. There are also mineralogical and isotopic differences between CAIs of the same mineralogical type: for example, (1) melilite in compact type A CAIs from CV chondrites is more åkermanitic than that in compact melilite-rich CAIs from CO and CR chondrites (Weber and Bischoff, 1997; Russell et al., 1998; Aléon et al., 2002a) and (2) the grossite-rich and hibonite-rich CAIs in CR chondrites are $^{16}$O-rich and have a canonical
Table 3  Distribution of types of CAIs, AOAs, accretionary rims, and aluminum-rich chondrules in type 2 and 3 chondrites.

<table>
<thead>
<tr>
<th>Object</th>
<th>CM</th>
<th>CO</th>
<th>CV</th>
<th>CR</th>
<th>CH</th>
<th>CB</th>
<th>Acfer 094</th>
<th>Adelaide</th>
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<td>Melilite-rich (type A)</td>
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<td>Al,Ti-px-rich (type B)</td>
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<td>Plagioclase-pyroxene-rich (type C)</td>
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<td>Grossite-rich</td>
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<td>Spinel + pyroxene-rich</td>
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<td>Pyy-hibonite spherules</td>
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<td>Fo-rich accretionary rims</td>
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<td>AOAs</td>
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<td>Aluminum-rich chondrules</td>
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Source: MacPherson et al. (1988) with additional data: CHs, Kimura et al. (1993); COs, Russell et al. (1998); CMs, MacPherson et al. (1984), Simon et al. (1994); CRs, Aléon et al. (2002a), Weissberg et al. (1993), Kalleneyn et al. (1994); CKs, Weber and Bischoff (1997), McSween (1977a), MacPherson and Delaney (1985), Kalleneyn et al. (1991), Keller et al. (1992), Noguchi (1993); H-L-LLs, Bischoff and Keil (1984), Russell et al. (2000), Kimura et al. (2002), Itoh et al. (2004a); ECs, Bischoff et al. (1985), Guan et al. (2000), Fagan et al. (2000); CBs, Krot et al. (2001a); Acfer 094, Adelaide, Krot (unpublished).

Note: r, rare; c, common; —, absent.

26Al/27Al ratio (Marhas et al., 2002; Aléon et al., 2002a), whereas those in CH chondrites are 16O-rich, but generally lack radiogenic 26Mg (26Mg*) (MacPherson et al., 1989; Kimura et al., 1993; Weber et al., 1995; McKeegan et al., 2000a). The grossite- and hibonite-rich CAIs in CB chondrites are 16O-poor (Krot et al., 2001a); no Al–Mg-isotopic measurements have been published yet.

1.07.5.1.2 Oxygen-isotopic compositions of CAIs

In situ ion microprobe analyses of oxygen-isotopic compositions of individual minerals in CAIs in the chondrite groups provide very important constraints on the origin of CAIs. CAIs from CV chondrites typically exhibit oxygen-isotope heterogeneity within an individual inclusion, with spinel, hibonite, and pyroxene enriched and anorthite and melilite depleted in 16O. At the same time, several coarse-grained igneous CAIs containing 16O-rich and 16O-poor melilite, anorthite and Al-Ti-diopside, and Al-Ti-diopside with oxygen-isotope zoning have been described in the Allende and Efremovka meteorites (e.g., Kim et al., 1998; Yurimoto et al., 1998; Itoh et al., 1999; Imai and Yurimoto, 2000). Based on these observations and experimental data on oxygen-isotope self-diffusion in CAI minerals (Ryerson and McKeegan, 1994), Yurimoto et al. (1998) concluded that coarse-grained CAIs in CV chondrites were initially 16O-rich and subsequently experienced oxygen-isotope exchange with 16O-poor nebular gas while partly molten during reheating. A few CAIs in CV chondrites appear to have experienced multiple heating events in nebular environments that fluctuated from 16O-rich, to 16O-poor, and back to 16O-rich (Yoshitake et al., 2005). 16O-poor compositions of secondary minerals (nepheline, sodalite, andradite, and hedenbergite) in CV CAIs (Cosarinsky et al., 2003) and oxygen-isotope heterogeneity in fine-grained spinel-rich CAIs that were probably not melted suggest that some oxygen-isotopic heterogeneity resulted from secondary alteration in asteroids (Aléon et al., 2002b; Fagan et al., 2002).

CAIs from CO chondrites (Figure 6) show a correlation between oxygen-isotopic composition and degree of thermal metamorphism: spinel, hibonite, melilite, diopside, anorthite, and olivine in most CAIs from CO3.0 chondrites Colony and Y-81020 are uniformly 16O-enriched, whereas melilite and secondary nepheline in CAIs from metamorphosed CO chondrites Kainsz (3.2) and Ornans (3.2) are 16O-depleted relative to spinel and diopside. These observations favor oxygen-isotope exchange during fluid–rock interaction in an asteroidal setting (Itoh et al., 2004a, b; Wasson et al., 2001). However, the 16O-poor compositions of some CAIs in CO3.0 chondrites (e.g., Yurimoto et al., 2001) suggest that some isotopic exchange also occurred in the solar nebula in the presence of 16O-poor gas.

CAIs in type 2 and 3 CR, CH, CB, CO, CM, ordinary, and enstatite chondrites are typically isotopically uniform (within 3–4%); both 16O-rich and 16O-poor CAIs have been found. Most CAIs in CR and CH chondrites are 16O-rich (Figure 7); the 16O-poor CAIs in CR,
CH, and CB chondrites show petrographic evidence for extensive melting (Aléon et al., 2002a; Krot et al., 2001a; McKeegan et al., 2006). CAIs in CM, ordinary, and enstatite chondrites are 16O-rich (\(\Delta^{17}O = -20\%\)). In CM chondrites, hibonites in spinel–hibonite spherules (SHIBs), which generally lack stable-isotopic anomalies in \(^{48}\)Ca and \(^{49,50}\)Ti, have canonical (\(^{26}\)Al/\(^{27}\)Al)\(_0\) and (\(^{41}\)Ca/\(^{40}\)Ca)\(_0\) ratios and group II REE patterns, whereas platy hibonites (PLACs), which generally have group III REE patterns, large (>10%) stable-isotopic anomalies in \(^{48}\)Ca and \(^{40}\)Ti, and lack \(^{26}\)Al and \(^{41}\)Ca, are similarly \(^{16}\)O-enriched. No obvious correlation between hibonite morphology and radiogenic \(^{26}\)Mg, Ca (\(\delta^{48}\)Ca) or Ti (\(\delta^{50}\)Ti) isotopic anomalies has been found (Sahijpal et al., 2000; Goswami et al., 2001).

To summarize, variations in oxygen-isotopic compositions within a single CAI in CV and CO chondrites require isotopic exchange, however, the exact mechanism of exchange remains poorly understood. Proposed mechanisms include gas–solid and/or gas–melt exchange in the solar nebula (e.g., Clayton, 1993; Yurimoto et al., 1998, 2000, 2001; Krot et al., 2005c), and solid–fluid exchange in an asteroidal setting (e.g., Wasson et al., 2001; Fagan et al., 2002, 2004). The presence of 16O-poor CAIs with igneous textures in primitive CR, CH, and CB chondrites suggests that in these cases oxygen-isotopic exchange occurred during melting. It remains unclear whether this exchange occurred in the CAI- or chondrule-forming regions and whether this exchange was late or early.

The oxygen-isotopic compositions of chondritic components are generally assumed to reflect isotopic variations among the different locations within the meteorite-forming regions of the solar nebula. However, since CAIs in most chondrite groups have similar 16O-rich isotopic compositions, it was inferred that CAIs formed in a single, restricted nebular locale and were then unevenly distributed to the regions where chondrites accreted after sorting by size and type (McKeegan et al., 1998; Guan et al., 2000). Although formation in a single restricted region appears to be generally accepted, sorting by size and type cannot explain the observed variations in mineralogy and isotope chemistry of CAIs in different chondrite groups. We suggest instead that CAI formation occurred multiple times in the CAI-forming region under diverse physicochemical conditions (e.g., dust/gas ratio, peak heating temperature, cooling rate, and number of recyclings) and that CAIs were subsequently isolated from the hot nebular gas at various ambient nebular temperatures. The isolation could be due to removal by stellar wind (e.g., Shu et al., 1996, 2001). The 16O-rich and 16O-poor CAIs reflect either temporal variations in oxygen-isotopic compositions of the nebular gas in the CAI-forming region(s) (e.g., Yurimoto et al., 2001) or radial transport of some CAI precursors into an 16O-poor gas prior to their melting (see also Scott and Krot, 2001;
Olivine-rich, accretionary rims around CAIs, which have grain sizes $4-20\ \mu m$, were first described in the altered CV chondrite Allende by MacPherson et al. (1985). In this meteorite, the accretionary rims have four layers that differ in texture and mineralogy. The innermost layer consists of either pyroxene needles, olivine, clumps of hedenbergite, and andradite or olivine “doughnuts” (i.e., crystals with central cavities). The next two layers outward both contain olivine plates and laths. The final layer separating accretionary rims from the Allende matrix contains clumps of andradite and hedenbergite surrounded by salitic pyroxene needles. Nepheline and Fe,Ni-sulfides are common constituents in all layers. Based on the observed disequilibrium mineral assemblages, abundant euhedral crystals with pore space between them, and rim thicknesses controlled by the underlying topography of their host inclusions, MacPherson et al. (1985) concluded that the layered accretionary rims in Allende are aggregates of gas–solid condensates which reflect significant fluctuations in physicochemical conditions in the solar nebula and grain/gas separation processes. Hiyagon (1998) analyzed the oxygen-isotope compositions of minerals in accretionary rims around two type A CAIs from Allende. Olivines in both accretionary rims are characterized by $^{16}$O-rich isotopic compositions ($\delta^{18}O = -28\%_o$, $\delta^{17}O = -30\%_o$), whereas wollastonite, andradite, and hedenbergite show much heavier oxygen-isotope compositions ($\delta^{18}O$ from $+2\%_o$ to $+10\%_o$, $\delta^{17}O$ from $-3\%_o$ to $+4\%_o$).

In the reduced CV chondrites, which are less altered than Allende, accretionary rims are

**Figure 7** (a, b) Oxygen-isotopic compositions of individual minerals in CAIs from CR chondrites. Most CAIs are $^{16}$O-rich and isotopically homogeneous; CAIs, which show petrographic evidence for extensive melting are less $^{16}$O-rich. Secondary phyllosilicates replacing $^{16}$O-rich mellile plot along terrestrial fractionation line. Data from Aléon et al. (2002a). (c, d) Oxygen-isotopic compositions of individual minerals in CAIs from CH chondrites show a bimodal distribution. The most refractory CAIs, which are composed of grossite, hibonite, spinel, perovskite, and mellile, are enriched in $^{16}$O; aluminum-diopside rims around these CAIs, pyroxene-spinel CAIs, and two mellile-rich CAIs surrounded by a forsterite layer are $^{16}$O-poor. Data from McKeegan et al. (2006). (e, f) Oxygen-isotopic compositions of individual minerals in CAIs from CB chondrites Hammadah al Hamra 237 and QUE 94411. The CAIs are rather homogeneous and $^{16}$O-poor. Data from Krot et al. (2001c).
not layered and consist of coarse-grained (20–40 μm), anhedral forsterite (Fa1–8 versus Fa8–50 in Allende), Fe,Ni-metal nodules, and fine-grained refractory components composed of aluminum-diopside, anorthite, spinel, and, in some cases, forsterite (Krot et al., 2001f, 2002b). These rims surround different types of CAIs: types A, B, and fine-grained spinel-rich (Figure 8). Forsterite grains in the accretionary rims are $^{18}$O-enriched similar to spinel, aluminum-diopside, and hibonite of the host CAIs (Figure 9).

Krot et al. (2001f, 2002b) concluded that forsterite-rich rims formed by accretion of high-temperature condensates in the CAI-forming regions. The rims were emplaced after high-temperature events experienced by the CAIs, such as melting and formation of Wark–Lovering rims (see Wark and Boynton, 2001), which must therefore have occurred in the CAI-forming region as well. Andradite, wollastonite, hedenbergite, and fayalitic olivine in the Allende rims formed by alteration under oxidizing conditions in the presence of $^{18}$O-poor fluid (Krot et al., 1995, 1998a, b, c, 2001e).

### 1.07.5.3 Amoeboid Olivine Aggregates

AOAs are irregularly shaped objects with fine grain sizes (5–20 μm) that occupy up to a few percent of type 2 and 3 carbonaceous chondrites (Table 3). AOAs are similar in size to co-accreted chondrules and CAIs being mostly 100–500 μm in size in CO (Chizmadia et al., 2002d).
up to 5 mm in size in CV (Komatsu et al., 2001), and typically $\approx 500 \mu m$ in CR chondrites (Aleón et al., 2002a). In the least altered chondrites, they are porous aggregates and their mineralogy matches that expected for high-temperature nebular condensates (Krot et al., 2004d). Unlike CAIs and chondrules, AOAs do not appear to show mineralogical and isotopic differences between groups and thus provide an excellent guide to the alteration history of the meteorite and its constituents.

1.07.5.3.1 Mineralogy and petrology of AOAs

AOAs, which were first described in the heavily altered Allende CV3 chondrite (Grossman and Steele, 1976), are best observed in the least altered chondrites, CO3.0, CR2, CH, CB chondrites, Adelaide, and Acfer 094 (Krot et al., 2004d and references therein). Here they consist of anhedral, fine-grained (1–20 $\mu m$) forsterite (Fa1–3), Fe,Ni-metal, and a refractory component composed of aluminum-diopside, spinel, anorthite, and rare melilite, or CAIs of similar mineralogy. AOAs in CO3.0 chondrites contain $\approx 8$ vol.\% metallic Fe,Ni: troilite is rare or absent (Chizmadia et al., 2002). The refractory objects in AOAs are characterized by significant variations in size (1–250 $\mu m$), shape (irregular, rounded), distribution (uniform, heterogeneous), modal mineralogy (spinel-rich, spinel-poor), and abundance (rare, abundant) (Figure 10). Forsterite grains typically contain numerous pores and tiny inclusions of aluminum-diopside. However, some AOAs show triple junctions between forsterite grains and coarse-grained shells surrounding finer-grained cores, indicating high-temperature annealing (Komatsu et al., 2001).

About 10\% of AOAs contain low-calcium pyroxene replacing forsterite at grain boundaries in AOA peripheries (Figure 5c), or rimming the AOA (Krot et al., 2004e). Although most AOAs show no clear evidence of being melted, those with low-Ca pyroxene rims are compact rather than porous and may have experienced small degrees of melting. Some AOAs appear to contain CAIs that have been melted (Figure 10).

Forsterite grains in AOAs in pristine chondrites show diverse compositions. Forsterite grains in Adelaide AOAs that lack low-Ca pyroxene are nearly pure (FeO $> 1$ wt.\%) with only small amounts of Cr$_2$O$_3$ ($< 0.3$ wt.\%) and MnO ($< 0.07$ wt.\%) whereas those in pyroxene-bearing AOAs are richer in FeO (1–4 wt.\%), Cr$_2$O$_3$ (0.2–0.6 wt.\%), and MnO (up to 0.8 wt.\%) (Krot et al., 2004d). Mn and Cr concentrations in AOAs in a CO3.0 chondrite (Yamato 81020) appear to be higher in fractured or peripheral regions and lowest in AOAs with high CaO concentrations (0.2–0.8 wt.\%) (Sugiura et al., 2004, 2006), This suggests that both Mn and Cr were introduced by gas–solid reactions after Ca-rich forsterite condensed, consistent with thermodynamic models (e.g., Weisberg et al., 2004).

Secondary nepheline, sodalite and ferrous olivine are common in AOAs in the altered and metamorphosed CV and CO chondrites, but are absent in AOAs from the unaltered chondrites. Olivines in AOAs from CV chondrites are generally more fayalitic than in the unaltered chondrites, with fayalite concentrations increasing from Leoville and Vigarano to Efremovka to Allende (Figure 11).
This sequence correlates with the degree of secondary alteration and thermal metamorphism experienced by CV chondrites (e.g., Krot et al., 1995, 1998a, b, c, 2001e; Komatsu et al., 2001). In CO3 chondrites, fayalite contents are well correlated with petrogic subtype (Chizmadia et al., 2002).

