Chondrites and the Protoplanetary Disk ASP Conference Series, Vol. 341, 2005 A. N. Krot, E. R. D. Scott, & B. Reipurth, eds.

## The Chondrite Types and their Origins

John A. Wood

Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, USA

Abstract. Recent advances in the dating of ferromagnesian chondrules are summarized, and the conclusion seems unavoidable (the author's earlier convictions notwithstanding) that chondrules comprising a given chondrite are the product of nebular activity extending over a million years or more. Continuing chondrule-forming activity, probably successive shock events, can explain the non-solar major element chemical compositions of the ordinary chondrites (OC): they are the cumulative effect of repeated small changes in the local system composition that accompanied each chondrule-forming event. In particular Fe,Ni metal was increasingly lost from the system with time, presumably by incorporation in planetesimals (most of them unsampled) at the nebular midplane. Fe/Si in the system progressed smoothly with time through values appropriate to the H, L, and LL OC groups. The parent bodies of each of these groups were accreted in a relatively short time, during which Fe/Si was essentially constant, then accretion effectively ceased, probably because the parent body was perturbed into an inclined orbit and no longer spent much time in the chondrule-rich nebular midplane. The perturbations are probably ascribable to the same density waves (gravitational irregularities) that created chondrule-forming shocks. Implementation of this concept is also explored for carbonaceous and enstatite chondrites. Maintenance of the differences in composition of the various chondrite types, which formed at differing radial distances, requires that turbulent diffusion was not effective in the zone of chondrite formation. Instead periodic disturbances by the nebular density waves were probably responsible for remixing solids from the midplane zone into the body of the nebula.

#### 1. Introduction

Chondritic meteorites, the oldest samples of planetary rock accessible to us, are divided into about a dozen classes based on differences in chemistry, mineralogy, and structure. It has long been understood that the several chondrite classes formed at different times and places in the solar nebula, and that the processes and conditions which produced them varied somewhat with time and radial distance in the nebula in a way that accounts for the observed differences in properties of the chondrites. A major goal of meteorite studies has been to understand the relationship between time, place, and properties of all the chondrite classes, not only for taxonomic purposes, but also to learn more about the processes that formed chondrites, through application of the principles of comparative anatomy. The present paper is a synthesis that attempts to advance this goal. Chondrites (with some exceptions) consist mostly of mm-scale chondrules. The discussion herein follows from the premise that chondrules were formed dispersed in the nebula when an earlier generation of dust-aggregations (chondrule precursors) were melted by transient energetic events. These chondrule-forming events appear most likely to have been nebular shock waves (section 2), a concept suggested by Wood (1963) and Suess & Thompson (1983).

Chondrites also contain refractory inclusions (Ca,Al-rich inclusions; CAIs) that formed at the inner edge of the protosolar disk, near the Sun (Shu et al. 1996; Wood 2004); these were transported from their site of formation to the radial distance of the asteroid belt either by an astrophysical x-wind (Shu et al. 1996) or by the outward diffusive effect of turbulence in the nebula (Cuzzi et al. 2003; but see section 3).

## 2. Chondrule-forming Shocks

Several possible sources have been suggested for the chondrule-forming shocks, but some mechanisms are more plausible than others. Wood (1984a) and Ruzmaikina & Ip (1994) treated the case of presolar precursors falling from the interstellar medium through the accretion shock into the solar nebula, but this model leaves the multigeneration chondrules (chondrules within chondrules) that are occasionally observed unaccounted for. Hood (1998) and Weidenschilling et al. (1998) noted that eccentrically orbiting planetesimals may have generated sufficiently strong bow shocks to melt chondrules in the nebula; but planetesimals of ~1000 km dimension are required, which would require chondrule formation to wait for the assembly of these relatively large objects and also of Jupiter, which is needed to perturb the planetesimals into eccentric orbits, whereas some chondrules appear to have been formed at the very beginning of the solar system (section 3). (It might also be argued that if planetesimals moved as rapidly through the nebular gas as this model requires, ablation from the planetesimal surfaces would probably produce chondrules more copiously than would the secondary effect of their bow shocks.)

A more durable concept has been the idea that the shocks were generated in the nebula by the passage of spiral density waves in a marginally gravitationally unstable disk (Hood & Horanyi 1991; Wood 1996; Boss 2000; Pickett et al. 2003; Boss & Durisen, this volume). Larson (2002) notes that tidal disturbances caused by early companion stars may create spiral density waves and associated nebular shocks that are capable of melting chondrules. An important property of systems of spiral density waves is that the relative velocity of the spiral pattern and the disk gas increases inward in the disk, from some corotation radius in the outer disk. This velocity difference defines the speed at which chondrule precursors (embedded in the gas) encounter shock waves (attached to the spiral pattern).

## 3. Ages of Chondrules and a New Paradigm

Improvements in techniques of dating the formation of typical (ferromagnesian) chondrules have been made in recent years, and the new data have made it appear that chondrules were formed over a protracted period of time, several Myr, in spite of the fact that accretion of nebular matter to the Sun is understood to have thinned the nebular gas density by orders of magnitude on this timescale (e.g., Briceño et al. 2001). The age data for ferromagnesian chondrules are summarized in Figure 1. The timescale that has emerged was presaged by similar conclusions resulting from earlier studies of Al-rich chondrules (e.g., Hutcheon et al. 2000). The fact that the chondrite Allende, with the oldest chondrules, is a representative of the class of chondrites (CV) having the largest content of CAIs, which were created and distributed very early in nebular history (section 1), is consistent with such a protracted history of chondrule formation and accretion.

