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Chondrules: Chemical, Petrographic and Chronologic Clues to Their Origin by Impact

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Abstract. Major element contents of chondrite groups were volatility controlled and established in a nebula after formation of Ca-Al-rich inclusions but before chondrules formed. Elemental abundances in chondrules tend to correlate with chemical affinity. Calcium was fractionated from Al by a planetary, not a nebular process. Chondrules were contemporaneous with igneous activity and aqueous and thermal metamorphism. Planetary bodies of varied size and structure co-existed during the first 50-80 million years of the Solar System, when chondrules formed and impact was common. We propose that most chondrules formed by impacts on differentiated bodies.

1. General Introduction

Chondrite meteorites are aggregate rocks that escaped melting since they formed in the nascent Solar System some 4565 million years (Ma) ago. They have near-solar elemental proportions that vary somewhat among the three main chondrite classes (see Scott & Krot, this volume): carbonaceous (atomic Mg/Si >1); ordinary (Mg/Si ~0.94), and enstatite (Mg/Si <0.9). The differences among the groups reflect differing reservoirs during accretion, due either to temporal or heliocentric effects. Some chondrites largely escaped the effects of parent body heating and fluid alteration. The constituents of these unequilibrated chondrites thus preserve clues to the process (es) that formed preplanetary matter and to the planetary accretion process itself. The defining constituents of chondrites are chondrules, which occur in all but the CI chondrites. Chondrules, therefore, were widespread within at least the innermost Solar System when planets were forming, and their origin is the subject of this chapter.

Chondrules by definition solidified from partially- to completely molten droplets. Thus chondrules generally are sub-spherical in shape (or were, prior to fragmentation or deformation), and most range in size from sub-mm to several mm in diameter (much larger and much smaller examples are known; see Connolly & Desch 2004; Krot & Rubin 1996). Chondrule compositions predominantly are rich in iron-magnesium silicates, although some are metal- and/or sulfide-rich. Excluded from this definition are calcium-aluminium-rich inclusions (CAIs), many of which also solidified from molten droplets but whose compositions are (as their name suggests) very different.

The "chondrule problem" is really two-fold: what process or processes established their bulk compositions, and what process or processes caused melting. Except for a narrow class of models that interpret chondrules as the products of direct melt condensation (as opposed to melting of solid precursors), these two aspects of chondrule petrogenesis are largely (but not completely) separate. The difficulty in the first instance is that the melting process destroys most or all physical traces of the material that was melted (e.g. Dodd 1981, p. 61). Even for the many chondrules that were incompletely melted and contain relict grains, such grains may well derive from an earlier episode of chondrite melting and need not represent the ultimate precursors (Jones 1996). In any case, heating certainly destroyed the record of the physical condition of the precursor material, so there is little direct evidence for the environment in which chondrules formed. Regarding the second part of the chondrule problem, only characteristics of the cooling and solidification part of the melting-solidification cycle are preserved in the final product; inferring the heat source is vastly more difficult.

Judging from the papers presented at chondrule conferences in 1982, 1994 and 2004, most workers interpret chondrule formation as occurring over a short timescale within the dusty protosolar nebula or accretion disk. Some argue for early formation with bodies of 20-3000 km diameter as intermediaries (Melosh et al. 2004; Sanders & Taylor, this volume). In contrast, we argue for chondrule formation over extended timescales by disruption of planetary bodies.

We review the chemical, physical, and isotopic properties of chondrules and their host chondrites that constrain theories of formation. Although chondrite bulk compositions are related to elemental volatility and presumably resulted from nebular processes, we argue that some chemical differences between chondrules cannot have been achieved by evaporation or condensation. Rather, they arose differently, possibly by crystal-liquid fractionation and core formation in planetary bodies. Chondrules are viewed as one component in an environment that included a range of bodies, and they evolved in a time-frame that also encompassed asteroidal metamorphism, melting, core formation, and massive asteroidal/planetary collisions.

2. Inconsistencies with a "Nebular" Chondrule Origin

2.1 Chondrite vs. Chondrule Chemical Fractionation

CI chondrites (the group that lacks chondrules) have bulk chemical compositions closest of all chondrites to that of the volatile-free Sun (Anders & Grevesse 1989). Relative to this "cosmic" composition, the compositions of the various chondrite groups record three kinds of chemical fractionation (Larimer & Anders 1970). The first is known as the refractory lithophile (= rock-forming) element fractionation. Refractory lithophile elements (e.g. Al, Ca, Ti) are enriched in the carbonaceous chondrites, in part by the addition of the early-formed CAIs to solids of "cosmic" composition (Larimer & Wasson 1988). Ordinary and enstatite chondrites, on the other hand, are depleted in refractory lithophiles (Larimer & Anders 1970). The second chemical fractionation established the Mg/Si ratios diagnostic of the chondrite classes. The third chemical fractionation involved the addition or removal of Fe, Ni and Co metal in "cosmic" proportions. Although the mechanisms by which these different chemical fractionations occurred are debated, it is generally agreed that fractionation between chondrite groups was a nebular process.