**1.07.5.3.2 Trace elements and isotopic composition of AOAs**

Trace element concentrations have been measured in 10 AOAs from Allende (Grossman et al., 1979). Most AOAs have unfractonated abundances of refractory lithophile and siderophile elements (2–20 × CI); two AOAs analyzed have group II REE patterns.

Oxygen-isotopic analysis of primary minerals (forsterite, aluminum-diopside, spinel, and anorthite) in AOAs from CM, CR, CB, and unmetamorphosed CO chondrites are uniformly enriched in $^{16}\text{O}$, whereas anorthite, melilitite, and secondary minerals (nepheline and sodalite) in AOAs from CVs and metamorphosed COs are $^{16}\text{O}$-depleted to various degrees (Hiyagon and Hashimoto, 1999a; Imai and Yurimoto, 2000, 2001; Itoh et al., 2002; Krot et al., 2001f, 2002b; Fagan et al., 2004) (Figure 12). Melilitite grains in AOAs from the reduced CV3 chondrite Efremovka are $^{16}\text{O}$-enriched relative to those from Allende, suggesting exchange during alteration (Fagan et al., 2004). Imai and Yurimoto (2000, 2001) reported two generations of olivines in Allende AOAs: primary forsteritic olivines, which are $^{16}\text{O}$-rich ($\Delta^{17}\text{O} \sim -20\%$), and secondary fayalitic olivines, which are $^{16}\text{O}$-poor ($\Delta^{17}\text{O} \sim -5\%$) and probably grew on the parent asteroid in the presence of $^{18}\text{O}$-poor fluid. Grain-boundary
Figure 11 Compositions of olivine in AOs from the reduced CV chondrites Vigarano (a), Leoville (b), Efremovka (c), oxidized CV chondrite Allende (d), CR chondrites (e), CH and CB chondrites (f), unique carbonaceous chondrites Adelaide (g), and Acfer 094 (h). Olivines in CRs, Adelaide, and Acfer 094 are magnesium-rich compared to olivines in CV AOs. Fayalite contents in olivines from CV AOs increase in the order Leoville and Vigarano, Efremovka, Allende; this is correlated with the degree of secondary alteration and thermal metamorphism experienced by CV chondrites. Data for Allende AOs are from Hashimoto and Grossman (1987); and for Efremovka, Leoville, and Vigarano AOs from Komatsu et al. (2001).
low-Ca pyroxene in AOA peripheries in primitive carbonaceous chondrites is $^{16}$O-rich ($\Delta^{17}$O < −20‰) whereas low-Ca pyroxene igneous rims on AOAs are $^{16}$O-poor ($\Delta^{17}$O ~ −5‰) (Krot et al., 2005b). Thus AOAs appear to have been modified in two different nebular environments, in addition to the final, presumably asteroidal environment where Na-rich phases were introduced.

Three AOAs in the CO3.0 chondrite Y-81020 that were studied for Al–Mg systematics showed $^{26}$Mg excesses corresponding to initial $^{26}$Al/$^{27}$Al ratios of (2.7±0.7)×10$^{-5}$, (2.9±1.5)×10$^{-5}$, and (3.2±1.5)×10$^{-5}$. Comparable excesses of $^{26}$Mg were not detected in the AOA-bearing chondrule (Itoh et al., 2002). The lower $^{26}$Al/$^{27}$Al ratios in AOAs compared to a canonical value of \(5 \times 10^{-5}\) found in most CAIs (e.g., MacPherson et al., 1995) suggest that either AOAs formed 0.1–0.5 Ma after CAIs or that $^{26}$Al was heterogeneously distributed in the CAI-forming region (Itoh et al., 2002).

Figure 12  Ion microprobe analyses of oxygen-isotopic compositions of individual minerals in AOAs from CR2 (a), CV3 (b), CM2 (c), and CO3 (d) chondrites. Key: fo, forsterit; cpx, Al-diopside; an, anorthite; sp, spinel; fas, Al–Ti-diopside; phyl, phyllosilicates; nph, nepheline; fo relict, relict AOA forsterite in chondrules; pig, chondrule pigeonite. Data for CR AOAs from Aléon et al. (2002a); CV AOAs are from Imai and Yurimoto (2000, 2001), Fagan et al. (2004), Hiyagon and Hashimoto (1999a), and Krot et al. (2002b); CM AOAs from Hiyagon and Hashimoto (1999b); CO AOAs from Itoh et al. (2002); CB AOA from Krot et al. (2001c).
1.07.5.3.3 Origin of amoeboid olivine aggregates

The mineralogy, petrology, $^{16}$O-rich compositions, depletion in moderately volatile elements, such as manganese, Cr, and Na, and the general absence of low-calcium pyroxenes associated with pristine AOAs strongly suggest that AOAs are aggregates of grains of forsterite, aluminum-diopside, spinel, anorthite, and Fe,Ni-metal that condensed in the nebula from an $^{16}$O-rich gaseous reservoir and aggregated with refractory objects (Krot et al., 2004d, e, 2005b; Weisberg et al., 2004). Mineralogical and chemical similarities between AOAs and forsterite-rich accretionary rims suggest that AOAs formed contemporaneously with these rims. Some refractory objects inside AOAs were melted prior to aggregation. AOAs subsequently experienced high-temperature annealing and solid-state recrystallization with only very minor melting and nebular alteration resulting in formation of anorthite and, in some cases, low-calcium pyroxene. The AOAs formed in the CAI-forming region(s) and they were either largely absent from chondrule-forming region(s) when chondrules formed, or the scales of the chondrule-forming events were small and their frequency low. Their preservation can be attributed to removal from the CAI-forming region prior to formation of low-calcium pyroxene by gas–solid reactions and/or kinetic inhibition of these reactions. Nevertheless, AOAs have preserved a record of nebular processing in $^{16}$O-rich and $^{16}$O-poor environments and may have been important precursor materials in the formation of several kinds of igneous, coarse-grained chondritic components such as refractory forsterite-rich objects and type I chondrules.

1.07.5.4 Aluminum-Rich Chondrules

Aluminum-rich chondrules are a diverse group of objects with igneous textures and $>10$ wt.% $\text{Al}_2\text{O}_3$ (Bischoff and Keil, 1984; Huss et al., 2001; MacPherson and Huss, 2005; Guan et al., 2006), which appear to have distinct origins from ferromagnesian chondrules (Section 1.07.5.5). Their mineralogy, bulk chemical compositions, oxygen, and Al–Mg isotope systematics suggest a close link between CAIs and aluminum-rich chondrules. Using the CaO–MgO–Al$_2$O$_3$–SiO$_2$ phase diagram (Figure 13), Huss et al. (2001) subdivided aluminum-rich chondrules in ordinary chondrites according to their bulk composition and mineralogy into three groups: “plagioclase-rich,” which plot in the anorthite (+ spinel) field on the liquidus and contain abundant euhedral calcic plagioclase crystals, “olivine-rich,” which plot in the forsterite (+ spinel) field and commonly contain large euhedral olivine phenocrysts, and “glassy,” which plot near the corundum–forsterite side of the ternary and are characterized by abundant transparent Na–Al-rich and calcium-poor glass that encloses a phenocryst assemblage of olivine, pyroxene, and spinel. In carbonaceous chondrites, however, Krot and Keil (2002) and Krot et al. (2002a) found a continuum between the plagioclase-rich and olivine-rich aluminum-rich chondrules: glassy aluminum-rich chondrules are absent (Figure 14). Because aluminum-rich chondrules in carbonaceous chondrites all have similar mineralogy (magnesian low-calcium pyroxene and forsterite phenocrysts, Fe,Ni-metal nodules, interstitial anorthitic plagioclase, Al–Ti–Cr-rich low-calcium and high-calcium pyroxenes, and crystalline mesostasis composed of silica, anorthite, and high-calcium pyroxene), Krot and Keil (2002) and Krot et al. (2002a) called them all plagioclase-rich chondrules, irrespective of modal mineralogy.

Because the aluminum-rich chondrules are compositionally most similar to CAIs and often contain aluminum-rich phases with high Al/Mg ratios (plagioclase and, occasionally, glass) which make them suitable for Al–Mg isotope studies, these chondrules received special attention (e.g., Kring and Boynton, 1990; Sheng et al., 1991; Hutcheon and Jones, 1995; Russell et al., 1996, 2000; Hutcheon et al., 1994, 2000; Marhas et al., 2002; Srinivasan et al., 2000a, b; Huss et al., 2001; Krot and Keil, 2002; Krot et al., 2001b, 2002a, c; Guan et al., 2006).

1.07.5.4.1 Isotopic and trace element studies of aluminum-rich chondrules

Oxygen-isotopic data for seven aluminum-rich chondrules from ordinary chondrites (Russell et al., 2000) are continuous with the ordinary chondrite ferromagnesian chondrule field above the terrestrial line, but extend it to more $^{18}$O-enriched values ($\delta^{18}$O = $-15.7 \pm 1.8\%$, $\delta^{17}$O = $-13.5 \pm 2.6\%$) along a mixing line of slope $= 0.83 \pm 0.09$ (Figure 15a). Two chondrules exhibit significant internal-isotopic heterogeneity indicative of partial exchange with a gaseous reservoir (Russell et al., 2000).
Porphyritic aluminum-rich chondrules are consistently $^{16}$O-rich relative to nonporphyritic ones, suggesting that degree of melting was a key factor during nebular exchange (Russell et al., 2000).

Oxygen-isotopic compositions of aluminum-rich chondrules from CR and CH chondrites (Krot et al., 2006a) are plotted in Figure 15b. Three out of six chondrules analyzed exhibit large internal-isotopic heterogeneity, whereas others are isotopically uniform; all chondrules have porphyritic textures. In contrast to aluminum-rich chondrules in ordinary chondrites, oxygen-isotopic heterogeneity is due to the presence of relict CAIs (Krot and Keil, 2002).

Aluminum–magnesium isotope measurements of aluminum-rich chondrules in ordinary and carbonaceous chondrites were summarized by Huss et al. (2001). About 10–15% of all aluminum-rich chondrules studied show $^{26}$Mg*. The inferred ($^{26}$Al/$^{27}$Al)$_b$ ratio of these chondrules is $\sim (0.5–2) \times 10^{-5}$, which is consistent with the values found in ferromagnesian chondrules from type 3.0–3.1 unequilibrated ordinary chondrites (Kita et al., 2000; McKeegan et al., 2000b; Mostefaoui et al., 2000, 2002).

Correlated in situ analyses of the oxygen- and magnesium-isotopic compositions of Al-rich chondrules from unequilibrated enstatite chondrites show that among 11 Al-rich chondrules measured for $^{26}$Al–$^{26}$Mg systematics, only one chondrule contains $^{26}$Mg* corresponding to the initial $^{26}$Al/$^{27}$Al ratio of $(6.8 \pm 2.4) \times 10^{-7}$ (Guan et al., 2006). The oxygen-isotopic compositions of five Al-rich chondrules on a three-oxygen-isotope diagram define a line of slope $\sim 0.6 \pm 0.1$ and overlap with the field defined by ferromagnesian chondrules in enstatite chondrites but extend to more $^{16}$O-rich compositions with a range in $\delta^{18}$O of about 12‰ (figure 3 in Guan et al., 2006).

The REEs in most aluminum-rich chondrules from carbonaceous chondrites studied are unfractionated (Kring and Boynton, 1990; Weisberg et al., 1991). However, some have highly fractionated group II and ultrarefractory patterns seen in refractory inclusions (Kring and Boynton, 1990; Misawa and Nakamura, 1988, 1996).
1.07.5.4.2 Origin of aluminum-rich chondrules

MacPherson and Russell (1997) and MacPherson and Huss (2005) discussed several possible models for the origin of aluminum-rich chondrules including impact melting of aluminous (evolved) parent body surface material, mixing of aluminous components with ferromagnesian chondrule precursors prior to chondrule formation, and volatilization. They concluded that (1) no single model appears capable of explaining the entire spectrum of...
Figure 15 Oxygen-isotopic compositions of individual minerals in (a) aluminum-rich chondrules from ordinary chondrites (Russell et al., 2000) and (b) CR carbonaceous chondrites (Krot et al., 2006a). Abbreviations: cpx, clinopyroxene; gl, glass; nph, nepheline; ol, olivine; opx, orthopyroxene; pl, plagioclase; px, pyroxene; sp, spinel.
aluminum-rich chondrule bulk compositions, (2) aluminum-rich chondrules are not intermediate in an evolutionary sense between known CAIs and chondrules, and (3) aluminum-rich chondrules are more closely related to normal chondrules, either by addition of an anorthite-like component to chondrule precursors or possibly, in some cases, by volatilization of chondrule or chondritic material of unusual oxygen-isotopic composition. Russell et al. (2000), MacPherson and Huss (2005), and Guan et al. (2006) concluded that “if aluminum-rich chondrules were mixtures of ferromagnesian chondrules and CAI material, their bulk chemical compositions would require them to exhibit larger $^{16}$O enrichments than we observe. Therefore, aluminum-rich chondrules are not simple mixtures of these two components.”

However, Krot and Keil (2002) and Krot et al. (2001b, 2002a) showed that ~15% of aluminum-rich chondrules from different carbonaceous chondrites are associated with relict CAIs (Figure 14). These relict CAIs are mineralogically similar to CAIs in AOAs and consist of anorthite, spinel, high-calcium pyroxene, and plagioclase; most of them were extensively melted during chondrule formation. Krot and colleagues inferred that aluminum-rich chondrules formed by melting of the ferromagnesian chondrule precursors (magnesian olivine and pyroxenes, Fe,Ni-metal) mixed with the refractory materials, including relict CAIs, composed of anorthite, spinel, high-calcium pyroxene, and forsterite. This mixing explains the relative enrichment of anorthite-rich chondrules in $^{16}$O compared to typical ferromagnesian chondrules (Figure 12), and the group II REE patterns of some of the aluminum-rich chondrules (Misawa and Nakamura, 1988, 1996; Kring and Boynton, 1990).

1.07.5.4.3 Relict CAIs and AOAs in ferromagnesian chondrules

Mineralogical observations indicate that CAIs outside chondrules show no clear evidence for being melted during a chondrule-forming event (Krot et al., 2002a, b, c, 2005d). Relict CAIs inside ferromagnesian chondrules are exceptionally rare. Only six relict CAIs have been described in ferromagnesian chondrules: Acfer 094 and Adelaide, the CH chondrites Acfer 182 and Patuxent Range 91546, the CV chondrite Allende, and the H3.4 ordinary chondrite Sharps (Bischoff and Keil, 1984; Misawa and Fujita, 1994; Krot et al., 2006b). Relict CAIs are also present in AOAs (Itoh et al., 2002; Hiyagon, 2000). These relict CAIs are very refractory, unlike those in aluminum-rich chondrules, being composed of hibonite, grossite, spinel, melilitite, perovskite, and platinum group metals (Figure 16). The relict CAIs in chondrules are corroded by host chondrule melts, but have largely preserved their $^{16}$O-rich isotopic signatures of typical CAIs (Figure 17a). The only relict OA observed inside a chondrule has also preserved its $^{16}$O-rich isotopic signature (Figure 17b). These observations indicate that some CAIs were present in the chondrule-forming regions and were melted together with chondrule precursors, suggesting that at least some CAIs formed before chondrules.

Magnesium isotope measurements of the relict CAIs and CAI- and AOA-bearing chondrules typically show no resolvable $^{26}$Mg* (Krot et al., 2002a; Itoh et al., 2002), implying upper limits for $^{26}$Al/$^{27}$Al$_I$ of $<1 \times 10^{-5}$ and $<5 \times 10^{-6}$. These data suggest either these CAIs formed without $^{26}$Al or their Al–Mg systems were reset during chondrule formation. If these CAIs formed initially with a canonical $^{26}$Al/$^{27}$Al$_I$ that was reset during chondrule melting, the host chondrules must have formed at least ~2 Myr after the CAIs.