The ages reported make it appear that chondrules were not formed by a single shock or a single brief epoch of shocks, but by shocks that recurred for millions of years; and that the chondrules occurring in a particular chondrite were not accreted promptly after formation, but remained suspended in the disk gas for millions of years. It would necessarily follow that the shocks which created chondrules were not global in extent, since this would have the effect of constantly resetting the ages of earlier generations of chondrules; instead the chondrule-forming events were relatively small and localized.



Figure 1. Ranges of ages for individual ferromagnesian chondrules (open circles) in six chondrites, with upper and lower limits of error bars shown. Sources: (1) McKeegan et al. (2000); (2) Kita et al. (2000); (3) Mostefaoui et al. (2002); (4) Tachibana et al. (2003); (5) Amelin et al. (2004); (6) Bizzarro et al. (2004); (7) Kurahashi et al. (2004); (8) Amelin et al. (2002). (5) and (8) report Pb-Pb ages; others are <sup>26</sup>Al-<sup>26</sup>Mg ages.

The data of Figure 1 are, of course, susceptible to error of interpretation. In particular, metamorphic resetting could make some chondrules appear to be younger than they are. If this effect could be removed, it might make the range of chondrule ages shorter than is shown. However, the evidence from Al-rich chondrules (Hutcheon et al. 2000), where <sup>26</sup>Mg\* is sought in anorthite crystals rather than glass, and where the high Mg concentration in these crystals is not consistent with metamorphic redistribution, is that chondrule formation continued over a period of  $\geq$ 4 Myr. The special contribution of Bizzarro et al. (2004) was to show that the period of chondrule formation also produced very old ferromagnesian chondrules, as old as CAIs; error caused by metamorphic resetting cannot be held responsible for these old ages. The present paper accepts the premise that the age ranges shown in Figure 1 and their differences are at least qualitatively correct, and they contribute to an understanding of different provenances of chondrite formation in the nebula.

A portion of the age ranges observed could be ascribed to mixing in parent bodies' regoliths of chondrules formed and (promptly) accreted at different times, instead of storage and mixing in the nebula; but it seems unlikely that regolith mixing could be deep enough, with the oldest chondrules remaining unconsolidated and accessible, to mingle chondrules with the range of ages seen in Figure 1 within what are now cm-scale sample volumes.

During their projected long period of storage in the nebula, turbulent diffusion (Cuzzi et al. 2003) would have radially mixed the chondrules in the nebula, swiftly and efficiently. This makes it hard to understand how the different chondrule populations that seem to have coexisted (Fig. 1), presumably at different radial distances, could have maintained their identities. It may mean that turbulent diffusion was not an effective process at all times and places in the nebula. Balbus & Hawley (2000) point out that magnetorotational instability would have been the principal agency of turbulence in the nebula, and this operates only at small and large radial distances where the gas is ionized and conductive because of (respectively) the heat of the proximate Sun and the transparency to cosmic rays of the outer disk. At the intermediate distances where chondrites formed there was nothing to cause sustained turbulence, and objects as large as chondrules tended to settle and accumulate in a zone near the midplane. However a premise of this paper is that every time the substance of the nebula passed through density waves, transient turbulence was generated. During these periods unaccreted solid matter from the midplane was remixed into the body of the nebula. Thereafter a new epoch of accretion of chondrites occurred at the nebular midplane, after a large enough density of chondrules (size-sorted during settling from the body of the nebula) had accumulated there. No significant amount of free nebular dust accumulated at the midplane; chondrite matrix consists of dust that gathered to chondrules and rimmed them as they settled through the nebula.

If turbulent diffusion is discounted, the x-wind (Shu et al. 1996) may have to be invoked to account for the transport of CAIs from the inner edge of the disk to what is now the asteroid belt; unless another transient source of disk-wide of turbulence, such as might have been generated by the earliest most copious accretion of interstellar matter, operated during the short time when CAIs were being formed and distributed.

The concept of formation of the ingredients of a particular chondrite parent body over a protracted period of time is the opposite of the view the author has consistently held in the past (e.g., Wood 1984b, 1985a,b, 2000). It offers new opportunities for understanding the processes that established the compositions of chondrite classes, and is different enough from earlier thinking (at least by the author) to constitute a new paradigm.

### 4. An Age - Radial Distance Framework for Chondrite Formation

If the chondrite classes formed at different times and places in the solar nebula, it is convenient to use a two-dimensional diagram as a framework to specify the separate provenances of the classes (Fig. 2). This figure is schematic; the radial distance axis is not quantified, and the dashed borders between the boxes signify that they are transitional as well as approximate.



Figure 2. Proposed age - radial distance framework for chondrite formation in the solar nebula; *schematic*. The distance axis is left qualitative. Position of the "snow line," an isotherm ( $\sim$ 160 K) outside which water ice can condense, is suggested.

Information about the time axis comes from the radiometric ages of chondrules (section 3). The time when accretion of a particular parent body began is a definite number, but one unknowable by us. Each parent body incorporated chondrules that had been formed before it nucleated, and it continued to gather chondrules that were formed later. It appears the accretion of each parent body did not continue for as long as the nebula contained accretable solid matter, but largely ended at a definite time (section 5), so the boxes in Figure 2 are shown with closed bottoms. They are open at the top because some fraction the chondrules being accreted, however small, was formed throughout the span of time extending back to  $t_0$ .

The place (radial distance) axis in Figure 2 is hard to quantify. In principle the stratigraphy of asteroid spectral classes (Gradie & Tedesco 1982), which can be correlated imperfectly with chondrite classes, should provide information, but in practice 4.5 Gyr of collisional and orbital evolution has created such broadening and overlap of the bands of orbits of asteroid spectral classes that little can be learned from spectroscopy about the mean distances at which particular chondrite parent bodies formed. However, the internal properties of chondrites provide two clues to radial distances of formation.