An important observation is that the fractionations exhibited by the bulk chondrite compositions are in some respects decoupled from those exhibited by chondrules. For example, the differing bulk compositions of the different chondrite groups are not the result of differing chondrule abundances. Consider the CM2 and CO3 carbonaceous chondrites, which have chondrule/matrix ratios of ~0.3 and ~1.3 respectively (Scott et al. 1996), and yet have similar major element chemistry (Wasson & Kallemeyn 1988) (Fig. 1a). Consider also the LL group chondrites, which contain abundant volatile-poor porphyritic chondrules (Alexander 1994) and yet are enriched in moderately volatile Mn, K and Na relative to chondrule-poor CM chondrites (Wasson & Kallemeyn 1988). We concur with Huss et al. (this volume) that major element fractionation between chondrite groups occurred before chondrules formed.

Another example of chondrule-chondrite chemical decoupling is in their respective Ca/Al ratios (Fig. 1). The solar (CI) Ca/Al value is 0.72 (Fig. 1a). Bulk chondrites exhibit an almost constant mean Ca/Al ratio (Fig. 1a), ranging from 0.76 (atomic) for R chondrites to 0.65 for the EL group. The range among individual meteorites is not much greater: 0.81-0.67 among 59 H, L and LL petrologic types 3-6 ordinary chondrites (Kallemeyn et al. 1989), and 0.82-0.66 among 16 CM, CO and CV chondrites (Kallemeyn & Wasson 1981). The respective individual chondrules, however, have a wider range of Ca/Al ratios (Figs. 1b-d). The Ca/Al ratios of 6 unaltered, FeO-poor chondrules from Murray (CM2) range from 1.23 to 0.31 (Fig. 1b). The range of Ca/Al in 5 chondrules in Allan Hills 85085 (CH3) is 0.99-0.48; that of PO chondrules in Semarkona is 0.94-0.55 (Fig. 1c). The range of Ca/Al, 0.84-0.55, in 9 Type IA and IAB chondrules from CR chondrites is greater than that of H, L, LL, CM, CO and CV chondrite groups. Finally, glass-rich chondrules in unequilibrated ordinary chondrites (UOCs) have extremely low Ca/Al ratios (Fig. 1d), the mean of 12 chondrules being 0.12 (Krot & Rubin 1994). It might be argued that because the data shown in these figures were collected using electron beam microanalysis of thin-sections, the random surface areas exposed for analysis are non-representative of the whole chondrules in many cases. However, instrumental neutron activation analyses (INAA) of bulk chondrules yield the same results. Twenty-nine chondrules (unclassified) from Semarkona (LL3.0) have atomic Ca/Al ratios in the range 0.90- 0.61 (Grossman & Wasson 1983). Moreover, different chondrule types give systematically different results. For example, in H3 chondrites the mean Ca/Al ratio of radial pyroxene chondrules is 0.96 whereas that of barred olivine chondrules is 0.33 (Fig.1c)