The only exception is the hibonite-rich relict CAI #9d from Adelaide (Figure 16d) that shows clear excesses of radiogenic $^{26}$Mg in hibonite that are correlated with $^{27}$Al/$^{24}$Mg ratio. The observed $^{26}$Mg* in hibonite together with spinel define an isochron with $^{26}$Al/$^{27}$Al$_I$ of $(3.7 \pm 0.5) \times 10^{-5}$. Melilitite in this CAI shows no $^{26}$Mg*, while a mixture of hibonite and melilitite shows an intermediate $^{26}$Mg excess that appears to plot on a mixing line connecting melilitie and the most $^{26}$Mg*-enriched hibonite. Two measurements of plagioclase in the host chondrule, which were made in the rim around the CAI, show no resolvable $^{26}$Mg* [$^{26}$Al/$^{27}$Al$_I$ < $5 \times 10^{-6}$]. Krot et al. (2006b) concluded that when CAI #9d was incorporated into the surrounding chondrule melt, diopside, melilitie (or anorthite), and spinel in its Wark–Lovering rim sequence began reacting with the surrounding chondrule melt to produce a layer of plagioclase, and melilitie in the interior of the inclusion-exchanged magnesium with the surrounding chondrule melt. The newly formed plagioclase and the melilitie inside the CAI no longer contain evidence of $^{26}$Mg*. This constrains the timing of the chondrule melting event to be at least 2 Myr after the CAI.
Figure 16  Backscattered electron images of chondrules containing relict refractory inclusions: #17 in Acfer 094 (a, b), #9d in Adelaide (c), #9 in Sharps (d), and #16 in PAT91546 (e). Relict CAI Acfer 094 (a, b) consists of hibonite (hib) with inclusions of perovskite (pv), a Zr-bearing phase (Zr-ph), and Re-, Ir-, Os-bearing (PGE) nuggets. It is surrounded by a shell of fine-grained, iron-spinel (sp). The host chondrule consists of ferrous olivine (ol), plagioclase mesostasis (pl), Fe,Ni-sulfides (sf), Cr-spinel, and relict grains of forsteritic olivine (fo). The relict CAI in Adelaide (c) consists of hibonite, perovskite, and melilite (mel); it is surrounded by a magnesium-spinel rim. Its host chondrule consists of forsteritic olivine, low-calcium pyroxene, glassy mesostasis, and kamacitic metal. The relict CAI in Sharps (d) consists of hibonite surrounded by iron-spinel and a nepheline-like phase (nph). Its host chondrule consists of forsteritic olivine, low-calcium pyroxene, high-calcium pyroxene, anorthitic mesostasis, and kamacitic metal. The relict CAI in PAT91546 (e) has a grossite (grs) core surrounded by a spinel (sp) rim. This CAI is surrounded by an igneous chondrule-like material composed of plagioclase (pl), low-Ca pyroxene (opx), high-Ca pyroxene (cpx), olivine (ol), and Fe,Ni-metal (met), mesostasis (mes) (after Krot et al., 2005d). (f) Relict AOA #1 in a type II chondrule from the CO3.0 chondrite Y-81020 (after Yurimoto and Wasson, 2002).
formed, because >80% of $^{26}$Al had decayed. Thus, Adelaide CAI #9d and its surrounding chondrule provide clear evidence of a $\geq 2$ Myr time gap between the formation of the CAI and its incorporation into the chondrule, and this conclusion does not require an assumption of homogeneously distributed $^{26}$Al in the chondrule-forming region (MacPherson et al., 1995).

1.07.5.4.4 Relict chondrules in igneous CAIs and igneous CAIs overgrown by chondrule material

Relict chondrules have been reported in three igneous CAIs—compact type A CAI A5 from Y-81020, coarse-grained, igneous, anorthite-rich (type C) CAIs ABC, and TS26 from Allende (Itoh and Yurimoto, 2003; Krot et al., 2005d).
No relict chondrules have been found inside AOAs or nonigneous CAIs.

CAI A5 has a melilite-rich core surrounded by a very fine-grained mantle composed of Al-diopside, spinel, and anorthite; the mantle contains igneously zoned pyroxene grains ranging in composition from enstatite to augite (Figure 18). The melilite and pyroxene grains are similarly $^{16}$O-depleted, whereas the mantle shows a wide compositional range and is $^{16}$O-enriched (Figure 17d). Itoh and Yurimoto (2003) concluded that the pyroxene grains are relict chondrule fragments incorporated into the host CAI prior to its final melting in the CAI-forming region. Alternatively, the lack of Wark–Lovering rim layers around the host CAI, the estimated fast cooling rate ($>100 \, \text{Ch}^{-1}$) during crystallization of the CAI mantle, and the wide range of oxygen-isotopic compositions of the CAI minerals overlapping with those of relict chondrule fragments, may indicate that this compound CAI-chondrule object experienced late-stage, incomplete melting and oxygen-isotopic exchange in an $^{16}$O-rich gaseous reservoir during chondrule formation (Russell et al., 2005).

Type C CAI ABC in its peripheral zone contains a relict olivine-pyroxene fragment that is corroded by Al-diopside and surrounded by a halo of high-Ca pyroxene (Figures 19a and 19b). Spinel and Al,Ti-diopside of the host CAI are $^{16}$O-enriched, whereas melilite, anorthite, olivine, and low-Ca pyroxene are $^{16}$O-depleted; Cr-spinel, high-Ca pyroxene, and Al,Ti-poor diopside have intermediate oxygen-isotopic compositions (Figure 17c). The CAI anorthite has a resolvable $^{26}\text{Mg}^*$ corresponding to the $(^{26}\text{Al}/^{27}\text{Al})_{\text{I}}$ ratio of $(4.7 \pm 1.4) \times 10^{-6}$.

TS26 is a mineralogically zoned type C CAI (Figures 19c and 19d). The coarse-grained core is surrounded by a thick, fine-grained mantle containing abundant relict grains of forsteritic olivine and low-Ca pyroxene; the Wark–Lovering rim layers are absent. Spinel and Al,Ti-diopside of the CAI core are $^{18}$O-rich, whereas melilite, anorthite, Al,Ti-poor diopside of the CAI mantle, and relict olivine and low-Ca pyroxene are $^{16}$O-depleted to various degrees (Figure 17c). Anorthite shows no resolvable $^{26}\text{Mg}^*$; the inferred $(^{26}\text{Al}/^{27}\text{Al})_{\text{I}}$ ratio is $<2.5 \times 10^{-6}$.

The relict nature of the olivine–pyroxene fragments in the periphery of the CAIs does not necessarily mean that they predated the CAIs. Instead, the $^{16}$O-poor oxygen in the periphery of the CAIs and resetting of their $^{26}$Al–$^{26}$Mg systematics, provide evidence that they experienced a late remelting event. During this event, incorporation of the chondrule-like, olivine–pyroxene material could have occurred (Krot et al., 2005d). This interpretation is consistent with some igneous CAIs being overgrown by chondrule-like material (Figures 19e and 19f). We note that the apparent discrepancy in interpretation of chondrule-bearing igneous CAIs (Itoh and Yurimoto, 2003; Krot et al., 2005d) is largely due to differences in definitions of CAI-formation. According to Itoh and Yurimoto (2003), all high-temperature processes that affected CAIs should be called CAI-forming events, whereas Krot et al.

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**Figure 18** Backscattered electron image of the chondrule-bearing CAI A5. The CAI consists of a polycrystalline melilite core surrounded by a porous mesostasis composed of a fine-grained mixture of Al-rich clinopyroxene (lighter area) and Al-rich glass (darker area). The mesostasis encloses a pyroxene assemblage dominated by enstatite with minor pigeonite and augite; troilite and Fe,Ni-metal (white spots) are scattered in the mesostasis near the pyroxene assemblage.
(2005d) define CAI-forming events as those which occurred in the CAI-forming regions, that is, regions with high ambient temperatures (>1350 K), relatively low pressure, $^{16}$O-rich nebular gas, and approximately solar redox conditions.

1.07.5.5 Refractory Forsterite-Rich Objects

A long-running controversy has existed over the origin of refractory forsterites 0.1–0.5 mm in size in type 2 and 3 ordinary and carbonaceous chondrites. Although most isolated olivines are probably formed by disaggregation of chondrules (McSween, 1977b; Roedder, 1981), Steele (1986, 1989) argued that the extremely forsteritic grains (Fa$_{>2}$) in carbonaceous chondrites, which have a blue cathodoluminescence color, high concentrations of CaO and Al$_2$O$_3$ (typically 0.5 and 0.25 wt.% respectively) and comprise a few percent of all olivines, did not crystallize in chondrules.

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**Figure 19** Combined elemental maps in Mg (red), Ca (green), and Al K$_\alpha$ (blue) X-rays (a, c, e) and back-scattered electron images (b, d, f) of the Allende type C CAIs associated with chondrule-like ferromagnesian silicates. (a, b) CAI ABC. (c, d) CAI TS26. (e, f) CAI 93. Regions outlined in “a,” “c,” and “d” are shown in detail in “b,” “d,” and “e,” respectively. an, anorthite and anorthitic plagioclase; cpx, high-Ca pyroxene; di, diopside; mel, melilite; nph, nepheline; px, low-Ca pyroxene; sec, secondary sod, sodalite; sp, spinel.

Reproduced by permission of Astronomical Society of the Pacific from Russell et al. (2005).
Steele suggested that the refractory forsterites may have condensed from the nebula, formed relict grains in chondrules, and were an important component of chondrulate precursor material. Weinbruch et al. (2000) showed that isolated refractory forsterites were more 16O-rich than olivines that crystallized in chondrules and also favored a condensation origin. However, Jones et al. (2000b) showed that there are rounded objects composed largely of a single large forsterite crystal with traces of low-Ca pyroxene and very little mesostasis that have compositions like those of the isolated forsterites. Jones et al. (2000b) inferred that these objects were chondrules, that relict forsterites from such objects were present in other type I chondrules, and that refractory 16O-rich forsterites were primitive nebular components. Pack et al. (2004, 2005) found <0.01–0.4 vol.% luminescent refractory forsterites in a variety of ordinary, carbonaceous, and R chondrites, and found no difference in their chemical and isotopic compositions. Highly refractory forsterites with >0.6 wt.% CaO and <0.5 wt.% FeO are enriched in 16O with Δ17O between −4‰ and −10‰, whereas moderately refractory and nonrefractory olivines range between −5‰ and +2‰. They inferred that the refractory forsterites come from a single common reservoir and that they formed in a reducing nebula gas of solar composition. The oxygen-isotopic and chemical compositions of the refractory forsterites lie beyond those at the FeO-poor end of the sequence defined by olivine-rich, FeO-poor type I chondrules and pyroxene-rich type IB chondrules (see Jones, 1994; Section 1.07.5.6.1). Melt inclusions in refractory forsterites are not in equilibrium with the olivine hosts—which either forsterite crystallized outside its stability field (McSween, 1977b), or because the melt reacted more readily with nebular gas than the crystallizing solids (Varela et al., 2005; Pack et al., 2004, 2005).

Refractory forsterite-rich objects are clearly a fascinating component of chondrites and may provide a possible link between refractory inclusions, especially AOAs, and chondrules. Their 16O-enriched composition points to an early solar nebula origin, though their formation ages have not been determined. Rounded, refractory forsterite-rich objects may be a kind of proto-type-I chondrules, as normal type I chondrules show evidence for gas–solid reactions during cooling (Section 1.07.5.6.5). However, Libourel and Krot (2006) described coarse-grained forsteritic aggregates with granoblastic textures inside type I chondrules in CV chondrites and inferred that these igneous objects, which are also 16O-enriched (Chaussidon et al., 2006), could not have formed in the solar nebula and may be derived from planetesimals that were disrupted. However, if these planetesimals existed, they have not supplied us with meteorites, as differentiated meteorites have Δ17O > −3‰ (Chapter 1.05). Whatever their origin, refractory 16O-enriched forsterites appear to be an important component of type I chondrule precursor materials.

### 1.07.5.6 Chondrules

Chondrules are igneous-textured particles composed mainly of olivine and low-calcium pyroxene crystals set in a feldspathic glass or microcrystalline matrix. (Chondrules with >10 wt.% Al2O3, which have closer links with CAIs are reviewed in Section 1.07.5.4.) Many chondrules with FeO-poor silicates also contain metallic Fe,Ni grains, often clustered near the periphery. Metal grains outside chondrules that are of comparable sizes to those inside have geochemical properties suggesting they were once ejected from or broken out of chondrules, or in the case of the CB group (where reduced chondrules lack metal), that metal and chondrules formed in the same environment. A close link between metal and reduced silicates is consistent with mineral–gas equilibration in the solar nebula as forsterite, enstatite, and metallic Fe,Ni are stable over similar temperature ranges (figure 2 of Chapter 1.15). The mineralogical, chemical, and isotopic properties of chondrules have been reviewed most recently by Jones et al. (2005).

Links between asteroids and chondrites suggest that chondrules are abundant in the inner part of the asteroid belt and that the terrestrial planets probably formed from chondritic materials. Thus, much of the mass that accreted in the inner solar system would have been derived from chondrules. In the absence of sticky organics, dry grains of silicate do not readily adhere so that chondrule formation may have been the process that triggered accretion in the inner solar system (e.g., Wood, 1996a; Cuzzi et al., 2001; Scott, 2002). Understanding the origin of chondrules has been a major goal of meteorite studies since chondrites were first described over 200 years ago.

#### 1.07.5.6.1 Chondrule textures, types, and thermal histories

Chondrule textures are conveniently divided into two types: porphyritic, which have large crystals of olivine and/or pyroxene in a fine-grained or glassy matrix, and nonporphyritic, which include those with cryptocrystalline,
radial-pyroxene, and barred-olivine textures (Figures 1 and 20). Table 4 shows how the proportions of different types vary considerably among the groups. Carbonaceous chondrites tend to have the highest fraction of porphyritic chondrules, but CH and CB groups are exceptions. Mean sizes and abundances of chondrules in each group are given in Table 1.

Laboratory experiments constrain the initial conditions and thermal history required for each textural type, but there are too many variables (e.g., initial state of chondrule, peak temperature, time at peak temperature, and cooling rate) to make very quantitative statements (Lofgren, 1996; Hewins, 1997; Hewins et al., 2005). Porphyritic chondrules crystallized from melts with many nuclei after incomplete melting of fine-grained, precursor materials (Lofgren, 1996; Connolly et al., 1998). Peak temperature and duration of heating are linked as porphyritic textures can be reproduced by heating fine-grained material to \( \approx 100^\circ \text{C} \) above the liquidus temperature (generally 1,350–1,800 \( ^\circ \text{C} \)) for 5 min, or just below the liquidus temperature for hours (Hewins and Connolly, 1996; Lofgren, 1996). Nonporphyritic chondrules crystallized from melts that were superheated above their liquidus for long enough to destroy all solids that could act as nuclei. For barred olivine and radial pyroxene chondrules, nucleation was probably induced by collision with solid grains (Connolly and Hewins, 1995).

Radial textured chondrules crystallized while cooling at 5–3,000 \( ^\circ \text{C} \text{Ch}^{-1} \), barred olivine chondrules at 500–3,000 \( ^\circ \text{C} \text{Ch}^{-1} \), and porphyritic chondrules at 5–100 \( ^\circ \text{C} \text{Ch}^{-1} \) (Desch and Connolly, 2002). Cooling rates above the liquidus may have been much higher; below the solidus, chondrules cooled more slowly at rates of 0.1–50 \( ^\circ \text{C} \text{Ch}^{-1} \) (Weinbruch et al., 2001).