One of these is based on differences in the proportions of chondrules that were completely melted, in the various classes (Table 1), which is a demonstration of the strength of shocks and the temperatures achieved during chondrule formation. As noted in section 2, shock velocity and thus strength is expected to have decreased outward in the nebula. As one illustration of this effect, if chondrule-forming shocks were associated with a density wave extending inward from an early-formed Jupiter, a possibility raised by Boss & Durisen (this volume), the shock velocity would have been the difference between the local Keplerian velocity of nebular gas and the pattern velocity of the density

wave (anchored at Jupiter). This difference would have been zero at Jupiter's radial distance, ~4.8 km/sec at 4 AU, and ~16.1 km/sec at 2 AU. Other sources of nebular shocks also have shock velocities that increase inward, for different reasons (for example, the velocities of eccentrically-orbiting planetesimals increase as they approach periapsis). The efficiency of shock-heating also increases with gas density and particle density, which increased inward.

Ordinary chondrites	16%
Carbonaceous chondrites	
CM	~5%
CR	<1%
CO	5%
CV	6%
Enstatite chondrites	
EH	18%
EL	~13%

Table 1. Proportions of completely melted (droplet) chondrules in chondrite groups, from Rubin & Wasson (1995), Rubin (2000).

Another often-referenced property related to radial distance is chondrites' content of the volatile components water and carbon (Table 2). In many cases the C is present in the form of organic compounds, and even where present as elemental carbon it probably entered chondrites as organic compounds which were subsequently pyrolized during metamorphism. The  $H_2O$  probably had its origin as nebular water ice (snow) that accreted along with silicate materials when the parent bodies formed. A simple-minded view would be that the farther out chondrite accretion occurred, the greater would be the concentrations of organic C and ice incorporated. If so, all other things being equal (e.g., depth of burial), the abundances of C and  $H_2O$  remaining after metamorphic evolution are approximate indicators of the radial distance of accretion.

Table 2. Volatile components in chondrite groups (representative values), from Mason (1963, 1971), Jarosewich (1966), Anders & Zadnick (1985.

	С	H <sub>2</sub> O
C1 (CI)	3.5%	20%
C2 (CM)	2.5%	13%
CR	1.5%	6%
C3 (CV, CO)	0.5%	1%
OC (Type 3)	0.5%	1%

Subsequent sections of this paper will discuss the rationale for the placement of boxes in Figure 2, and the differences in formative processes and their products that gave rise to the various chondrite classes.

#### 5. Ordinary Chondrites

There is an honorable tradition of studying patterns of chemical fractionations in chondrites relative to the solar composition in an effort to understand formative processes and reasons for the differences between chondrite classes (e.g., Larimer & Anders 1970; Wasson 1972). Following that precedent, the present paper begins by comparing abundances of the refractory elements Ca and Al (normalized to Si) in ordinary chondrites (OC), with abundance patterns in the solar photosphere (Fig. 3). It is seen that the OC are systematically depleted in refractory elements by ~20%, relative to solar.



Figure 3. Abundances of the two principal refractory elements, Ca and Al, normalized to Si, in the three ordinary chondrite classes and the solar photosphere. Abundances in chondrites in Figures 3, 4, and 5 are from Jarosewich (1990). Photospheric abundances in all figures of this paper are from Grevesse & Sauval (1998).

A similar plot based on the most-abundant cationic elements Mg, Fe, and Si (Fig. 4) displays a surprisingly extended and regular pattern of Fe depletion, ranging from almost no depletion at all for some H chondrites to a nearly 50% depletion for some LL chondrites. Mg is depleted by a small and almost-constant amount (~5%) that is closely correlated with the amount of Fe depletion. Iron depletions in OC correlate with depletions of Ni (Fig. 5), showing that subtraction from the system of Fe in the form of metal was responsible for the observed Fe depletions. (The trend of data in Figure 5 does not pass through the origin because chondrites also have other Fe-bearing phases that do not contain Ni.)

This plot of individual chondrite compositions is more revealing than plots of mean compositions for the H, L, and LL groups because it shows that the chondrites lie along a remarkably smooth and constrained compositional trend. The regularity of the trend strongly suggests the working of an evolutionary process, which by the continuing withdrawal of metal from the nebular system caused the composition of residual condensed

# 960 *Wood*

matter to migrate leftward in Figure 4 from the vicinity of solar, to H, then L, then LL OC compositions.



Figure 4. Abundance ratios of the three most abundant cationic elements (Mg, Fe, and Si), normalized as in Figure 3, in OC and the Sun.



Figure 5. Ni/Si plotted against Fe/Si, showing that Fe and Ni fractionations correlate, and loss of metal phase containing both elements must have been responsible. Some LL chondrites lost practically all of their solar complement of Ni.

Interestingly, the refractory-element depletions of Figure 3 do not correlate with the Fe/Mg trend. Depletions of Ca and Al in Figure 3 are approximately constant, and not obviously related to membership in the H, L, and LL groups. An early process, not repeated during the subsequent evolution of the nebular mineral system, appears to have operated to deplete the system in Ca and Al (~20%) and Mg (~5%).

The present paper will argue that the evolution of the nebular mineral system, in particular the loss of Fe,Ni metal, resulted from the action of repeated chondrule-forming shock waves on precursor dust-clumps and unaccreted earlier-formed chondrules, within box "OC" of Figure 2, as follows.