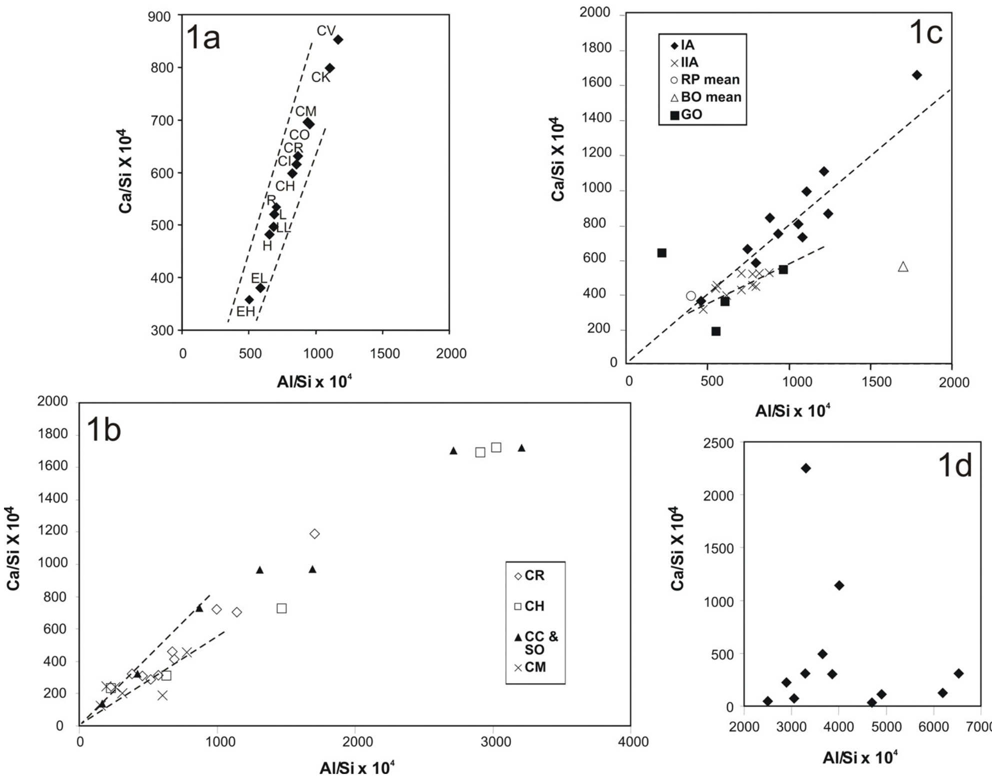

Figure 1. Ca/Si vs Al/Si atomic ratios of chondrites and chondrules. (a) Mean ratios of chondrite groups (data of Hutchison 2004). Lines have Ca/Al ratios of 0.82 and 0.66, the upper and lower limits of individual H, L, LL, CM, CO and CV chondrites (Kallemeyn & Wasson 1981; Kallemeyn et al. 1989). (b) Ratios in individual chondrules from carbonaceous chondrites: FeO-poor chondrules in CR chondrites (Connolly et al. 2001); various chondrule types in Allan Hills 85085, CH3 (Weisberg et al. 1988); cryptocrystalline (CC) and skeletal olivine (SO) chondrules in two CB_b chondrites (Krot et al. 2001); pristine chondrules in Murray, CM2 (Rubin & Wasson 1986). Dashed reference lines of Ca/Al atomic ratios of 0.82 and 0.66, the limits in chondrites. (c) Ratios in individual FeO-poor (Jones & Scott 1989) and FeO-rich (Jones 1990) PO chondrules from Semarkona, LL3.0; mean ratios in 8 radial pyroxene (RP) chondrules and 7 barred olivine (BO) chondrules from H3 chondrites (Lux et al. 1981); ratios in 4 granular olivine chondrules (Weisberg & Prinz 1996). Separate regression lines are drawn through the FeO-poor and FeO-rich chondrules (d) Individual glass-rich chondrules in type 3 ordinary chondrites (Krot & Rubin 1994).

(Lux et al. 1981). In Semarkona, Type IA (FeO-poor) chondrules define a different slope from type IIA (FeO-rich) chondrules (Fig. 1c; Jones 1990). Differences in Ca/Al ratio are, therefore, not an artifact of sampling. Rather, the differing chondrule varieties formed from different precursors. At least in the case of Semarkona, the observations of Jones & Scott (1989) and Jones (1990) argue that the chondrules were neither aqueously altered nor thermally metamorphosed, so secondary processing was not the cause of Ca/Al fractionation. We conclude that variations in Ca/Al ratios are a primary feature of chondrules, and those variations are different than exist in bulk chondrites.

One other striking contrast between chondrites and chondrules exists, namely in how volatile and refractory elements correlate. In many (commonly glassy) chondrules, enrichment in refractory Al paradoxically is accompanied by enrichment in moderately volatile Na rather than refractory Ca. Aluminium is associated with the Na in chondrule mesostases. Similarly, Al is also correlated with more volatile Cr in rare chromite-rich chondrules (Krot et al. 1993), and the elements occur together in spinel minerals ($M^{2+}M_2^{3+}O_4$; M = divalent Mg or Fe, and trivalent Al, Fe or Cr). Thus, in chondrules, elements tend to be associated on the basis of shared chemical affinity rather than volatility, in contrast to the situation among chondrites. Possible causes of the elemental enrichments or depletions in chondrules are discussed below.