Porphyritic chondrules are classified into type I, which are FeO-poor in unmetamorphosed chondrites, and type II, which are FeO-rich. Type I chondrules account for \( > 95\% \) of chondrules in CO, CV, CR (Figure 1a), and CM chondrites and olivine-rich varieties were probably abundant in the material that accreted to form the Earth (Hewins and Herzberg, 1996). Types I and II are both subdivided into A, which are olivine-rich (\( > 90 \) modal percent olivine), and B, which are pyroxene-rich (Jones, 1990, 1994, 1996a, b). Olivines in type IA chondrules in unmetamorphosed chondrites are mostly \( \text{Fa}_{0.3-5} \) and \( \text{Fa}_{2-10} \) in IB; type II chondrules olivines are \( \text{Fa}_{10-20} \) in ordinary chondrites and up to \( \text{Fa}_{50} \) in carbonaceous chondrites. Rounded type I chondrules commonly have low-calcium pyroxene rims, glassy mesostases, and grains of metallic Fe,Ni, whereas type II chondrules lack these features, contain small chromites and commonly have larger olivines (Figure 20; Scott and Taylor, 1983). Type I and II chondrules can be identified from these features in many type 2–6 chondrites so that metamorphic and alteration effects can be tracked (McCoy et al., 1991; Hanowski and Brearley, 2001). Type I chondrules also occur as finer grained, irregularly shaped aggregates, which

![Figure 20 Backscattered electron images of three chondrules in Tieschitz (H/L3.6) chondrite. (a) Type IA porphyritic chondrule composed largely of forsteritic olivine (ol), mesostasis (mes), metallic Fe,Ni droplets (met) (white). Dusty olivines are relict, FeO-rich olivines that crystallized elsewhere and formed tiny metallic Fe,Ni particles when heated in the chondrule melt. (b) Type IIA porphyritic chondrule containing large euhedral, FeO-bearing, olivine phenocrysts, dark mesostasis (mes), and white sulfide droplets (sf). (c) Nonporphyritic chondrule containing fine pyroxene crystals that appear to radiate from the upper edge of the chondrule.](image-url)
represent partly melted dust aggregates or aggregates of partly melted particles (e.g., Rubin and Wasson, 2005). In ordinary chondrites, which have very diverse textured chondrules, all chondrules having olivines with Fa < 10 may be referred to as type I by some authors (Hewins, 1997).

Chondrules have also been classified using their cathodoluminescence properties and the compositions of olivines and mesostases (Sears et al., 1995a). For unmetamorphosed chondrites, groups A and B in this scheme correspond to types I and II. During metamorphism, the cathodoluminescence properties and chondrule group change. The merits of the two schemes were reviewed by Scott et al. (1994) and Sears et al. (1995b). Grossman and Brearley (2005) caution that the classification criteria based on the compositions of chondrule mesostases need to be revised because of Na loss during electron probe analysis.

1.07.5.6.2 Compositions of chondrules

Chemical compositions of chondrules have been determined from extracted samples using neutron activation analysis and by in situ analysis in polished sections using electron microprobe and ion probe analysis (e.g., see Gooding et al., 1980; Grossman et al., 1988; Alexander, 1995). Chondrules typically show flat refractory abundances that are relatively close to the mean chondrite value and abundances of moderately volatile elements that scatter more widely about the mean. Type II chondrules are relatively unfractonated with near-CI levels of refractories and moderately volatile elements. However, type I chondrules show systematic depletions of moderately volatile elements and a broader spread of refractory abundances with the silicon-rich type IB chondrules being poorer in refractories than the silicon-poor type IA chondrules (Figure 21). The source of the fractionations in type I chondrules is discussed below.

Oxygen-isotopic compositions of large individual chondrules suggest that chondrules formed from several different reservoirs that were poorer in 16O than the CAI source (Figure 22). Chondrules in ordinary chondrites generally plot above the terrestrial fractionation line, enstatite chondrule chondrules plot on or near the line, and carbonaceous chondrite chondrules lie below. Ion probe analyses for oxygen isotopes in olivine show that most ferromagnesian chondrules have relatively homogeneous compositions due to exchange between

<table>
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<tr>
<th>Type/group</th>
<th>CM</th>
<th>CO</th>
<th>CV</th>
<th>CR</th>
<th>CH</th>
<th>CB,</th>
<th>CK</th>
<th>H–L–LL</th>
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<td>~1</td>
<td>&gt;99</td>
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<td>82</td>
<td>~87</td>
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<td>95</td>
<td>94</td>
<td>96–98</td>
<td>20</td>
<td>~1</td>
<td>&gt;99</td>
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<td></td>
<td></td>
<td>4</td>
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<td>5</td>
<td></td>
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<tr>
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<td>6.3</td>
<td>2–4</td>
<td>80</td>
<td>~99</td>
<td>&lt;1</td>
<td>16</td>
<td>18</td>
<td>~13</td>
<td>~8</td>
</tr>
</tbody>
</table>


*a Includes radial pyroxene and glass chondrules.

Figure 21 Elemental abundances in type IA chondrules, which are olivine-rich and type IB and IAB chondrules, which are pyroxene rich, from the Semarkona (LL3.0) chondrite normalized to CI chondrites and silicon. Type IA chondrules are enriched in refractories relative to IAB and IB. For moderately volatile elements, all type I chondrules are depleted, with most IA showing larger depletions than types IB and IAB. Reproduced by permission of Elsevier from Jones (1994).
chondrule melt and nebula gas; but some type I chondrules have $^{16}O$-rich forsterites that were probably present in precursor materials (see references in Scott and Krot, 2001; Jones et al., 2004; Krot et al., 2006a). Chondrules are isotopically homogeneous in comparison to CAIs: $^{50}$Ti anomalies (see Niemeyer, 1988) and mass fractionation effects (e.g., Clayton et al., 1985; Misawa and Fujita, 2000; Alexander and Wang, 2001; Alexander et al., 2000) are much smaller than those in many CAIs. Inferred initial concentrations of $^{26}$Al in chondrules and $^{207}$Pb/$^{206}$Pb dating suggest that chondrules formed 1–4 Ma after CAIs (Kita et al., 2000; Mostefaoui et al., 2002; Amelin et al., 2002). See Gilmour (2002), Gilmour et al. (2006), Kita et al. (2005), and Chapter 1.16 for reviews of chondrule formation ages.

Effects of secondary processes in modifying volatile elements (Grossman et al., 2000, 2002) and oxygen isotopes in chondrules, especially in ordinary chondrites (Bridges et al., 1998; Franchi et al., 2001) require further study (see Chapter 1.09).

Trapped and cosmogenic noble gases in chondrules offer clues to their irradiation history and formation but not definitive constraints (see Chapter 1.14). Trapped noble gases are generally absent or rare in chondrules, but significant amounts of trapped $^{36}$Ar, $^{84}$Kr, and $^{132}$Xe from a so-called subsolar component were found in chondrules in an EH3/4 chondrite (Okazaki et al., 2001). This component is intermediate in composition between that of the Sun and the major trapped component in type 1–3 chondrites (“Q-type” gases) and occurs in E4–6 chondrites (Patzer and Schultz, 2002b), CR2, CH3, CB$3$, and K3 chondrites (see Bischoff et al., 1993). Okazaki et al. (2001) inferred that solar wind had been implanted into chondrule precursor material near the protosun and then fractionated during melting to leave a subsolar pattern. However, subsolar noble gases are present in several other sites suggesting that the subsolar gases were redistributed (Busemann et al., 2002). Further laser microprobe analyses of chondrules and other components in the most pristine chondrites are clearly needed to establish which chondrules, if any, acquired solar gases from the nebula or were irradiated by high-energy particles near the inner edge of the disk.

1.07.5.6.3 Compound chondrules, relict grains, and chondrule rims

Chondrules in all groups except CB and CH show evidence for collisions: with each other while partly molten and with solid grains while molten and solid. Compound chondrules form by collisions of partly molten chondrules and their abundance gives some constraint on the number density of chondrules in the region where they formed. Unfortunately, there are large uncertainties in chondrule speed and the provenance of the joined chondrules, which make estimates of the chondrule density very uncertain. About 1–2% of chondrules in ordinary and CV chondrites are compound (Wasson et al., 1995; Akaki and Nakamura, 2005). In over half of these, the chondrules that collided have such similar compositions that they could have been derived from a single large droplet. Other compound chondrules may have formed by part melting of a porous aggregate containing an embedded chondrule: relatively few compound chondrules probably formed by random collisions. However, Ciesla et al. (2004b) infer that at least 5% of chondrules are compound and that chondrules formed where solids were concentrated by $>45$ times above the canonical solar nebula value, possibly at the nebula midplane.

Foreign grains in chondrules appear to have been derived from other chondrules (Jones, 1996b). Relict low-FeO olivines from type I chondrules can be found in high-FeO, type II chondrules and vice versa, indicating that chondrule formation was a repeated process and that material was recycled through the chondrule furnace (e.g., Kunihiro et al., 2004b, 2005a).

Chondrules may have two types of rims: fine-grained matrix rims and coarse-grained igneous
rims: both are missing in CH and CB chondrites. Matrix rims vary in composition but the variations are uncorrelated with chondrule composition (Section 1.07.5.7). However, the compositions of igneous rims are related to those of the host chondrule: type I chondrules have igneous rims that are FeO poor, while type II chondrules have FeO-rich rims (Krot and Wasson, 1995). The igneous rims formed by collisions between chondrules and smaller partly molten particles, or solid particles with diverse oxygen-isotopic compositions that were accreted and later incompletely melted (Nagashima et al., 2003).

From the abundances of igneous rims, compound chondrules, and relict grains and the dearth of unmelted, chondrule-sized dustballs, we infer that collisions between partly melted objects and remelting of aggregates from such collisions were important processes that enabled chondrules to form from fine particles.

1.07.5.6.4 Closed-system crystallization

Understanding whether chondrules acted as open or closed systems during chondrule formation is crucial for elucidating their origin (Sears et al., 1996). Type II chondrules appear to be good candidates for closed system crystallization, as chemical zoning profiles across their phenocrysts are consistent with fractional crystallization (Jones, 1990; Jones and Lofgren, 1993). Type II chondrules contain significant concentrations of sodium and other volatile elements that would have been readily lost if the chondrules had been molten for more than a few minutes (Yu and Hewins, 1998). Such chondrules are commonly considered as archetypal chondrules formed by closed-system melting. Although most workers infer that type II chondrules resulted from single heating events, Wasson and Rubin (2003) argue for multiple events with low degrees of melting, which we infer that collisions between partly melted objects and remelting of aggregates from such collisions were important processes that enabled chondrules to form from fine particles.

1.07.5.6.5 Open-system crystallization

Unlike the archetypal chondrules, type I chondrules show a variety of evidence for volatility-controlled chemical fractionations that may have occurred during chondrule formation. Hewins et al. (1997) studied microporphyritic and cryptoporphyritic type I chondrules in Semarkona (LL3.0), which have irregularly shaped interstitial metal grains rather than the rounded droplets in mesostasis common in coarser type I chondrules. They found an inverse correlation between grain size and abundance for the moderately volatile elements, sodium, potassium, and sulfur, as well as iron and nickel (Figure 23). Hewins et al. inferred that volatilization increased with the extent of melting of a fine-grained precursor having a chondritic composition. Alternatively, these very fine-grained chondrules may have formed by aggregation of partly melted particles that scavenged volatiles with an efficiency that depended on their grain size. Despite the large increase in alkali concentrations from type IA to type IB chondrules, they do not show any systematic variation in K isotopic composition (Alexander and Grossman, 2005).

Mesostases in some type IA chondrules in Semarkona show volatility-related chemical zoning (Matsunami et al., 1993; Nagahara et al., 1999). Mesostasis near the rims is higher in volatiles and lower in refractories than mesostasis near the core. Matsunami et al. invoked recondensation and reduction processes in the solar nebula. The chemical variations across type I chondrules and those in microporphyritic and cryptoporphyritic type I chondrules (Figure 23) mimic the fractionation patterns shown by the bulk chemical data for
chondrules in the IA–IB sequence (Figure 21), suggesting single-process-controlled chemical variations within and among type I chondrules. The concentration of pyroxene phenocrysts around the periphery of many type I chondrules was reproduced experimentally by Tissandier et al. (2002), who allowed melt to react with gaseous SiO during crystallization. They inferred that such gas–melt interactions were prevalent during chondrule formation, and invoked high dust–gas ratios to stabilize chondrule melts in the nebula (Ebel and Grossman, 2000). Further evidence for gas–melt interactions is provided by silicon-rich, igneous rims on many type I chondrules in CR2 chondrites (Krot et al., 2004b). These rims contain high-calcium and low-calcium pyroxene, glassy mesostasis, Fe,Ni, and silica, with high concentrations of chromium and manganese and low concentrations of aluminum and calcium in high-calcium pyroxene (Figure 24). Mesostasis zoning follows that in the ordinary chondrites with silicon, sodium, potassium, and manganese increasing and calcium, magnesium, aluminum, and chromium decreasing from the olivine-rich core, through the pyroxene-rich rim to the silicon-rich rim. FeO remains nearly constant. Krot et al. (2004b) infer that gas–melt fractional condensation or gas–solid condensation followed by remelting produced these chemical fractionations. Isolation of early-formed forsterite condensates may have resulted naturally from crystallization, as forsterite would have equilibrated with the nebula more slowly than the melt.

Formation of chondrules from a gas–melt impact plume, some by gas–melt condensation, was proposed for chondrules in CBn chondrites, which have unusual textures and compositions (Krot et al., 2001d, 2006c). The chondrules are cryptocrystalline or skeletal olivine, lack igneous or fine-grained rims and relict grains, and do not form compound objects (Figure 25). They clearly formed from total melts in a dust-free environment. Some cryptocrystalline chondrules are embedded in zoned metal grains, which have compositional profiles consistent with nebular condensation (Krot et al., 2001d, 2006c). Chondrules have uniform flat refractory element abundances but the variation ((0.02–3)/C2 CI) is far wider than in other chondrites (Figure 26). The depletions of refractory elements relative to silicon in the cryptocrystalline chondrules indicate that silicon or the refractory elements, or both, condensed into chondrules or their precursors. The near-CI bulk abundances of refractory elements in the chondrites favor closed-system fractional condensation. Moderately volatile elements in chondrules show large depletions (Figure 26) that are inversely correlated with condensation temperature, as for bulk chondrites (Figure 3) and type I chondrules (Figure 21). Chondrule textures are consistent with condensation of melts.

1.07.5.6.6 Chondrules that formed on asteroids

Chondrites contain a small fraction of chondrules that may have formed on asteroids. One rare type of chondrule (~0.1%) in type 4–6 ordinary chondrite breccias is composed largely of plagioclase (or mesostasis of plagioclase composition) and chromite (Krot et al., 2001d, 2006c). Chondrules that formed on asteroids

Figure 23  Elemental abundances in microporphyritic and cryptoporphyritic type I chondrules in Semarkona showing an inverse correlation between grain size (in micrometer) and abundance for the moderately volatile elements (chromium to sulfur). Hewins et al. (1997) attribute this to volatilization during melting. Reproduced by permission of National Institute of Polar Research from Hewins et al. (1997).
1993). Krot and Rubin (1993) suggest that these chondrules may have formed by impact melting as they find impact melts with similar compositions inside shocked ordinary chondrites and such chondrules are absent in type 3 chondrites. In addition, some chromite-rich chondrules contain chromite-rich aggregates, which appear to be fragments of equilibrated chondrites. Other possible impact products were described in LL chondrites, which are mostly breccias, by Wlotzka et al. (1983). They found microporphyritic potassium-rich clasts with highly variable K/Na ratios that are totally unlike chondrules in type 3 chondrites. Large chondrules and clasts in Julesberg (L3) may also be impact melt products according to Ruzicka et al. (1998).

1.07.5.7 Metal and Troilite

Two kinds of metal are found in chondrites: grains composed of refractory elements (iridium, osmium, ruthenium, molybdenum, tungsten, and rhenium), which condense along with the refractory oxides above $\sim 1,600 \text{ K at } 10^{-4} \text{ atm}$, and grains composed predominantly of iron, cobalt, and nickel, which condense with forsterite and enstatite at $\sim 1,350–1,450 \text{ K}$ (Campbell et al., 2005). The former are associated with CAIs (Palme and Wlotzka, 1976) and the latter with chondrules, typically type I or FeO-poor chondrules (B&J, 1998, pp. 244–278). Unfortunately, few chondrites preserve a good record of the formation history of their metal grains because subsequent low-temperature reactions commonly formed oxides and sulfides and thermal metamorphism allowed kamacite to exsolve from taenite. Most refractory nuggets have been studied in Allende CAI, where rampant oxidation and sulfurization and redistribution of volatile tungsten and molybdenum compounds have severely compromised the high-temperature nebular record (Palme et al., 1994).

Most grains of metallic Fe,Ni and troilite outside chondrules were probably lost from chondrules when they were molten. The sizes of prominent grains are roughly correlated with chondrule size (Skinner and Leenhouts, 1993; Kuebler et al., 1999; Schneider et al., 2003),
but were probably modified by shock after compaction. Grains of metallic Fe,Ni in most unshocked type 3–6 chondrites provide a record of slow cooling at $\sim 1–1,000 \text{ K Myr}^{-1}$ through the temperature range $\sim 550–350^\circ \text{C}$, when kamacite and taenite ceased to equilibrate (Wood, 1967). In most type 2 and 3.0–3.3 chondrites, metallic Fe,Ni grains typically contain concentrations of 0.1–1% chromium, silicon, and phosphorus, which are not found in type 4–6 chondrites, and reflect high-temperature processing prior to accretion.