*a. Early depletion of Al and Ca.* Particularly energetic shock waves are postulated in earliest times, which locally heated precursor aggregations to high enough temperatures to vaporize significant amounts of Mg, Fe, Si, and more volatile elements. Many of the resulting chondrules, enriched to some degree in Al and Ca, sank to the nebular midplane and were removed from the system by being incorporated in planetesimals, which we have not sampled. Their loss changed the bulk composition of the residual nebular matter from which later generations of chondrules would be made.

*b. Later, less-energetic chondrule formation.* Subsequent chondrule forming shocks acted on precursors whose Ca/Si and Al/Si (and to a lesser degree Mg/Si) had been offset from the solar values by the amounts seen in Figure 3 and at the right end of the sequence of points in Figure 4. This later chondrule-forming activity was not energetic enough to further deplete the refractory element content of the residual nebular dust more than slightly, enough to account for the small positive slope seen in the sequence of points in Figure 4 (which is a time sequence, with the leftmost points representing the youngest chondritic matter).

*c. Metal separation during chondrule formation.* Carbon incorporated in chondrule precursors reduced Fe oxides and silicates in the precursors, forming molten metal. Some of this immiscible metal separated from the molten chondrules as relatively large metal droplets. (The observed distribution of metal in Renazzo, a CR chondrite, is consistent with such a process (Connolly et al. 2001). However, it should be noted that Cohen & Hewins (2004) were unable to reproduce the effect experimentally at nebular gas pressures.)

*d. Physical fractionation during settling in the nebula.* Processed objects in the nebula with the greatest (density x diameter), principally chondrules greater in diameter than some cutoff value and large metal grains, were able to sink and concentrate near the nebular midplane. The density  $\times$  diameter criterion may have militated against porous chondrule-precursor aggregations reaching the midplane, accounting for their absence in chondrites. Over a period of time metal loss from the nebula was more efficient than that of metal-poor chondrules, so the residual nebular system, and chondritic planetesimals later formed from it, became increasingly depleted in Fe and Ni.

Major-element fractionations associated with chondrule formation were earlier suggested by Sears et al. (1992), DeHart et al. (1992), and Haack & Scott (1993).

The process proposed would appear to have testable consequences. Chondrules should be progressively younger in the sequence H-L-LL, and they should be younger the less deeply they were buried in their parent bodies. Tachibana et al. (2003) describe a (weak) trend toward more Si in younger LL chondrules, and Dodd (1976) argued that H3 and LL3 chondrites (least deeply-buried, hence youngest) tend to be Fe-poor relative to

(older) H and LL chondrites of higher petrologic grade. A plot of petrologic grade vs. Fe/Si (Fig. 6) based on the more recent and homogeneous data set of Jarosewich (1990) shows a weak effect for H3 (3 out of 8 H3 chondrite points are depleted in Fe), but no effect for LL3. For the most part this plot shows Fe/Si to be essentially independent of petrologic grade (depth), demonstrating that the time scale for accretion of the OC parent bodies was small compared with the time scale of fractionation of metal from silicates in the nebula.



Figure 6. Petrologic grades of chondrites in the Fe/Si fractionation trend of Figure 4, plotted against Fe/Si. Points with grades 4, 5, and 6 have had 0.5 added to their grades to place them in the middle of the range for their grade instead of at a boundary between grades.

Three discrete parent bodies formed sequentially on the Fe/Si chemical evolution track. Why did the accretion of each body end? Why didn't material with progressively smaller Fe/Si continue to join (e.g.) the H group parent body? Why didn't material with substantially smaller Fe/Si, of the type that later nucleated the L group parent body, also accrete onto the H group parent body? This did not happen; the accretion of each of the three OC parent bodies was effectively terminated. What could accomplish this, yet leave the parent bodies in the asteroid belt from which their debris emanates today? The answer must be that after a period of growth in the nebular midplane, during which they achieved their final sizes, the OC parent bodies were perturbed into orbits of sufficient inclination that they spent little time thereafter in the midplane zone with its rich population of accretable matter.

The most probable source of the needed perturbations was the same nebular density waves (gravitational irregularities) that have been held responsible for the chondruleforming shocks. Perturbation by the passage of one spiral arm may have sufficed to take an OC parent body out of the ecliptic plane, or the effects of a series of density waves may have been required. The relatively short time scale of growth of the OC parent bodies from matter of essentially constant mean composition bore some relationship to the local Keplerian velocity, which determined how often disk material encountered potentially perturbing density waves. The span of OC chondrule ages in Figure 1 does not define the accretion time of the LL parent body, because accretion was not efficient enough to exhaust the nebula's stock of old chondrules.

The finite dispersion of Fe/Si values at all petrologic grades in Figures 4 and 6 could be an effect of hierarchical accretion, reflecting fractionation that occurred during the gradual growth of aggregations too small to be decoupled from the nebular gas and perturbed out of the midplane; only final accretion of these aggregations was on the short (Keplerian) timescale suggested here.

Presumably many chondritic parent bodies were formed in this fashion, the arguments of Meibom & Clark (1999) notwithstanding, of which we have sampled only three that are located near the 3:1 or  $v_6$  Jupiter resonances, which selectively perturb their debris into Earth-crossing orbits (Gaffey 2000). Substantial periods of time separated the accretion of these bodies; the H and L group parent bodies, at least, did not form end-to-end in the Fe/Si fractionation trend.

The OC box in Figure 2 is placed rightward of the snow line because these chondrites show evidence of aqueous alteration (e.g., Grossman et al. 2000), meaning they must have accreted ice along with their more refractory constituents.

### 6. Carbonaceous Chondrites

Abundances of Ca and Al in carbonaceous chondrites (CC) are shown in Figure 7. Far from displaying depletions of refractory elements, most of these chondrites have excesses ascribable to the CAIs they incorporated, derived from an external source (section 1). In a plot of Mg/Si vs. Fe/Si (Fig. 8) almost all CC show some Fe depletion, but very little compared with that in OC (Fig. 4). Any Mg loss that may have occurred, analogous to that in Figure 4, is masked by the gains in Mg from CAIs introduced.