2.2. The Duration of Chondrule Heating is Unconstrained

If chondrules formed by melting of solid precursors in a nebular environment, experimental results indicate that a thermal spike is required to produce the range of observed textures and compositions, either a few minutes at 1500−1850°C or hours at perhaps to 1400−1750°C (Hewins et al. this volume). Evaporation of FeO and SiO_2 from melts could yield more magnesian compositions in chondrules without the need for the very high temperatures that might otherwise be demanded, so PO chondrules may have formed at 1400−1600°C.

On the other hand, if chondrules formed by the break-up of internally heated partly molten bodies, there is no need for a sudden temperature spike. Impact, however, would have caused additional local heating. It is thus essential to include heating rate in discussions of chondrule origins. Consider, for example, how so-called flash heating would affect objects of different sizes. Would rapid heating of fine-grained precursors yield the same internal temperature in 0.1 mm and 10 mm objects? Would a small object vaporize while a large object melted at, say, 1750°C? If the peak temperature had been uniform throughout small chondrules, would we not see evidence of temperature gradients in cm-sized, ones? Had heating been rapid, we would expect to find some objects with dusty, unmelted or sintered cores grading outwards into melted rims, or the reverse, objects with melted cores grading outwards to dusty rims, depending on the heating mechanism. Such gradations have not been observed.

It has been proposed that rare agglomeratic or granular olivine chondrules, and certain rims around mainly porphyritic chondrules, were flash-heated (see below). The rims, however, formed in secondary events that acted on chondrules that had already undergone primary melting and solidification. Agglomeratic types excepted, throughout their size-range chondrules exhibit no textural evidence of temperature gradients incurred during primary melting. Some chondrules have chilled margins consistent with rapid cooling, such as an outer olivine "shell" around many barred olivine chondrules. No chondrules have unmelted or partially melted interiors that grade outwards into more highly melted margins, or the reverse, unmelted or partially melted rims that grade into more highly melted interiors.

Rubin & Krot (1996) suggested that survival of partially resorbed relict grains (derived from earlier generations of chondrule melts; Jones 1996) in some porphyritic chondrules requires rapid heating. If, however, the grains are xenocrysts that were introduced into pre-existing melts or partial melts, rapid heating may not be required. In fact, adding crystalline material to chondrule melts has been proposed as a means of promoting crystallization (see Connolly & Desch 2004). Survival of relict grains in chondrules probably requires cooling rates towards the higher end of the postulated range, 10 - 1000°C/hr (Hewins et al. this volume), rather than rapid heating.

Coarse-grained (Rubin 1984) and igneous (Krot & Wasson 1995) chondrule rims and microchondrule-bearing chondrule rims (Krot & Rubin 1996) have been cited as support for chondrule formation by rapid heating. In ordinary chondrites, igneous rims have sharp contacts with their host chondrules; rims on low-FeO chondrules mainly formed by melting the host chondrule, whereas those around high-FeO chondrules "appear to consist largely of melted matrix-like materials" (Krot & Wasson 1995). Rare FeO-poor chondrules in highly unequilibrated L and LL chondrites have rims of "fine-grained FeO-rich matrix-like material" that contain microchondrules (Krot & Rubin 1996). The microchondrules consist mainly of magnesian Ca-poor pyroxene, as in the host chondrules, but some others consist of Fe-rich olivine. Host chondrules have pyroxene-rich surfaces that are "irregular and show evidence of remelting" (Krot & Rubin 1996). Rubin & Krot (1996) recognize that chondrules are the products of multiple heating, but the lack of gradational contacts between chondrule interiors and melted or partially melted rims suggests that these rims formed by secondary heating of "previously formed chondrules or chondrule fragments" (Rubin & Krot 1996). Thus, the primary heating of chondrules was unrelated to rim formation. Chondrule melting was more pervasive, suggesting a longer heating duration than the event that formed the rims.

2.3. Most Chondrules in UOCs are Abraded Remnants of Larger Objects

In some UOCs, chondrules with abraded margins outnumber whole solidified droplets by about 3:1 (Dodd 1981, pp. 121-122). Abrasion may have been caused by impact or disturbance during compaction on parent bodies. Regardless, petrofabric analysis has revealed that in some porphyritic olivine chondrules, the long axes of olivine phenocrysts have "a linear preferred orientation ... thought to reflect flowage of a partly crystalline parent magma" (Dodd 1969). Such chondrules were interpreted as solidified pieces from larger semi-molten magma bodies, rather than as melt droplets.