The most pristine metallic Fe,Ni grains are found in the CR–CH–CB clan (Krot et al., 2002c). Most metal grains with $>8\%$ Ni lack coexisting low-nickel kamacite and high-nickel taenite showing that these chondrites were not heated above $\sim 300^\circ \text{C}$ for more than a year (Reisener et al., 2000). Metal grains are not present in most chondrules in CH chondrites, which are cryptocrystalline, and are entirely absent from chondrules in CB chondrites.

### 1.07.5.7.1 CR chondrite metallic Fe,Ni

CR2 chondrites contain 5–8 vol.% metallic Fe,Ni grains in type I chondrules and between them, which are not associated with troilite. Grains outside chondrules were probably once

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**Figure 25** Combined elemental map in magnesium (red), calcium (green), and Al K$_{\alpha}$ (blue) X-rays (a, c) and backscattered electron images (b, d) of two barred or skeletal olivine chondrules, and a combined X-ray map (e) and NiK$_{\alpha}$ scanning map (f) of a zoned Fe,Ni metal grain with an enclosed cryptocrystalline chondrule (CC) in the CB$_{6}$ chondrite HaH 237. The chondrules, which contain forsteritic olivine (ol), low-calcium pyroxene (px), high-calcium pyroxene (cpx), and mesostasis (mes), lack rims and relict grains and clearly formed in a dust-free environment from total melts. Reproduced by permission of the University of Arizona on behalf of The Meteoritical Society from Krot et al. (2002c).
associated with chondrules. Metal grains have bulk concentrations of 4–15 wt.% Ni, solar Co/Ni ratios and up to 1% chromium and phosphorus (Weisberg et al., 1993). Grains at chondrule cores have higher nickel concentrations than those at the rims (Figure 24c) and all grains are depleted in moderately volatile elements (Connolly et al., 2001). Kong and Palme (1999) noted that Renazzo metal grains are covered with layers of carbon, which appear to have evolved at low temperatures. Two kinds of processes have been invoked to account for the origin and composition of the metal grains: condensation as nebular solids or recondensation during chondrule formation (Grossman and Olsen, 1974; Weisberg et al., 1993; Connolly et al., 2001) and silicate–metal equilibration and reduction during chondrule formation (Scott and Taylor, 1983; Zanda et al., 1994). Given that the silicate portions of type I chondrules in CR2 chondrites have retained a record of condensation processes, it seems likely that the metallic portions have also, and that both kinds of processes were involved in making CR metal.

### 1.07.5.7.2 CH and CB chondrite metallic Fe,Ni

Between 0.01% and 1% of the metal grains in CH chondrites (Meibom et al., 1999, 2000) and all the zoned metal grains in CB$_6$ chondrites (Meibom et al., 2001; Campbell et al., 2001) have radial chemical zoning patterns that are consistent with formation as solid nebular condensates above 1,200 K (Figure 27). Fractional condensation models suggest that grains in QUE 94411 formed under a variety of oxidation conditions with enhanced dust–gas ratios of 10–40 times solar prior to vaporization (Petaev et al., 2001). Kinetic growth models suggest growth timescales of 1–4 days at cooling rates of a few degrees per hour and removal from hot gas before temperatures fell below ~1,200 K (Meibom et al., 2001). The tiny fraction of appropriately zoned grains in CH chondrites might have condensed in convective...
updrafts in the nebula and been transported outward to cooler regions by convection (Meibom et al., 2000). However, the large fraction of zoned grains in CB$_6$ chondrites requires a more efficient transport mechanism such as an X-wind (Meibom et al., 2001; Shu et al., 2001).

CB chondrites also contain relatively homogeneous metal grains with micrometer-sized troilite droplets. Large grains in CB$_6$ chondrites have near-solar Co/Ni ratios and 0.1–1 wt.% Cr and P and were among the first metallic grains to be tagged as nebular condensates (Newsom and Drake, 1979; Weisberg et al., 1990). Moderately volatile siderophile elements gallium, germanium, arsenic, and antimony are depleted by factors of up to $10^3$ from CI levels (Campbell et al., 2002). Condensation models suggest that the precursor gas was enriched in metals by a factor of $10^7$ above solar levels prior to condensation. Hypervelocity impacts between asteroids or disruption of molten planetesimals might provide an appropriate environment for the condensation of CB$_6$ metal as molten sulfur-bearing droplets (Campbell et al., 2002; Rubin et al., 2003; Krot et al., 2005a). However, the presence of CAIs in CB$_6$ chondrites and the intimate mixture of zoned and sulfur-bearing metallic Fe,Ni grains in CB$_6$ chondrites suggest that components from diverse sources were accreted to form the CB chondrites.

1.07.5.7.3 Troilite

Troilite in chondrites may have condensed below $\sim 650 \text{ K}$ by reaction of nebular gas with metallic Fe,Ni, or crystallized from Fe–Ni–S melts in chondrules or during secondary processing in asteroids. Whether any metal grains in chondrites have preserved nebular signatures is questionable as sulfur is readily mobilized during metamorphism and shock (Lauretta et al., 1997). Criteria for identifying nebular sulfide condensates (Lauretta et al., 1998) and igneous sulfides (Rubin et al., 1999; Kong et al., 2000) have been proposed. Rubin et al. (1999) found that 13% of the chondrules in Semarkona (LL3.0) contain metal-troilite nodules with igneous textures inside phenocrysts. They inferred that these chondrules were heated only briefly in the nebula, otherwise sulfur would have been lost. Lauretta et al. (2001) infer that troilite and fayalite rims on metal grains in Bishunpur (LL3.1) formed in a totally different way at $\sim 1,200 \text{ K}$ in a dust-enriched nebula.

1.07.5.8 Matrix Material

Matrix material is best defined as the optically opaque mixture of mineral grains 10 nm to 5 $\mu$m in size that rims chondrules, CAIs, and other components and fills in the interstices between them (Scott et al., 1988). Matrix grains are generally distinguished from fragments of chondrules, CAIs, and other components by their distinctive sizes, shapes, and textures. Minerals found in matrices include silicones, oxides, sulfides, metallic Fe,Ni, and especially in type 2 chondrites, phyllosilicates, and carbonates (Table 5). Matrices are broadly chondritic in composition though richer in FeO than chondrules and have refractory abundances that deviate more from bulk chondrite values (McSween and Richardson, 1977; Brearley, 1996; Bland et al., 2005; Huss et al., 2005). Matrix typically accounts for 5–50 vol.% of the chondrite (Table 1).

In the least altered chondrites, matrix rims, which are also called fine-grained rims, are similar in chemical composition and mineralogy to the interstitial matrix material, though matrix rims may be finer-grained and lack clastic material. Compositions of rims on chondrules and on CAIs appear indistinguishable. Rims are not uniform in width (Figure 28), but rim thickness is correlated with chondrule size within a chondrite group (Metzler et al., 1992; Paque and Cuzzi, 1997). However, matrix rims are absent in the CH, CB, and K chondrite groups. Clearly, matrix rims around chondritic components were acquired after the components formed and before final lithification of these components into a rock. (Note that some rims around altered mineral grains appear to have formed in situ by cementation of interstitial material during aqueous alteration.) Most authors envisage that the chondritic components acquired their rims by accreting dust in the nebula (e.g., Morfill et al., 1998; Liffman and Toscano, 2000; Cuzzi et al., 2001; Cuzzi, 2004), though some argue that rims form in asteroidal regoliths (e.g., Symes et al., 1998; Tomeoka and Tanimura, 2000; Trigo-Rodriguez et al., 2006).

Although chondrules and CAIs may have acquired transient, fluffy rims in the nebula, the identical nature of well-compacted rims on objects that formed at different times and places suggests that rim acquisition and compaction may have been delayed until planetesimal accretion.

Millimeter-to-submillimeter lumps of matrix-rich material are present in many chondrites. Lumps that are mineralogically similar to nearby matrix occurrences are probably pieces of rims or aggregates of interstitial material. However, heavily altered matrix-rich lumps called dark clasts with distinctive mineralogies probably have a different origin (Section 1.07.5.8.10). In CH and CB chondrites, all the matrix material is present as dark
clasts; there are no matrix rims or interstitial material.

According to Anders and Kerridge (1988), “controversy permeates every aspect of the study of matrix material, from definition of matrix to theories of its origin.” Although controversy remains, major progress has been made in identifying matrix components and understanding their origin. Since matrix is commonly richer in volatiles than other components, it is commonly referred to as the “low-temperature component” of chondrites. But this is a misnomer as it is composed of diverse materials that formed under different conditions. Prior to detailed TEM studies and the acquisition of mineralogical and isotopic evidence for aqueous alteration on asteroids, all matrix minerals in carbonaceous chondrites including magnetite, carbonates, and phyllosilicates were thought to have condensed in the solar nebula (see McSween, 1979; see Chapter 1.09). However, matrix minerals in most chondrites are now thought to be a complex mixture of presolar materials and nebular condensates that were mixed with fine chondrule fragments and experienced aqueous alteration and metamorphism (e.g., Scott et al., 1988). However, nebular mechanisms for forming magnetite and phyllosilicates are still being studied (Hong and Fegley, 1998; Ciesla et al., 2003). Matrix investigations are handicapped by the extremely fine-grained nature of the constituents and the difficulty of distinguishing primary and secondary mineralogical features (Brearley, 1996). The fine grain size (commonly as small as 50–100 nm), high porosity, and permeability of matrix ensure that it is more susceptible to alteration by aqueous fluids and metamorphism in asteroids than other chondritic components.

Most of the matrix data that we review are chemical and mineralogical as there is little isotopic information about individual matrix grains. Bulk oxygen-isotopic compositions for matrix samples commonly differ from those of associated chondrules (e.g., Scott et al., 1988), but lack of oxygen-isotope data for samples of key chondrites and specific matrix components severely limits inferences about matrix origins.

### Table 5 Mineralogy of chondrite matrices.

<table>
<thead>
<tr>
<th>Group</th>
<th>Phases</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonaceous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI</td>
<td>Serpentine, saponite, ferrihydrite, magnetite, Ca–Mg carbonate, pyrrhotite</td>
<td>1</td>
</tr>
<tr>
<td>CM</td>
<td>Serpentine, tochilinite, pyrrhotite, amorphous phase, calcite</td>
<td>1</td>
</tr>
<tr>
<td>CR2</td>
<td>Olivine, serpentine, saponite, minor magnetite, Fe,S, pentlandite, pyrrhotite, calcite</td>
<td>2</td>
</tr>
<tr>
<td>CO3.0: ALHA77307</td>
<td>Amorphous silicate, Fo_{90–99}, low-calcium pyroxene, Fe,Ni metal, magnetite, sulfides</td>
<td>3</td>
</tr>
<tr>
<td>CO3.1–3.6</td>
<td>Fayalitic olivine, minor phyllosilicates, and ferric oxide</td>
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</tr>
<tr>
<td>CV3 reduced</td>
<td>Fayalitic olivine, low-calcium pyroxene, low-nickel metal, FeS</td>
<td>5</td>
</tr>
<tr>
<td>CV3 oxidized:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bali-like</td>
<td>Fayalitic olivine, phyllosilicate, fayalite, Ca–Fe pyroxene, pentlandite, magnetite</td>
<td>6</td>
</tr>
<tr>
<td>Allende-like</td>
<td>Fayalitic olivine, Ca–Fe pyroxene, nepheline, pentlandite</td>
<td>7</td>
</tr>
<tr>
<td>Ungrouped C:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acfer 094</td>
<td>Amorphous silicate, forsterite, enstatite, pyrrhotite, ferrihydrite, traces of phyllosilicate</td>
<td>8</td>
</tr>
<tr>
<td>Adelaide</td>
<td>Fayalitic olivine, amorphous silicate, enstatite, pentlandite, and magnetite</td>
<td>9</td>
</tr>
<tr>
<td>Ordinary</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LL3.0: Semarkona</td>
<td>Smectite, fayalitic olivine, forsterite, enstatite, calcite, magnetite</td>
<td>10</td>
</tr>
<tr>
<td>H, L, LL 3.1–3.6</td>
<td>Fayalitic olivine, amorphous material, pyroxene, albite, Fe,Ni metal</td>
<td>11</td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K3: Kakangari</td>
<td>Enstatite, forsterite, albite, ferrihydrite, troilite, Fe,Ni metal</td>
<td>12</td>
</tr>
</tbody>
</table>

References: 1, Zolensky et al. (1993); 2, Endress et al. (1994); 3, Brearley (1993); 4, Brearley and Jones (1998); 5, Lee et al., (1996); 6, Keller et al., (1994); 7, Scott et al. (1988); 8, Greshake (1997); 9, Brearley (1991); 10, Alexander et al. (1989a); 11, Alexander et al. (1989b); 12, Brearley (1989).
Other reviews of chondrite matrices have addressed aqueous alteration in the matrices of carbonaceous chondrites (Buseck and Hua, 1993; see also Chapter 1.09), matrix mineralogies and origins (Scott et al., 1988; Huss et al., 2005), possible relations between matrix and chondrules (Brearley, 1996), the diverse mineralogy of matrices in different chondrite groups (B&J, 1998, pp. 191–244) and relations between matrices of primitive chondrites and cometary silicates (Nuth et al., 2005). Here we focus on geochemical and mineralogical features in type 1–3 chondrites that offer the best insights into the origin of the components of matrix and chondrites and the relationship between matrix and chondrules. Unfortunately, well-characterized matrix material from E3 and R3 chondrites is lacking.

Some important constituents of matrix material are discussed elsewhere: presolar grains (see Chapter 1.02), carbon and organic phases (see Chapter 1.10), and noble gases (see Chapter 1.14). The abundances and nature of these constituents in chondrite matrices provide valuable clues to the thermal and alteration history of specific matrix samples.

1.07.5.8.1 CI1 chondrites

CI1 chondrites contain neither chondrules nor refractory inclusions and have generally been considered as virtually pure matrix material. They are composed almost entirely of phyllosilicates, oxides, sulfides, carbonates, and other minerals (Table 5) that were once widely thought to be nebular condensates but are now known to be products of aqueous alteration (B&J, 1998, p. 192). CI1 chondrites contain 65 wt.% of serpentine–saponite intergrowths, which are too fine-scale for accurate analysis, 10% magnetite, 7% pyrrhotite, 5% poorly crystalline ferrihydrite (5Fe2O3·9H2O), and smaller amounts of pentlandite and other phases (Bland et al., 2002; B&J, 1998, p. 192). Carbonates constitute ~5% of the meteorites; the largest have been dated by 53Mn–53Cr isotope systematics at ~6–20 Ma after CAI formation (Endress et al., 1996).

CI1 chondrites also contain a small fraction of isolated olivine and pyroxene grains up to 400 μm in size with chemical, oxygen-isotopic compositions, and rounded inclusions of metallic Fe,Ni and trapped melt indicating that they were derived from chondrules (Leshin et al., 1997). Brearley and Jones (1998) estimate the abundance of olivine and pyroxene at <1 vol.%, but X-ray diffraction studies by Bland et al. (2002) indicate 7 wt.% olivine. The difference probably reflects a high abundance of olivine crystallites embedded in phyllosilicates (P. A. Bland, private communication). CI1 chondrites also contain rare refractory grains with oxygen-isotopic compositions comparable to those in CAIs (see Scott and Krot, 2001).

Why do the most highly altered chondrites provide the best match with the composition of the solar photosphere? We have yet to answer this question satisfactorily, but many factors are probably responsible. First, chondrules that are deficient in volatiles relative to matrix material were scarce in the CI precursor material. Second, the rocks appear to have been affected by closed-system alteration. The prominent sulfate veins in CI1 chondrites appear to have formed in fractures on Earth (Gounelle and Zolensky, 2001) and not in the parent body, so it is likely that aqueous solutions did not percolate through the rock. Third, CI1 chondrites are unique fine-grained breccias as they are entirely composed of diverse, altered lithic fragments less than a few hundred micrometers in size (Morlok et al., 2002). They appear to be very representative samples of one or more...
asteroids that were thoroughly scrambled. Fourth, they probably formed further from the Sun than other chondrite groups and therefore acquired higher concentrations of carbonaceous, volatile-rich material.