It is well known that chondrules are much smaller in CO than in CV chondrites, in spite of the fact that the chemistry of the two groups is almost identical. The position of the small-chondrule CO field beneath (i.e., later than) the large-chondrule CV field in Figure 2 probably resulted from the decrease of nebular gas density with time, along with the maximum size of objects that could settle to the midplane in a given time. The decrease undoubtedly was gradual with time through the CO and CV boxes, not a step-function as the two discrete boxes in Figure 2 imply; CV and CO chondrites simply derive from two parent bodies that accreted at different times on the trend of decreasing gas density. The intervals of time during which each parent body accreted probably were limited by the perturbing effect of nebular density waves, as section 5 suggests for OC.

Fields for CM and CI chondrites are shown progressively farther out in Figure 2, consistent with their greater contents of carbon and water (Table 2) and with conventional wisdom. Positions of these boxes in Figure 2 are fictional and meaningless. The temporal position of the CR field conforms to the age of Acfer 059 in Figure 1, but the radial distance of the box is equivocal: the placement shown is consistent with the intermediate content of C and  $H_2O$  of CR chondrites (Table 1), but not with their smaller content of melted chondrules than CM (Table 2).

Wood



Figure 7. Ca/Si vs. Al/Si in carbonaceous chondrites. Letters plotted denote examples of CI, CM, CV, CO, and CR chondrites, with the "C" omitted. Chondrite compositions in Figures 7 and 8 are from Mason (1963), Clarke et al. (1970), Fuchs et al. (1973), and Kracher et al. (1985).



Figure 8. Mg/Si vs. Fe/Si in carbonaceous chondrites. Labeling convention as in Figure 7.

## 7. Enstatite Chondrites

Enstatite chondrites (EC) have the most extreme properties encountered among chondrites, and their formation is hardest to rationalize. Their reduced state, manifested by

964

their Fe<sup>2+</sup>-poor olivine and pyroxene, the Si content of their metal, and the presence of minerals unique to reducing environments (e.g., oldhamite, daubreelite, sinoite, niningerite), is well known. However, chondrules and their constituent minerals in E3 chondrites are not uniformly reduced; there is evidence of an earlier generation of more OClike minerals that reacted with a new, more reducing environment to form EC (Rambaldi et al. 1984; Lusby et al. 1987; Ikeda 1989).

Baedecker & Wasson (1975) noted that loss of refractory elements and of an oxidizing agent ( $H_2O$ ) from the formation site of EC was required to account for their properties. Larimer & Bartholomay (1979) showed that an increase of nebular C/O (as by loss of  $H_2O$ ) would account for the unusual mineralogy of EC.

Abundances of the refractory elements Ca and Al in enstatite chondrites are shown in Figure 9; they are even more depleted in EC than in OC, which are shown for comparison. Magnesium is similarly more depleted in EC than OC (Fig. 10). Fractionations of Fe/Si are shown in Figure 10. These are of the same scale as fractionations in OC, and again Fe/Si correlates with Ni/Si (not shown), so metal fractionation is the agency of these effects. In the case of EC, however, not only losses of metal are seen (EL) but also gains of metal, so that sometimes Fe/Si exceeds the solar value (EH).



Figure 9. Ca/Si vs. Al/Si in enstatite chondrites. "L" and "H" denote EL and EH chondrites. Positions of OC, from Figure 3, are also shown for comparison. Enstatite chondrite compositions in Figures 9 and 10 are from Mason (1966).

A four-stage process of formation is proposed to account for the complexities of enstatite chondrites:

a. Early loss of refractory elements. As in the case of OC formation, an initial stage of very-high-temperature processing distilled protochondrules in the nebula, which rained out to the midplane where they were accreted and removed from the system. The effect operated even more strongly and effectively than in the OC region, producing an ~20% depletion of Mg, as well as even larger losses of Ca.

*b. Later, less-energetic chondrule-formation.* Subsequent shocks formed chondrules (including Type II chondrules with ferrous silicate minerals) much like OC chondrules. Droplets of Fe,Ni metal probably separated from these, as was suggested for OC (section 5).



Figure 10. Mg/Si vs. Fe/Si in enstatite chondrites. Labeling convention as in Figure 8. Again, OC compositions from Figure 4 are shown for comparison.

*c. Physical fractionation during settling in the nebula.* In this case, there was no net loss of metal during the settling of chondrules and metal droplets to the midplane, but a metal/silicate fractionation did occur internally in the system during settling, the products of which are preserved in the form of metal-poor (EL) and metal-rich (EH) chondrites. These aliquots appear to have accreted into separate parent bodies, not two layers on a single body (or family of congruent bodies), since many examples are known of EL3 and EH3 chondrites, both of which represent near-surface material. Chondrule-forming activity which produced the metal-rich EH parent bodies may have depleted the residual nebula in metal enough to account for subsequent formation of metal-poor EL planetesimals.

*d. Another stage of thermal processing in the midplane, prior to accretion.* The nonsolar bulk composition of the midplane layer would produce a novel suite of minerals, if another shock wave impinged on that zone while chondrules and other solids were still dispersed in it. Petaev & Wood (2001) found that a 100× enhancement of chondritic dust and a 20× enhancement of refractory organic material, relative to the "gas" and "ice" components of Wood & Hashimoto (1993), produces an environment in which the classic EC minerals are stable between 1120 K and 500 K, even though C/O and H/O in the system have less than their solar values. Incomplete reaction of this environment with the Fe<sup>2+</sup>-bearing chondrules produced in stage *b* yielded the partly-reacted and decomposed lithologies described by Ikeda (1989) and other authors.

The vaguely indicated provenance for formation of these chondrites is labeled EC in

Figure 2. It is placed inside those of the other chondrite types because of ECs' higher content of melted chondrules (Table 1), and the postulated higher-energy processing that depleted the refractory elements in the system to a greater degree than in OC. Shukolyukov & Lugmair (2004) argue that the abundance of radiogenic <sup>53</sup>Cr in EC is consistent with their formation inside the present asteroid belt. Little is known about the ages of EC or their chondrules. Guan et al. (2002) describe an Al-rich chondrule in EH3 chondrite Sahara 97072 whose level of <sup>26</sup>Mg\* indicates formation ~2 My after *t*<sub>0</sub>. The presence in E3 chondrites of CAIs (Kimura et al. 2001) rules out very late accretion.

#### 8. Carbon in the Nebula

Carbon, in the form of organic carbonaceous compounds, played a key role in the formation of chondrites generally and chondritic reduced metal in particular. Two classes of organic compounds would have been present in the nebula. The first comprised those compounds that formed in the presolar molecular cloud and the diffuse interstellar cloud that preceded it, and coated interstellar dust grains that joined the nebula (Kouche et al. 2002; Kudo et al. 2002; Nakano et al. 2003). These compounds would have been destroyed by pyrolysis at <450K in the chondrule-forming shocks. In the cooling postshock system, assuming the formation of graphite and methane was inhibited, C may have formed a second, different, set of compounds, again at temperatures <450K (Zolotov & Shock, 2001). Section 5 postulates that organic C incorporated in chondrule precursors was the reducing agent that created Fe,Ni metal blebs in the chondrules; it may also have been the sticking agent that bound chondrule precursors together.

There is no way of knowing whether the organic compounds in chondrule precursors were of presolar or nebular origin, since they were destroyed by the chondruleforming events. It is possible that the nature of the carbonaceous compounds defined two discrete categories of chondrule precursors. We can speculate that precursors which aggregated farther from the Sun were more generously endowed with presolar organic compounds, and these formed more highly reduced Type I chondrules when they melted. Perhaps Type II chondrule precursors, aggregated at an interior position, incorporated nebular organic compounds in smaller amounts and achieved less reduction of Fe. The distribution of Types I and II chondrules in a given chondrite tends to be bimodal (e.g., Takagi et al. 2004).

Besides this putative C in chondrule precursors, the matrices of primitive chondrites are known to contain organic carbon and C in the form of nanodiamonds. Alexander et al. (1998) argue from the approximately constant ratio of nanodiamonds to total organic C in matrices, and from the extreme range of isotopic compositions of N in them, that most of the organic material present ( $\geq$ 70%) formed in the interstellar medium, not via local synthesis in the nebula. This poses a problem, because neither the organic material nor the nanodiamonds now in chondrite matrices would have survived the high temperatures of chondrule-forming events. These components must have been resupplied to the region of chondrite formation at a rate sufficient to maintain the observed concentrations of organic compounds and diamonds in the dust that became incorporated as matrix into the chondrite parent bodies when they accreted. The source of resupply cannot have been the outer nebula because dispersed organic material, diamonds, chondrules, and mineral dust cannot move radially relative to one another, all being coupled to the gas. The source of additional organic matter and nanodiamonds must have been the continuing accretion

## 968 Wood

of interstellar matter to the nebula. The rate of accretion to the disk decreased with time, but so did the mass of the nebula the accreted matter was added to.

Here a conundrum reveals itself. For the pattern of chondrite chemical evolution described in section 5 to operate requires that differentiated matter (chondrules and metal grains) was subtracted from the nebula faster than interstellar mineral dust was added to it; otherwise the Fe content of the residual nebula could not diminish. But for chondrites to contain the approximately constant abundances of nanodiamonds and (apparently) presolar organic C observed by Alexander et al. (1998) appears to require that addition of new interstellar material to the nebula kept pace with losses, so that a steady-state concentration of unprocessed matter (which, however, would include newly-acquired Fe and also refractory elements) was maintained. The solution may lie in recognition that much of the material processed in chondrule-forming shocks was not precursors freshly aggregated from (Fe-rich) dust, but old unaccreted chondrules that had gone through repeated cycles of shock-melting, during which Fe metal progressively separated from them and became vulnerable to selective loss by accretion. Newly-infallen interstellar dust supplied the presolar C that is found in chondrite matrices, but the Fe budget of the system was dominated by recycled chondrules.

### 9. Differentiated Meteorites

Figure 2 includes a box labeled "Differentiated meteorites," in which those meteorite types resulting from igneous activity would have formed. The bottom of the field cuts off at less than 2 Myr because planetesimals accreting later than that would not contain enough live <sup>26</sup>Al for decay of the latter to heat them to the melting temperature (Wood 2000). Figure 1 suggests material was available in the nebula for accretion into planetesimals early enough to experience <sup>26</sup>Al-melting, even if the CV, CO, and LL3 parent bodies did not accrete that soon. Levels of <sup>26</sup>Mg\* found by Srinivasan et al. (1999) in the Piplia Kalan eucrite are consistent with <sup>26</sup>Al as the heat source that produced melting in the eucrite parent body. Comparable evidence of <sup>26</sup>Al in most HED meteorites is missing, presumably because of diffusive resetting during the crustal metamorphism their source region experienced (e.g., Yamaguchi et al. 1996), caused either by burial beneath later lava flows or within a crater ejecta blanket (Sears et al. 1997).