### 1.07.5.8.2 CM2 chondrite matrices

In CM2 chondrites, the interstitial matrix material and the matrix rims around chondrules are very similar mineralogically (Zolensky et al., 1993). Matrices are dominated by phyllosilicates, which are also present in chondrules and CAIs, and formed as a result of aqueous alteration, but the location is controversial (see Chapter 1.09). Phyllosilicates are mostly 10–100 nm in size and are largely serpentine with diverse morphologies, degrees of crystallinity, and compositions (Barber, 1981; Zolensky et al., 1993). Crystals of the Fe$^{3+}$-rich serpentine, clinochlore, reach up to 1–10 μm in size and may be intergrown with tochilinite, (Fe,Mg)(OH)$_2$ (see B&J, 1998, p. 202). Metzler et al. (1992), Bischoff (1998), and Lauretta et al. (2000) argue that alteration occurred mainly in small precursor planetesimals prior to accretion of the CM body. Hanowski and Brearley (2000, 2001) disagree pointing to the occurrence of cross-cutting veins of alteration minerals, loss of calcium from chondrule mesostases and deposition as carbonate in the surrounding matrix, and other features favoring in situ alteration on asteroids.

CM2 matrices also contain small olivine grains down to 0.1 μm in size, which are close to Fo$_{100}$ in composition (Barber, 1981). These forsterites lack defects, are sometimes euhedral, and appear to have formed before the phyllosilicates (Barber, 1981; B&J, 1998, p. 216). Euhedral Fa$_{40-50}$ olivines are also embedded in phyllosilicate (Lauretta et al., 2000). Pyroxenes are rarer and are dominantly magnesium-rich, Fs$_{<2}$ (Brearley, 1995). Some olivines and pyroxenes are especially enriched in manganese (1–2 wt.% MnO) and are comparable in composition to the low iron, high manganese olivines and pyroxenes present in IDPs (Klöck et al., 1989). These were called LIME silicates (low-iron, manganese enriched) by Klöck et al., who argued that they are nebular condensates.

As much as 15% of CM matrices may be amorphous silicate, which is associated with comparable volumes of very poorly crystalline phyllosilicates (Barber, 1981). In ALH81002, 5 vol.% of the matrix rims are composed of amorphous regions a few micrometers across that are rich in silicon, aluminum, magnesium, iron, and presumably oxygen, and contain 5–40 nm grains of iron-rich olivines and metallic Fe,Ni (Lauretta et al., 2000). Chizmadia and Brearley (2003) found more abundant amorphous material in the CM2 chondrite, Y 791198. (Origins of matrix components are reviewed in Section 1.07.5.8.11.)

Rim thickness appears to be correlated with object size (Metzler et al., 1992). However, rims around grains of calcite, tochilinite, and other alteration products may be artifacts of alteration rather than preaccretionary features. Trigo-Rodriguez et al. (2006) infer that the “primary accretionary rocks” of Metzler et al. (1992) did not form in the nebula but rather in asteroidal regoliths. Hua et al. (2002) compared the concentrations of trace and minor elements in matrix rims around different types of chondrules and other objects in two CM chondrites and found no relationship between bulk compositions of rims and enclosed objects. Abundances of moderately volatile elements in CM matrices are depleted relative to CI chondrites, but enriched relative to bulk CM chondrites (Bland et al., 2005; Figure 29).

### 1.07.5.8.3 CR2 chondrite matrices

CR2 chondrite matrices are predominantly composed of olivine with grain sizes of 0.2–0.3 μm accompanied by intergrowths of serpentine and saponite with dimensions of 20–300 nm and minor sulfide and magnetite grains 0.1–25 μm in size (Zolensky et al., 1993; Endress et al., 1994). CR2 chondrites also contain ~3 vol.% of more altered matrix lumps mostly 0.1–1 mm in size, which are similar in bulk composition to the other matrix material (Endress et al., 1994). However, phyllosilicates, magnetite, and chondrule fragments are more abundant in the matrix lumps than in other matrix material, and sulfides are richer in nickel suggesting that the lumps are chondritic clasts that formed in a totally different environment.

### 1.07.5.8.4 CO3 chondrite matrices

The matrix of the type 3.0 CO chondrite, ALHA77307, is very different mineralogically from matrices in CO3.1–3.6 chondrites (Table 5). It is largely composed of amorphous silicate material (Figure 30), which forms discrete regions 1–5 μm in size, and 30–40 vol.% of heterogeneously distributed tiny olivine crystals and crystal aggregates (Brearley, 1993). Matrix rims around chondrules and refractory inclusions are fairly homogeneous (Figure 31), mineralogically and chemically indistinguishable, and nearly isochemical with interstitial material (Brearley et al., 1995; Chizmadia et al., 2005). Rims are slightly lower in manganese and
Chondritic Components

Figure 29  Elemental abundances in matrices of CM, CV, CR, and CO chondrites normalized to bulk CI chondrites using the refractory element Yb; data from Bland et al. (2005); figure from Huss et al. (2005). Matrices, like bulk chondrites, show increasing depletions with increasing elemental volatility. However, matrices are less depleted than bulk chondrites. Siderophile and chalcophile elements in CM, CO, and CV chondrites tend to have higher abundances than adjacent lithophiles, which are marked by gray bands. Reproduced by permission of Astronomical Society of the Pacific from Huss et al. (2005).
calcium than interstitial matrix (Table 6). As in other chondrites, matrix material is broadly chondritic in composition but aluminum, nickel, and potassium are enriched relative to silicon and CI chondrites, and calcium and titanium are depleted. Moderately volatile elements are typically enriched relative to bulk CO chondrite by factors of 2–3 (Figure 31; see also Bland et al., 2005).

The amorphous phase in the ALHA77307 matrix is heterogeneous on the submicrometer scale but homogeneous on a 10 μm scale (Table 6). It is mostly composed of silicon, iron, magnesium, and oxygen with relatively high concentrations of aluminum, nickel, sulfur, and phosphorus. Its Ca/Al ratio is much lower than those in chondrule mesostases, which are closer to chondritic values, precluding an origin from chondrule glass (Brearley, 1993). Brearley’s chemical and textural studies also suggest that the amorphous component was not formed by shock melting of matrix material, as Bunch et al. (1991) proposed for the matrix rims. In some areas, the amorphous phase appears to show incipient formation of phyllosilicates.

Three types of olivine occur in the amorphous phase of ALHA77307 (Brearley, 1993): (1) abundant irregularly shaped and poorly crystalline olivines 0.2–300 nm in size with Fo10–70; (2) well-crystallized, subhedral, larger forsterite crystals 200 nm to 4 μm in size (Fo95–98); and

![Figure 30](image1.png)  
**Figure 30** Transmission electron micrograph of the matrix in ALHA77307 (CO3.0) showing that it is largely composed of amorphous material with embedded crystallites of kamacite (Kam), pyrrhotite (FeS), olivine (OL), and low-calcium pyroxene (Pyx). Matrices of all carbonaceous chondrites probably resembled this matrix material prior to asteroidal alteration and metamorphism. Reproduced by permission of Elsevier from Brearley (1993).

![Figure 31](image2.png)  
**Figure 31** Elemental abundances in matrix material in CO3 chondrites normalized to bulk chondrite: data for rims on chondrules in ALHA77307 (type 3.0) obtained by synchrotron X-ray fluorescence microprobe analysis (Brearley et al., 1995) and for bulk matrix in Ornans (type 3.3) analyzed by instrumental neutron activation (data from Rubin and Wasson, 1988). Chondrule rims in ALHA77307 are uniform in composition but deviate significantly from the bulk chondrite composition. Matrix in Ornans is relatively unfractionated. Reproduced by permission of Elsevier from Brearley et al. (1995).
micrometer-sized, isolated crystals and similar-sized aggregates of 100 nm grains of well-crystallized manganese-rich forsterites, with up to 2 wt.% MnO. Pyroxene, which is not as abundant as olivine, is mostly poor in calcium and iron and also occurs in several varieties. Orthopyroxene forms angular crystals 1–1.5 mm in size and is intergrown with clinopyroxene in aggregates of 0.2–0.3 mm crystals.

High-resolution TEM images of an intergrowth indicate cooling from the protopyroxene stability field above 1,000–5,000 °C (Jones and Brearley, 1988).

Manganese-rich enstatite crystals are ~0.1 μm in size, largely clinoenstatite, indicative of rapid cooling from above 1,000 °C at >1,000 °C h⁻¹ (Jones and Brearley, 1988). Manganese-rich enstatite crystals are ~0.1 μm in size, largely clinoenstatite, indicative of rapid cooling from above 1,000 °C at >1,000 °C h⁻¹, and are associated with manganese-rich olivines in micrometer-sized aggregates.

Some amorphous regions in ALHA77307 contain rounded grains of kamacite with 4–5% Ni and nickel-bearing sulfides, which are both <200 nm in size. Elsewhere, magnetite occurs as crystals as small as 50 nm and aggregates <10 μm in size. The close proximity of magnetite-rich and metal-sulfide-rich regions suggests that they formed separately under very different conditions in the nebula (Brearley, 1993). From a weak correlation between the Mg/(Mg + Fe) ratios of the olivines and the adjacent amorphous material, Brearley (1993) proposed that the olivines had crystallized from the amorphous phase during low-temperature annealing. However, the very different properties of the magneisian and ferroan olivines suggest they formed under different conditions. Presumably, the larger, highly crystalline forsterites crystallized at higher temperatures. Brearley (1993) argued against a condensation origin for the iron-poor, manganese-rich silicates as proposed by Klöck et al. (1989), and suggested that they formed by annealing of amorphous material.

Matrices in the more metamorphosed CO3.1–3.6 chondrites are unlike the ALHA77307 matrix as they are dominated by submicrometer grains of FeO-rich olivine Fo40–60 with minor pyroxene, spinels and metallic Fe,Ni (see B&J, 1998, pp. 217–220). In Lancé and Ornans, the matrix, like the mesostasis in chondrules, also contains minor phyllosilicates and other alteration products. Lancé matrix contains magnesium-rich serpentine and poorly crystalline material between FeO-rich olivines (Keller and Buseck, 1990). Hydrous ferric oxides are also present on grain boundaries in Kainsaz and Warrenton indicating incipient alteration. Matrix olivines in type Z3.4 chondrites have more equilibrated compositions than those in types 3.1–3.3 (B&J, 1998, p. 220). Ornans matrix is close to bulk CO composition (Rubin and Wasson, 1988; Figure 31).

The evidence that CO3 chondrites form a metamorphic sequence (Scott and Jones, 1990; B&J, 1998, p. 38) suggests that they all originally contained matrix material like that in ALHA77307. The amorphous material in ALHA77307, which shows only incipient formation of fayalitic olivine and phyllosilicates, could have been readily replaced by fayalitic olivine by further fluid-assisted metamorphism to produce the type 3.1–3.6 matrices. Additional studies are needed to see if the minor feldspathic

<table>
<thead>
<tr>
<th>Weight%</th>
<th>Interstitial matrix</th>
<th>Matrix rims</th>
<th>Amorphous phase</th>
<th>Amorphous phase</th>
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<tbody>
<tr>
<td></td>
<td>areas ALHA77307</td>
<td>chondrules</td>
<td>ALHA77307</td>
<td>Acfer 094 matrix</td>
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<td></td>
<td></td>
<td>ALHA77307</td>
<td>(CO3.0)</td>
<td>(ungrouped)</td>
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<tr>
<td>No. anal.</td>
<td>36</td>
<td>106</td>
<td>8</td>
<td>6</td>
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<tr>
<td>SiO₂</td>
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<td>33.3 (0.7)</td>
<td>53 (9)</td>
<td>47 (4)</td>
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<tr>
<td>TiO₂</td>
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<td>4.7 (0.3)</td>
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<td>37.3 (2.1)</td>
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<td>MnO</td>
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<td>0.6 (~0.2)</td>
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<td>MgO</td>
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<td>15.8 (0.8)</td>
<td>8.3 (1.7)</td>
<td>10.1 (3)</td>
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<td>CaO</td>
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<td>0.41 (0.38)</td>
<td>1.4 (0.4)</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.32 (0.06)</td>
<td>0.25 (0.06)</td>
<td>NA</td>
<td>~0.7</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.11 (0.02)</td>
<td>0.14 (0.05)</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>NiO</td>
<td>3.4 (0.4)</td>
<td>3.9 (0.7)</td>
<td>4.7 (2.6)</td>
<td>5.2 (2.2)</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.32 (0.09)</td>
<td>0.25 (0.09)</td>
<td>3.6 (2.1)</td>
<td>NA</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.4 (0.8)</td>
<td>3.0 (0.6)</td>
<td>4.5 (2.8)</td>
<td>4.0 (2.0)</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Sources: Brearley (1993) and Greshake (1997).
Note: Matrix analyzed by electron microprobe: amorphous phase by analytical transmission electron microscopy. Totals are normalized to 100%. Figures in parentheses are 1σ of means of analyzed regions for matrix and 1σ of analyses for amorphous phase.
NA, not analyzed.
component between FeO-rich olivines in types 3.1–3.6 (B&J, 1998, p. 217) is related to the amorphous component in ALHA77307.

1.07.5.8.5 CK3 chondrite matrices

Matrices of CK4–6 chondrites are composed largely of olivine, low-calcium pyroxene and plagioclase grains that are mostly 20–100 μm in size with minor magnetite and sulfide (B&J, 1998, p. 239). CK3 chondrite matrices appear to resemble those in CV3 chondrites, which are discussed below. Matrix textures in the Kobe CK4 chondrite were interpreted by Tomeoka et al. (2001) to result from partial melting during shock metamorphism, although Kobe itself is only classified as a shock stage S2.

1.07.5.8.6 CV3 chondrite matrices

Matrix material in CV3 chondrites occurs as rims on chondrules and other components, as well as interstitial material, which is coarser grained. The volume of a matrix rim is approximately equal to the volume of the enclosed chondrule (Paque and Cuzzi, 1997). Matrices are mineralogically diverse but are dominated by iron-rich olivine, Fa30–60, which is coarser than in other chondrite groups. It forms elongate grains up to 20 μm in length and subhedral finer grains <100 nm to 3 μm in the interstices (B&J, 1998, p. 220; Watt et al., 2006). Olivines contain planar defects and small inclusions of sulfide, metal or magnetite, and poorly graphitized carbon (Tomeoka and Buseck, 1990; Keller et al., 1994; Brearley, 1999). Reduced CV3 chondrites appear to be the least altered as they have abundant metallic Fe,Ni rather than magnetite: minor matrix minerals include low-calcium pyroxene, metallic, Fe,Ni, and FeS. In the Bali-like oxidized CV3 chondrites, matrices lack metal and contain abundant phyllosilicates, fayalite (Fa>95), calcium-rich pyroxene, pentlandite, and magnetite in addition to iron-rich olivine (Figure 32a). In the Allende-like oxidized CV3s, hydrated silicates and fayalite are rare or absent, but Ca–Fe-rich pyroxene, nepheline, and pentlandite are abundant, and magnetite is present (Krot et al., 1995, 1998a, b, c, 2001f; Brearley, 1999; B&J, 1998, pp. 220–225) (Figure 32b).

Proponents of a nebular origin for the secondary minerals in oxidized CV3 chondrites argue that fayalitic olivine condensed in the solar nebula at high fO2, following evaporation of chondritic dust, and coated preexisting chondrules (Nagahara et al., 1988; Palme and Fegley, 1990; Weinbruch et al., 1990). Kimura and Ikeda (1998) infer that anhydrous alteration minerals like nepheline in Allende formed at ~600–800 °C whereas estimates from zoning in olivine point to maximum temperatures of ~400–550 °C. They, therefore, conclude that the anhydrous alteration occurred prior to accretion of the chondritic components. Brenker et al. (2000) who studied aggregates of andradite and hedenbergite 20–50 μm in size in the Allende matrix, infer that the Ca–Fe-rich pyroxene cooled rapidly from >1,050 °C at >10 °C h⁻¹. They argue that a localized nebular environment is more compatible with this thermal history than an asteroidal environment.