The outer edge of the differentiated meteorites field in Figure 2 cuts off at the snow line, because incorporation of a substantial amount of ice in accreting planetesimals would provide a thermal buffer that prevented temperatures from rising to the melting range even in early-formed bodies (Wood & Pellas 1991).

#### 10. Conclusions

I consider that this paper makes two important contributions. The first is acknowledgment that chondrule-formation continued for a very long time (by early-solar-system standards), essentially for as long as the gaseous nebula endured, and that repeated chondrule-forming events had the effect of gradually changing the bulk chemistry of the system, especially in the region of OC formation. The Mg/Si vs. Fe/Si track in Figure 4 is a compelling record of a portion of the changes that occurred.

The H, L, and LL groups of OC formed in separate parent bodies. Each group includes the full range of petrologic types, including near-surface type-3 material, so they cannot have shared parent bodies. Fe/Si is essentially constant in each of these groups, so the groups' parent bodies must have accreted rapidly, on a time scale short compared with that of the chemical evolution described in the last paragraph, after which accretion onto those bodies largely ceased. The second contribution alluded to is the conclusion that accretion halted when the parent bodies were perturbed into inclined orbits that removed them from the "feeding zone" at the nebular midplane, and that the most likely perturbing influence was the same density waves that created chondrule-forming shocks. The relatively short accretion times of the parent bodies appear to measure the time it took for these objects to encounter enough gravitational disturbances to achieve this degree of perturbation.

Chondrite formation was probably closely linked to the presence of density waves (spiral arms) in a marginally gravitationally unstable nebula, in several ways. First, density waves probably generated shocks that melted dust aggregations into chondrules. Second, the density waves periodically created transient turbulence that remixed solid matter from the nebular midplane into the body of the nebula. Third, density waves gravitationally perturbed the orbits of chondrite parent bodies out of the nebular midplane.

Acknowledgments. I am grateful to Conel Alexander for a very constructive review of this paper, which evolved through many exuviations; and also to Sasha Krot and Misha Petaev for their helpful advice. The research reported was supported entirely by the Smithsonian Institution Astrophysical Observatory.

More generally and importantly, I want to express my heartfelt thanks to the international meteoritics community, which constituted my professional home and family for 48 years, for their sustained friendship and support. I have been blessed. Most of all, I am forever indebted to Klaus Keil, Sasha Krot, Ed Scott, and the rest of the SOEST mafia for giving me the enviable sendoff described in this volume. Aloha!

#### References

- Alexander, C. M. O'D., Russell, S. S., Arden, J. W., Ash, R. D., Grady, M. M., & Pillinger, C. T. 1998, Meteorit. Planet. Sci., 33, 603
- Amelin, Y., Krot, A. N., Hutcheon, I. D., & Ulyanov, A. A. 2002, Science, 297, 1678
- Amelin, Y., Krot, A., & Twelker, E. 2004, Geochim. Cosmochim. Acta, 68. Suppl. 1, A759
- Anders, E., & Zadnik, M. G. 1985, Geochim. Cosmochim. Acta, 49, 1281
- Baedecker, P. A., & Wasson, J. T. 1975, Geochim. Cosmochim. Acta, 39, 735
- Balbus, S. A., & Hawley, J. F. 2000, Space Sci. Rev., 92, 39
- Bizarro, M., Baker, J. A., & Haack, H. 2004, Nature, 431, 275
- Boss, A. P. 2002, ApJ, 576, 462
- Briceño, C., Vivas, A., Calvet, N., Hartmann, L., Pacheco, R., Herrera, D., Romero, L., Berlind, P., Sánchez, G., Snyder, J. A., & Andrews, P. 2001, Science, 291, 93
- Clarke, R. S. Jr., Jarosewich, E., Mason, B., Nelen, J., Gómez, M., & Hyde, J. R. 1970, Smithsonian Contribs. Earth Sci., 5, 53 pp.
- Cohen, B. A., & Hewins, R. H. 2004, Geochim. Cosmochim. Acta, 68, 1677
- Connolly, H. C. Jr., Huss, G. R., & Wasserburg, G. J. 2001, Geochim. Cosmochim. Acta, 65, 4567
- Cuzzi, J. N., Davis, S. S., & Dobrovolskis, A. R. 2003, Icarus, 166, 385
- DeHart, J. M., Lofgren, G. E., Jie, L., Benoit, P. H., & Sears, D. W. G. 1992, Geochim. Cosmochim. Acta, 56, 3791
- Dodd, R. T. 1976, Earth Planet. Sci. Lett., 28, 479
- Fuchs, L. H., Olsen, E., & Jensen, K. J. 1973, Smithsonian Contribs. Earth Sci., No. 10, 39 pp.