Evidence favoring progressive alteration in asteroids includes fayalite veins that cross-cut chondrules and matrices, replacement of chondrules by fayalite-rich matrix material in
dark inclusions, and comparable alteration minerals in chondrules and matrices (Krot et al., 1995, 1998a, b, c, 2001f; Kimura and Ikeda, 1998). In Bali-like CV3s, saponite replaces calcium-rich minerals in chondrules and CAIs; magnetite is replaced by fayalite and calcium-rich pyroxene. In Allende-like CV3s, fayalitic olivine replaces low-calcium pyroxene; magnetite–sulfide grains in matrices and chondrules are replaced by fayalitic olivine and calcium-rich pyroxenes; nepheline and calcium-rich pyroxene form veins in and around CAIs and dark inclusions. Isotopic data also favor asteroidal sites for alteration. Coexisting magnetite and fayalite in Mokoia show large mass fractionation in oxygen isotopes, consistent with aqueous alteration (Choi et al., 2000). Nepheline lacks evidence for $^{28}$Mg excesses indicating formation $>3–5$ Myr after CAI formation (MacPherson et al., 1995). $^{53}$Mn–$^{53}$Cr isotope systematics suggest that fayalite formed $7–16$ Myr after CAIs (Hutcheon et al., 1998).

The mineralogy of CV3 chondrite matrices prior to alteration is not clear. The two reduced CV3 chondrites that have been studied are TEM are not ideal samples. In Leoville, which is moderately shocked, Nakamura et al. (1992) found aggregates of rounded, 10–100 nm olivine grains with interstitial amorphous material, but attributed this to shock. In Vigarano, which is a breccia of altered and unaltered material (Lee et al., 1996), oxygen-isotopic mapping of the matrix revealed $^{16}$O-rich forsterite grains 2 μm in size that may be fragments of AOA or related objects, as well as similar-sized $^{18}$O-poor fayalite and enstatite grains (Kunihoro et al., 2005b). Clearly this technique is essential for unraveling the origins of matrix components.

1.07.5.8.7 Matrix of ungrouped C chondrites, Acfer 094, and Adelaide

These two chondrites are among the least altered and metamorphosed chondrites and like ALHA77307, their matrices contain presolar silicates (Nagashima et al., 2004; Kobayashi et al., 2005). Acfer 094, which is closely linked to the CO and CM groups, has abundant matrix material and higher concentrations of presolar SiC than any other chondrite (Newton et al., 1995). Its matrix is composed of 30 vol.% forsterites 10–300 nm in size and Fa$_{0-2}$ in composition, 40% amorphous material, and 20% enstatite with Fs$_{0-3}$ and grain sizes of 200–300 nm (Greshake, 1997). The enstatites show intergrowths of ortho- and clinoenstatite indicating rapid cooling at $\sim 1,000 \text{ C}^{-1}$. Minor components included 5% sulfides, <1% phyllosilicates, and <2% ferrihydrite.

The highly unusual combination of amorphous material and forsterite in Acfer 094 matches that in the CO3.0 chondrite, ALH77307. The amorphous phases in the two chondrites are compositionally similar (Table 6) and both contain submicrometer enstatites and forsterites with high concentrations of MnO (0.6–2 wt.%; Greshake, 1997). These concentrations are higher than in chondrules and comparable to those in high-manganese, low-iron silicates reported in IDPs by Klöck et al. (1989). Acfer 094, like ALH77307, contains <1% phyllosilicate in the amorphous material and 100–300 nm sulfide grains (pyrrhotite and minor pentlandite) as in ALHA77307, but it lacks matrix metal grains. Since ferrihydrite is present in the amorphous material in Acfer 094, metal may once have been present. Greshake (1997) proposed that the amorphous material was a presolar or solar condensate and that the FeO-poor silicates formed in the solar nebula by condensation or annealing of amorphous material.

Adelaide, which also has links to CO and CM groups, has a matrix that lacks phyllosilicates and is dominated by fayalitic olivine Fa$_{31-84}$ occurring as aggregates of 100–200 nm crystals and platy and corroded single crystals (Brearley, 1991). Amorphous material, which is rich in iron and sulfur, is present but is less abundant than in ALHA77307. High-manganese enstatite forms 1–1.5 μm clusters of 100–500 nm crystals but forsterites are absent. Pentlandite forms aggregates of 10–30 nm crystals and magnetite occurs as 400–6,500 nm clusters of 100 nm grains.

1.07.5.8.8 H–L–LL3 chondrite matrices

Matrix material in type 3 ordinary chondrites forms rims on chondrules, metal grains, and other components and occurs as lumps (B&J, 1998, pp. 231–237). In the LL3.0 chondrite, Semarkona, matrix consists largely of phyllosilicates formed by aqueous alteration with fine-grained olivine Fa$_{3-38}$ and low-calcium pyroxene, calcite, and magnetite (Alexander et al., 1989a). Magnetite grains show large mass fractionation of oxygen isotopes suggesting that a limited supply of aqueous fluid was largely consumed during asteroidal alteration (Choi et al., 1998). Klöck et al. (1989) identified an additional population of forsterites Fa$_{<1}$ and enstatites Fs$_{<2}$ having MnO concentrations of 0–1.4 wt.% that are correlated with FeO. The high-manganese silicates are comparable in composition to the iron-poor, manganese-rich silicates identified in IDPs (Klöck et al., 1989).
Matrices in type 3.1–3.6 chondrites are largely composed of FeO-rich olivines, which may have skeletal or elongate morphologies, and an amorphous feldspathic phase (Nagahara, 1984; B&J, 1998, pp. 231–237). The origins of these phases are uncertain. Alexander et al. (1989b) argued that interchondrule matrix and matrix rims in ordinary chondrites were derived from broken chondrules, contrary to Brearley et al. (1989), who suggested an origin by annealing of amorphous material. Ikeda et al. (1981) identified two types of matrix in ordinary chondrites with abundant amorphous material, one containing Fe,Ni droplets 10–100 nm in size. They speculated that the amorphous material formed by shock. Fayalitic olivine (Fa54–94) occurs in the matrices of Krymka (LL3.1) and Bishunpur where it rims metal grains (Weisberg et al., 1997; Lauretta et al., 2001). These authors argued that it formed in the solar nebula, not during aqueous or hydrothermal alteration. Strong evidence for asteroidal alteration is present in Tieschitz (H3.6), which contains nepheline and albite in veins between chondrules and in chondrule mesostases (Hutchison et al., 1998). This so-called white matrix formed when aqueous fluids attacked chondrule mesostases forming voids.

1.07.5.8.9 K3 chondrite matrix (Kakangari)

Kakangari has many unusual properties as chondrules and matrix both contain enstatite and forsterite, and matrix silicates are more magnesian than those in chondrules (Weisberg et al., 1996; B&J, 1998, p. 82). Matrix and chondrules have similar bulk chemical compositions though matrix is richer in $^{16}$O (Weisberg et al., 1996).

Kakangari matrix contains mostly euhedral to subhedral crystals with grain sizes of 200 nm to 1.5 µm, which occur as individual crystals and polycrystalline units or clusters 2–8 µm in size, some of which have well-annealed textures. It is composed of 50 vol.% enstatite, Fs2–5, ~20 vol.% forsterite, Fa0–3, 10 vol.% albite crystals 250–1,000 nm in size, Or21–30, and <1 vol.% anorthite up to 500 nm in size. Minor phases include chromium-spinel, troilite grains 1–5 µm in size and ~10 vol.% ferrhydrite, which forms acicular aggregates up to 2 µm in length in pores. The lower FeO concentrations in olivine relative to coexisting pyroxene in matrix and chondrules as in EH3 chondrites, suggest that reduction occurred during cooling as olivine diffusion rates are faster than those in pyroxene (Scott and Taylor, 1983; B&J, 1998, pp. 72–74).

Olivine occurs mainly as inclusions in enstatite and is also found in albite, spinel, and troilitie (Brearley, 1989). At least three kinds of polycrystalline clusters appear to have formed separately: (1) enstatite-rich units with forsterite inclusions, (2) coarser versions with albite and olivine inclusions, and (3) forsterite–anorthite units with no enstatite. Enstatite crystals are intergrowths of ortho- and clinopyroxene and their microstructures indicate cooling from >1,000 °C at ~1,000 °C h$^{-1}$. Brearley (1989) suggests that the Kakangari matrix formed from amorphous or partly crystalline particles <10 µm in size that were annealed at 1,100–1,200 °C or possibly higher, and then rapidly cooled in an hour. The chondrules in Kakangari could have formed from similar material that was heated to higher temperatures, partly melted, and quenched at comparable rates, provided that the chondrules acquired lower $^{16}$O concentrations when molten.

The bulk composition of Kakangari suggests that the hypothesized precursor material for the chondrules and matrix had near-CI levels of moderately volatile elements that were not lost during high-temperature processing. Reduction probably occurred during this processing.

1.07.5.8.10 Heavily altered, matrix-rich lithic clasts

Heavily altered, matrix-rich chondritic clasts are very different from the most common lithic clasts in chondrites, which are fragments of chondrules and CAIs or lithic fragments resembling the host rock. They are also unlike rare foreign chondritic clasts that are shocked and appear to have impacted the parent body at high speed after accretion, e.g., an LL chondrite clast in an H chondrite (Lipschutz et al., 1989).

Altered, matrix-rich chondritic clasts are similar in size to chondrules and CAIs in the host chondrite, unshocked, and appear to have been gently incorporated into the host material at an early stage. Prior to incorporation, they were aqueously altered in a different location. They occupy a few volume% of CR2 (see Section 1.07.5.7.3). CV3, CO3, CH, and CB chondrites. In CV3s they tend to have fewer and smaller chondrules than the host chondrites and some are rimmed by matrix material (Kracher et al., 1985; Johnson et al., 1990). Although Palme et al. (1989) and Weisberg and Prinz (1998) argued that some are unaltered aggregates of nebular condensates, there is now abundant evidence favoring formation by asteroidal alteration (Kojima et al., 1993; Kojima and Tomeoka, 1996; Krot et al., 1997, 1998a, b, c, 2001e). I–Xe ages of some CV3 clasts confirm that they were altered.
1.07.5.8.11 Origins of matrix phases

Unaltered carbonaceous chondrite matrices are composed largely of amorphous silicate and submicrometer forsterites and enstatites and micrometer-sized aggregates of such crystals (Scott and Krot, 2005a; Nuth et al., 2005). In addition, they contain up to a few volume percent of carbonaceous material, sulfides, parts per million levels of presolar silicate and oxide grains (see Chapter 1.02), and solar refractory grains. Micrometer-sized corundum, spinel, and hibonite grains of solar-system origin are much more common than presolar grains (e.g., Virag et al., 1991; Strebel et al., 2000; Nittler et al., 1994) and probably formed as dust in the CAI-forming region (Scott and Krot, 2005a), or elsewhere when CAIs were forming.

Not enough is known about unaltered matrices in ordinary and enstatite chondrites to infer their detailed mineralogy. However, enstatite chondrite matrices probably resemble the matrix of Kakangari in having enstatite, metallic Fe,Ni, and sulfide as important constituents in addition to parts per million levels of presolar grains (Ebata et al., 2006).

Amorphous ferromagnesian silicate is best preserved in the matrices of ALHA77307, Acfer 094, and Adelaide, though it is absent in Kakangari. It is more fractionated than bulk matrix with higher Al/Ca, Ni/Si, and P/Si than CI chondrites. Metallic Fe,Ni is abundant only in the ALHA77307 matrix but it may have been altered in the other chondrites. Related amorphous material may be present in CM, CO, and ordinary chondrites. The aluminum-rich nature of amorphous material may account for the high Al/Ca ratio of some matrix materials (Figure 27), the depletion of refractory elements with respect to aluminum in matrix materials in ordinary chondrites (Alexander, 1995), and the low Ca/Al ratio of certain chondrites like Adelaide and Kakangari (Brearly, 1991). The cause of the enrichment of aluminum, nickel, and phosphorus in amorphous matrix is uncertain as these elements have different geochemical properties. This amorphous material did not form from quenched melt from chondrule mesostases, by impact in situ or elsewhere, or by dehydration of phyllosilicates. It appears to have accreted into chondrule rims as small particles (1–5 μm in size in ALHA77307).

Forsterites Fa<5 and enstatites Fa<5, which are 10–300 nm in size, are found in the matrices of CM chondrites, ALHA77307, Acfer 094, and probably also in Semarkona, for which grain sizes were not reported. Enstatites and forsterite grains with higher FeO concentrations tend to be MnO-rich (0.6–2 wt.%). Intergrowths of ortho- and clinoenstatite and forsterite-enstatite associations indicate that all magnesium silicates cooled from >1,300 K at ~10^3 to 10^4 °C·s^-1 as micrometer- and submicrometer-sized grains prior to accretion. Oxygen-isotopic mapping of micrometer-sized grains shows that primitive matrices contain ~10–100 ppm of presolar silicates (Nagashima et al., 2004). Therefore, the vast majority of iron-poor matrix silicates must have formed in the solar nebula.
Primitive chondrite matrices are surprisingly similar to porous chondritic aggregate IDPs in that both contain amorphous material, FeO-poor olivines, and pyroxenes, some of which are MnO-rich (Klöck et al., 1989), refractory oxides, and presolar silicate and oxide grains (Scott and Krot, 2005a; Nuth et al., 2005). Oort cloud and Jupiter-family comets also contain amorphous and crystalline FeO-poor olivines and pyroxenes (Hanner, 1999; Wooden et al., 2005; Harker et al., 2005), and the same minerals are observed in disks around protostars (see Nuth et al., 2005). 16O-rich refractory micrograins are present in micrometeorites and chondritic aggregate IDPs suggesting additional links between chondrite matrices and particles from the outer solar system (Greshake et al., 1996; Engrand and Maurette, 1998; Engrand et al., 1999). The amorphous aggregates in ALHA77307 that are rich in metal and sulfide may be related to the glass with embedded metal and sulfide (GEMS) grains that are a major constituent of porous chondritic IDPs and resemble amorphous interstellar grains (Bradley et al., 1999; Rietmeijer, 1998, 2002). However GEMS are richer in SiO2 and much smaller: 100–500 nm in size with kamacite and sulfide grains that are <5 nm in size, cf. <200 nm in ALH77307. GEMS may have formed by amorphization of interstellar grains by cosmic-ray irradiation (like amorphous rims on some lunar grains) or by shocks (Bradley, 1994; Bradley et al., 1999; Chapter 1.26). However, nearly all GEMS have solar-like oxygen-isotopic compositions and are more likely to be solar-system products (Messenger et al., 2003). Amorphous silicate material is known to condense around evolved stars (Hill et al., 2001), and the amorphous matrix material may be a solar-system analog.

Two high-temperature processes have been proposed for magnesian silicates in matrices: disequilibrium condensation (Klöck et al., 1989; Nagahara et al., 1988; Greshake, 1997) and annealing of amorphous condensate particles (Brearley, 1993; Greshake, 1997). Annealing experiments suggest that magnesium-rich silicates can crystallize from amorphous condensates in a few hours at 1,050 K, or a year or more below 1,000 K (Hallenbeck et al., 2000; Rietmeijer et al., 2002). If the magnesian silicates formed close to the protosun by annealing or condensation, they could have been lofted across the disk by outflows powered by reconnecting magnetic field lines, turbulence, or radiation pressure (Liffman and Brown, 1996b; Shu et al., 1996, 2001; Nuth et al., 2002). Alternatively, Harker and Desch (2002) suggest that magnesian silicates in comets formed at 5–10 AU by annealing caused by nebular shocks. We infer that magnesian silicates were ubiquitous in the solar nebula at 2–10 AU as a result of high-temperature processing and quenching in hours or days (Scott and Krot, 2005a). The similarity of the cooling rates inferred for the magnesian silicates in the matrix and for chondrules suggests that matrix silicates and chondrules may have been formed in related events.

Submicrometer fayalitic olivines are heterogeneously distributed in the matrices of primitive chondrites. In Acfer 094 they are absent but the ALHA77307 matrix contains 30–40 vol.%, which probably formed in situ by low-temperature annealing of amorphous material (Brearley, 1993). Submicrometer-sized fayalitic olivines are also present in matrices of CO3.1–3.6, type 3 ordinary chondrites and the interstices of larger olivines in CV3 chondrites. An origin for these olivines by annealing of amorphous material also appears plausible but the evidence is weak. In some instances (e.g., in ALH77307) annealing and crystallization of olivines may have started prior to accretion, as Kakangari matrix grains were extensively annealed before chondrules and matrix accreted. However, for the coarse, abundant fayalitic grains and pure fayalite in CV3 chondrites, an asteroidal origin is indicated as their formation required an aqueous fluid (Krot et al., 2004f). Although fayalitic olivine has been inferred to have been a major constituent of the solar nebula (e.g., Nagahara et al., 1994; Ozawa and Nagahara, 2001), we find no firm evidence from chondrite matrices that any “crystalline,” FeO-rich silicate formed in the solar nebula.

Chemical differences between matrix and chondrules suggest that nearly all chondrules could not have formed from matrix material. For example, matrix material is typically richer in FeO than chondrules, and mean refractory elemental abundances deviate further from CI levels than for chondrules. Some authors argue from chemical differences that chondrules and matrices are chemically complementary and therefore formed in the same location. For example, Fe/Si ratios in chondrules and matrix are lower and higher, respectively, than CI ratios whereas the bulk compositions of CM, CO, CV, and other chondrites are close to solar implying that chondrules and matrix were chemically fractionated from one another (Wood, 1996a). The case for Fe/Si is not very convincing, however, as there is a wide range of CI-normalized Fe/Si ratios from 0.4 in LL chondrites to ≥2 in CH and CB chondrites. However, for other elements, a stronger case can be made. CI-normalized, mean Ti/Al ratios for matrix and chondrules in the Renazzo CR2 chondrite are 0.5 and 1.5, respectively, whereas
bulk Ti/Al ratios for CR and other chondrites are within 10% of CI levels (Klerner and Palme, 2000). Palme and Klerner (2000) infer that chondrules and matrix formed from a single reservoir that behaved as a closed system during condensation and processing of refractory elements. Bland et al. (2005) infer that matrices and chondrules have complementary enrichments and depletions of volatile siderophile and chalcophile elements due to exchange in the nebular region where chondrules formed.

1.07.6 FORMATION AND ACCRETION OF CHONDRITIC COMPONENTS

Several common themes have emerged from this review of chondritic components. Type 3 chondrites, for example, are more affected by alteration than generally realized. Only a handful of chondrites meet the minimal requirements for pristine chondrites, and none of these escaped the imprint of asteroidal modification. Whether this alteration occurred in parent bodies, as we infer, or in the nebula, the alteration environment was quite different from that at the location where each component formed.

Mean sizes of chondrules, CAIs, amoeboid olivine inclusions, dark clasts, and possibly metallic Fe,Ni grains tend to be correlated among the chondrite groups. Thus, in groups with relatively small chondrules, all components tend to be relatively small. This sorting process occurred after all components formed, possibly during turbulent accretion triggered by chondrule formation (Cuzzi et al., 2001). Aerodynamic sorting should cause metal particles to accrete with larger chondrules, as particles are sorted according to the product of their radius and density (Kuebler et al., 1999). However, Akridge and Sears (1999) have also argued for aerodynamic sorting but they proposed that components were sorted in an asteroidal regolith during degassing.

Many different processes were involved in making each chondritic component. Unaltered chondrite matrices may contain at least five different types of micrometer-to-nanometer-sized components, which formed in diverse environments: amorphous FeO-rich silicate, forsterite and enstatite crystals, refractory grains, presolar grains, and carbonaceous material. Chondrules formed by several nebular processes (closed-system melting, condensation, and possibly evaporation) and at least one asteroidal process (impact melting in regoliths). CAIs are largely fine-grained condensates or coarse-grained igneous objects that probably formed from fine-grained precursors. An exception to this preference for complexity is provided by the amoeboid olivine inclusions: all AOAs could have formed by the same basic process: nebular condensation with only minor subsequent thermal processing. Aluminum-rich chondrules may provide a second exception, at least within carbonaceous chondrites.

Each chondrite component appears to have been manufactured predominantly by brief high-temperature processes. Chondrules and igneous CAIs have textures indicating cooling in minutes or hours. Many enstatite grains in matrices contain ortho–clino intergrowths like those in chondrules, and cooled in less than a few hours. Metal grains in CH chondrites cooled from high temperatures in days, at most. However, the generation of group II REE pattern characteristic of many fine-grained CAIs is one process that required longer timescales of many years (Palme and Boynton, 1993).

The high-temperature processes that formed chondritic components typically involved gas–solid or gas–liquid exchange over part of the temperature range 1,200–2,000 K. Rapid cooling in the formation environment or removal to cooler localities ensured an extraordinary diversity of mineralogical and chemical compositions among chondritic components. Chemical fractionations during brief high-temperature processing were so ubiquitous and extensive that they may be largely responsible for at least four of the major chemical variations shown by chondrites: variations in refractory and moderately volatile elements, metal–silicate ratios, and forsterite–enstatite variations.

The search for nebular condensates among chondrites has generated several interesting but seemingly false leads including wollastonite needles (e.g., Kerridge, 1993) and blue-luminescing enstatite rims (Weisberg et al., 1994; Hsu and Crozaz, 1998). FeO-rich matrix silicates are also unlikely to be nebular condensates. They appear to have formed predominantly by asteroidal processes, though some may have formed by nebular annealing of FeO-rich amorphous material.

In the final section, we review the heat sources that may have operated in the early solar system to produce such diverse chondritic components.

1.07.7 HEATING MECHANISMS IN THE EARLY SOLAR SYSTEM

A wide variety of components in chondrites and chondritic IDPs were processed at high temperatures in the solar nebula over a period of several million years, and several heating mechanisms were probably involved. Possible
heating mechanisms for making chondrules have been reviewed by Cassen (1996), Boss (1996), Rubin (2000), and Ciesla (2005), and for CAIs and chondrules by Jones et al. (2000a). Most heating models have focused on chondrule origins, but Shu et al. (1996, 2001) address both CAI and chondrule formation close to the protosun; Hood (1998) and Desch and Connolly (2002) consider mechanisms for separately melting ferromagnesian and refractory aggregates to make chondrules and igneous CAIs. Richter et al. (2006) infer that igneous CAIs may have experienced nebula conditions like those calculated for chondrule-forming shocks. Russell et al. (2005) conclude that refractory inclusions formed at the inner edge of the accretion disk whereas chondrules formed close to the site where chondrules accreted.

Three kinds of processes have been invoked for forming chondrules: melting of dust aggregates (generally considered to be the standard model), condensation of melts, or melts and crystals (Ebel and Grossman, 2000; Krot et al., 2001d; Varela et al., 2005), and impacts into solid or partly molten bodies (e.g., Symes et al., 1998; Sanders, 1996). As discussed above, we believe that all three processes formed chondrules, and that the standard model cannot account for olivine- and pyroxene-rich chondrules.

Rubin (2000) has reviewed models for forming chondrules and their consistency with various petrologic constraints (Table 7): condensation, exothermic chemical reactions, jetting during nebular collisions between particles, ablation in protoplanetary atmospheres, nebular lightning (Desch and Cuzzi, 2000), supernova shock waves, aerodynamic drag heating at the accretion edge of the disk, magnetic reconnection flares, gas dynamic shock waves (Section 1.07.7.1), bow shocks from early formed planetesimals (Hood, 1998; Weidenschilling et al., 1998; Ciesla et al., 2004a), FU Orionis outbursts, bipolar outflows (Section 1.07.7.2), gamma-ray bursts (Duggan et al., 2003), radiative heating (Eisenhour and Buseck, 1995), and impacts into asteroidal regoliths and molten planetesimals (Section 1.07.7.3). Additional mechanisms include shocks in the envelopes of giant protoplanets (Nelson and Ruffert, 2005), current sheets in magnetically active nebula regions (Joung et al., 2004), and ablation of 1–500 m-sized planetesimals by shock (Genge, 2000). Note that the constraints listed in Table 7 apply to what we have called, “archetypal chondrules,” which are most closely represented by type II chondrules. Chronological and magnetic constraints are not included in Table 7.

Below we review three models that are currently popular: nebular shocks, jets and outflows near the protosun, and impacts on planetesimals.

1.07.7.1 Nebular Shocks

Nebular shock waves are discontinuities between hot compressed gas moving faster than the local sound speed \( \sqrt{300/T} \, \text{cm s}^{-1} \) and cooler, less dense, slowly moving gas (Cassen, 1996). Particles overtaken by shocks are suddenly enveloped in a blast of wind moving at several kilometers per second, which subjects the particles to frictional heating. Particles are also heated by radiation from the shock front before they are overtaken and by conduction from hot gas. Desch and Connolly (2002) find that cooling rates in the range 10–1,000 °C Ch\(^{-1}\) can be produced without invoking shocks of unreasonable speeds. They studied a range of shock speeds (5–10 km s\(^{-1}\)) and gas densities and found conditions under which chondrules would partially melt, conditions that would cause dust to evaporate, and at the higher shock speeds, conditions that would evaporate chondrules. The shock model appears to be capable of forming droplets of the correct size (Connolly and Love, 1998; Susa and Nakamoto, 2002; Miura and Nakamoto, 2005), it seems consistent with many petrologic constraints from archetypal chondrules (Table 7), and predicts a correlation between cooling rate and the concentration of chondrules, which appears consistent with compound chondrule statistics (Desch and Connolly, 2002). Shock heating models have also been investigated by Iida et al. (2001) and Ciesla and Hood (2002) and are reviewed by Desch et al. (2005). Constraints on shock models from the presence of iron–sulfide inclusions in chondrules are discussed by Uesugi et al. (2005).

A major problem for the shock model has been to find a source of powerful, pervasive, and repeatable shocks. Several have been proposed: clumpy material falling into the nebula (Tanaka et al., 1998), bow shocks from planetesimals scattered by Jupiter (Hood, 1998; Weidenschilling et al., 1998), spiral-arm instabilities in the solar nebula (Wood, 1996b), X-ray flares (Nakamoto et al., 2005), and close encounters with sibling protostars (Bally et al., 2005). Boss and Durisen (2005) infer that clumps and spiral arms could generate ~10 km s\(^{-1}\) shocks in the asteroid belt (Chapter 1.04).

1.07.7.2 Jets and Outflows

Two types of jet or outflow models have been proposed. Liffman and Brown (1996a, b)
Table 7  Review by Rubin (2000) of chondrule-formation models and their consistency with petrologic and geochemical constraints.

<table>
<thead>
<tr>
<th></th>
<th>Oxygen isotopes</th>
<th>Incomplete melting</th>
<th>Evaporation during long-term heating</th>
<th>Relict grains and moderate volatiles</th>
<th>Rapid cooling</th>
<th>Chondrule abundance</th>
<th>Chondrule size$^a$</th>
<th>Multiple heating</th>
<th>Microchondrules in rims</th>
<th>Primary troilite</th>
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<tr>
<td>Condensation</td>
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<tr>
<td>Exothermic chemical reactions</td>
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<td>+</td>
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<td>−</td>
<td>−</td>
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<tr>
<td>Jetting</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
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<tr>
<td>Meteor ablation</td>
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<td>+</td>
<td>+</td>
<td>−</td>
<td>−</td>
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<tr>
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<tr>
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<td>?</td>
<td>−</td>
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<tr>
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<td>FU Orionis outbursts</td>
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<td>−</td>
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<tr>
<td>Bipolar outflows</td>
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<td>+</td>
<td>?</td>
<td>−</td>
<td>+</td>
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<tr>
<td>Radiative heating</td>
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<td>+</td>
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<tr>
<td>Planetesimal collision</td>
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<td>−</td>
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<td>−</td>
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<tr>
<td>Impact-melting in parent-body regolith</td>
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<td>+</td>
<td>+</td>
<td>−</td>
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<td>−</td>
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<td>−</td>
<td>−</td>
<td>+</td>
</tr>
</tbody>
</table>

$^a$Chondrule size distribution within a group is much narrower than the total variation shown by all chondrites.

Note: +, consistent; −, inconsistent; ?, possibly consistent after ad hoc modifications; /, not applicable.
suggested that chondrules formed in a bipolar outflow by ablation of planetesimals and were then injected into the asteroid belt. Size sorting of metal grains and chondrules can occur in jet-flow models (Liffman, 2005), and the observed correlation between rim thickness and chondrule size may have arisen when chondrules reentered the dusty nebula at hypersonic speeds (Liffman and Toscano, 2000).

Shu et al. (1996, 2001) proposed that chondrules and CAIs formed at the inner edge of the protostellar disk (see Chapter 1.04). About 0.05 AU from the protosun, the rotation rate of the disk matches that of the protostar and the disk is terminated. Inflowing gas is ionized and either whipped into the protostar by the star’s magnetic field, or ejected in the bipolar outflows, while rocks spiral inward until they evaporate or are launched by the winds. CAIs are thought to form during quiescent conditions, whereas chondrules form when the position of the inner edge of the disk fluctuates due to intense flares from the protosun. Shu and colleagues suggest that CAIs and chondrules are hurled outward by the so-called X-wind, which they infer powers the bipolar outflows. CAIs and chondrules fall back onto the disk at several astronomical units or beyond and are available for accretion into asteroids and planets or recycling back to the inner edge of the disk. Smaller particles fall back at greater distances from the protosun. Detailed thermal histories for chondrules and CAIs have not been calculated for this model.

1.07.7.3 Impacts on Planetesimals

Four kinds of impacts have been proposed to form chondrules: hypervelocity impacts between solid bodies that melt regolith material (e.g., Symes et al., 1998; Sears, 2005; Bridges et al., 1998), hypervelocity impacts on Vesta-sized and larger, partly molten bodies (Hutchison et al., 2005), impacts onto already molten planetesimals at lower speeds that puncture the planet spewing forth molten drops of silicate and metal (Sanders, 1996; Sanders and Taylor, 2005), and specifically for CB chondrites, an impact between undifferentiated Moon-to-Mars-sized bodies that generated a plume of melt and vapor (Rubin et al., 2003; Krot et al., 2005a).

Many factors suggest that the vast majority of chondrules could not form by impact in regoliths (Taylor et al., 1983). Molten droplets are rare on the regolith of Vesta, the presumed parent of the eucrites, and meteorite evidence suggests that chondrule-free asteroids did not form in the inner part of the asteroid belt (Scott, 2002). (See Sears, 1998 for a contrary view.) However, the chromite-rich chondrules present in brecciated type 4–6 ordinary chondrites (Krot and Rubin, 1993) and perhaps a few percent of other chondrules in H, L, and LL chondrites probably did form this way after the chondritic bodies had accreted. Since impact melt will be ejected at speeds of several kilometers per second, much faster than the escape velocity of the asteroid (less than a few hundred meters per second), most impact melt will not re-accrete to the target asteroid. Impact melt should be rarer on the surface of asteroids than on the Moon (Taylor et al., 1983).

Any asteroid more than ~15 km in radius that accreted <1–1.5 Myr after CAIs formed would have melted <3 Myr later, given the evidence that $^{26}$Al was relatively homogeneously distributed with an $^{26}$Al/$^{27}$Al ratio of ~$5 \times 10^{-5}$ when CAIs formed (e.g., Yoshino et al., 2003; Hevey and Sanders, 2006). The parent asteroids of differentiated asteroids appear to have formed at this stage before the chondrite parent bodies, and several suffered catastrophic impacts during or soon after igneous differentiation (Keil et al., 1994). Sanders (1996) argues that chondrules formed in major impacts on molten planetesimals with thin crusts, and that convection was vigorous enough to prevent gravitational segregation of melted Fe,Ni droplets to the core (see also Yoshino et al., 2003; Sanders and Taylor, 2005). This model envisages that molten metal–silicate droplets were dispersed into the solar nebula and that they accreted long after they had cooled and mixed with impact droplets from other asteroidal impacts, nebula dust, CAIs, and material from the cool unmelted crust of the target asteroids. The advantages of this model are that abundant chondrules are generated, the model readily accommodates the several Ma interval between CAI and chondrule formation, and, provided gas loss occurred, it could explain why many chondrules lost volatiles (Lugmair and Shukolyukov, 2001). Issues that require further study are discussed by Sanders and Taylor (2005).

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