- Gaffey, M. J. 2000, Lunar Planet. Sci., 31, 1092
- Gradie, J., & Tedesco, E. 1982, Science, 216, 1405
- Grevesse, N., & Sauval, A. J. 1998, Space Sci. Rev., 85, 161
- Grossman, J. N., Alexander, C. M. O'D., Wang, J., & Brearley, A. J. 2000, Meteorit. Planet. Sci., 35, 467
- Guan, Y., Huss, G. R., MacPherson, G. J., & Leshin, L. A. 2002, Lunar Planet. Sci., 33, 2034
- Haack, H., & Scott, E. R. D. 1993, Meteoritics, 28, 358
- Hood, L. L. 1998, Meteorit. Planet. Sci., 33, 97
- Hood, L. L., & Horanyi, M. 1991, Icarus, 93, 259
- Hutcheon, I. D., Krot, A. N., & Ulyanov, A. A. 2000, Lunar Planet. Sci., 31, 1869
- Ikeda, Y. 1989, Proc. NIPR Symp. Antarct. Meteorites, 2, 75
- Jarosewich, E. 1966, Geochim. Cosmochim. Acta, 30, 1261
- Jarosewich, E. 1990, Meteoritics, 25, 323
- Kimura, M., Hiyagon, H., Lin, Y., & Nakajima, H. 2001, Symp. Antarct. Meteorites, 26, 52
- Kita, N. T., Nagahara, H., Togashi, S., & Morishita, Y. 2000. Geochim. Cosmochim. Acta, 64, 3913
- Kouche, A., Kudo, T., Nakano, H., Arakawa, M., Watanabe , N., Sirono, S.-I., Higa, M., & Maeno, N. 2002, ApJ, 566, L121
- Kracher, A., Keil, K., Kallemeyn, G. W., Wasson, J. T., Clayton, R. N., & Huss, G. I. 1985, Proc. Lunar Planet. Sci. Conf. 16th, J. Geophys. Res., 90. Suppl., D123
- Kudo, T., Kouchi, A., Arakawa, M., & Nakano, H. 2002, Meteorit. Planet. Sci., 37, 1975
- Kurahashi, E., Kita, N. T., Nagahara, H., & Morishita, Y. 2004, Lunar Planet. Sci., 35, 1476
- Larimer, J. W., & Anders, E., 1970, Geochim. Cosmochim. Acta, 34, 367
- Larimer, J. W., & Bartholomay, M. 1979, Geochim. Cosmochim. Acta, 43, 1455
- Larson, R. B. 2002, MNRAS, 332, 155
- Lusby, D., Scott, E. R. D., & Keil, K. 1987, Proc. Lunar Planet. Sci. Conf. 17th, J. Geophys. Res., 92 Suppl., E679
- Mason, B. 1963, Space Sci. Rev., 1, 621
- Mason, B. 1966, Geochim. Cosmochim. Acta, 30, 23
- Mason, B. 1971, Meteoritics, 6, 59
- McKeegan, K. D., Greenwood, J. P., Leshin, L. A., & Cosarinsky, M. 2000, Lunar Planet. Sci., 31, 2009
- Meibom, A., & Clark, B. E., 1999, Meteorit. Planet. Sci., 34, 7
- Mostefaoui, S., Kita, N. T., Togashi, S., Tachibana, S., Nagahara, H., & Morishita, Y. 2002, Meteorit. Planet. Sci., 37, 421
- Nakano, H., Kouchi, A., Tachibana, S., & Tsuchiyama, A. 2003, ApJ., 592, 1252
- Petaev, M. I., & Wood, J. A. 2001, Meteorit. Planet. Sci., 36 Suppl., A162
- Pickett, B. K., Mejia, A. C., Durisen, R. H., Cassen, P. M., Berry, D. K., & Link, R. P. 2003, ApJ, 590, 1060
- Rambaldi, E. R., Housley, R. M., & Rajan, R. S. 1984, Nature, 311, 138
- Rubin, A. E. 2000, Earth Sci. Rev., 50, 3
- Rubin, A. E., & Wasson, J. T. 1995, Meteoritics, 30, 569
- Ruzmaikina, T. V., & Ip, W. H. 1994, Icarus, 112, 430
- Sears, D. W. G., Jie, L., Benoit, P. H., DeHart, J. M., & Lofgren, G. E., 1992, Nature, 357, 207
- Sears, D. W. G., Symes, S. J. K., Batchelor, J. D., Akridge, D. G., & Benoit, P. H. 1997, Meteorit. Planet. Sci., 32, 917
- Shu, F. H., Shang, H., & Lee, T. 1996, Science, 271, 1545
- Shukolyukov, A., & Lugmair, G. W. 2004, Geochim. Cosmochim. Acta, 68, 2875
- Srinivasan, G., Goswami, J. N., & Bhandari, N. 1999, Science, 284, 1348
- Suess, H. E., & Thompson, W. B. 1983, in Chondrules and their Origins, ed. E. A. King (Houston: Lunar Planet. Institute), 243

- Tachibana, S., Nagahara, H., Mostefaoui, S., & Kita, N. T. 2003, Meteorit. Planet. Sci., 38, 939
- Takagi, M., Huber, H., Rubin, A. E., & Wasson, J. T. 2004, Meteorit. Planet. Sci., 39 Suppl., A103
- Wasson, J. T. 1972, Rev. Geophys. Space Phys., 10, 711
- Weidenschilling, S. J., Marzari, F., & Hood, L. L. 1998, Science, 279, 681
- Wood, J. A. 1963, Sci. Amer., 209, 64
- Wood, J. A. 1984a, Earth Planet. Sci. Lett., 70, 11
- Wood, J. A. 1984b, Meteoritics, 19, 339
- Wood, J. A. 1985a, in Protostars and Planets II, eds. D. C. Black, & M. S. Matthews (Tucson: Univ. Arizona Press), 687
- Wood, J. A. 1985b, Meteoritics, 30, 601
- Wood, J. A. 1996, Meteorit. Planet. Sci., 31, 641
- Wood, J. A. 2000, Space Sci. Rev., 92, 97
- Wood, J. A. 2004, Geochim. Cosmochim. Acta, 68, 4007
- Wood, J. A., & Hashimoto, A., 1993, Geochim. Cosmochim. Acta, 57, 2377
- Wood, J. A., & Pellas, P. 1991, in The Sun in Time, eds. C. P. Sonett, M. S. Giampapa, & M. S. Matthews (Tucson: Univ. Arizona Press), 740
- Yamaguchi, A., Taylor, G. J., & Keil, K., 1996, Icarus, 124, 97
- Zolotov, M. Yu., & Shock, E. L. 2001, Icarus, 150, 323