2.4. CAIs, Igneous and Metamorphic Rocks and Low-Temperature Matrix Coexisted with Chondrules

It is well known that chondrules occur in chondrites together with clear products of very early nebular processes, such as CAIs (Russell et al., MacPherson et al., and

Jones et al. this volume). There can be no doubt that CAIs were present throughout the chondrite- accreting regions, even though CAIs probably formed in a different location from ferromagnesian chondrules (Krot et al. 2002). Fine-grained matrices in the least metamorphosed carbonaceous, ordinary and enstatite chondrites also contain tiny diamond, silicon carbide, and graphite grains whose isotopic ratios or fractionated noble gases are indicative of a presolar origin (Huss & Lewis 1994, 1995).

What is less-well remembered is that chondrules also coexist in chondrites along with products of much *later*, parent body, processes such as melting and metamorphism. Fragments of igneous rock occur in members of many chondrite groups: CO (Kurat & Kracher 1980), CV (Kennedy & Hutcheon 1992), H/L, L and LL (Hutchison 1992; Kennedy et al. 1992; Bridges et al. 1995). Dodd (1981) cites examples of metamorphosed chondrules or lithic clasts in UOCs. Mezö-Madaras is an L chondrite composed of (1-10) cm equilibrated L chondrite clasts in dark, chondrule-rich material of petrographic type 3. It is a fragmental breccia whose components had different thermal histories (Binns 1968), but see section 2.5, below.

Igneous and metamorphosed lithic and mineral clasts, chondrules, matrix, CAIs, sulfide and metal coexisted and accreted together to form chondrite parent bodies. To identify processes that were contemporaneous with chondrule formation, we discuss the times when these components formed. This should help us evaluate potential chondrule-forming mechanisms.

2.5. Chondrule Formation, Igneous Activity, Thermal and Aqueous Metamorphism and Core Formation Overlapped in Time

Diverse kinds of radiometric age data have been used to argue that chondrules must have formed in the solar nebula prior to formation of any asteroid- or planet-sized bodies. In fact, the situation is not so simple.

CAIs are the oldest measured objects that formed in the Solar System, and ages of other primitive objects are commonly compared to those of CAIs. Unfortunately, the precise relative timing of events that were separated in time by only a few Ma in the early Solar System is difficult to achieve using absolute radiometric age dating.

Short-lived radionuclides that were present in the solar nebula provide the means to achieve relative (not absolute) age differences as short as 10^5 years in some cases. One widely applied system, based on the decay of ^{26}Al to ^{26}Mg, indicates that many, but by no means all (MacPherson et al. 1995), "normal" CAIs formed ~1.5 Ma before the onset of chondrule formation (Kita et al. and Russell et al. this volume). This is derived from the fact that the inferred initial ^{26}Al/^{27}Al ratios in CAIs, typically ~5×10^{-5}, are several times higher than ratios measured in chondrules. However, the short half-life of ^{26}Al, 0.73 Ma, restricts the chronologic usefulness of this system to the earliest ~4 Ma of chondrule history. After ~4 Ma most of the ^{26}Al had decayed, so the method is incapable of yielding precise ages for objects formed after this time and merely sets upper limits (Huss et al. 2001; Mostefaoui et al. 2002). Additionally, interpretation of the Al-Mg isotopic system in terms of chronology within a chondrule or CAI is unambiguous only when the ^{26}Mg/^{24}Mg ratios (from which ^{26}Mg excesses, due to the in situ decay of former ^{26}Al, are measured) in the constituent phases correlate with ^{27}Al/^{24}Mg to give an "isochron" relationship. In CAIs, Mg-rich phases coexist with phases having high Al/Mg ratios, and it is in the latter where in situ decay of radiogenic ^{26}Mg has produced *measurably* high ^{26}Mg/^{24}Mg ratios. Isochron relationships are reasonably well exhibited by many CAIs. Similarly, in chondrules the Al largely resides in Mg-poor glassy mesostasis or plagioclase, and these are the sites where ^{26}Mg excesses can readily be measured. However, many chondrules do *not* show good isochron relationships and instead simply show well-resolved ^{26}Mg excesses. If (as is commonly believed) chondrule recycling introduced relict olivine grains into later generations (Jones 1996), those grains must have been accompanied by "parentless" radiogenic ^{26}Mg from mesostases and, possibly, from plagioclase. The relict olivines did not dissolve completely or equilibrate with their new chondrule melts, so Mg from the olivines need not have completely "swamped" excess ^{26}Mg. Therefore excesses of ^{26}Mg in such chondrules, without an isochron relationship, do not require that the most recent melting episode occurred when ^{26}Al was "live". The Al-Mg method dates the onset of chondrule formation, but not its cessation.

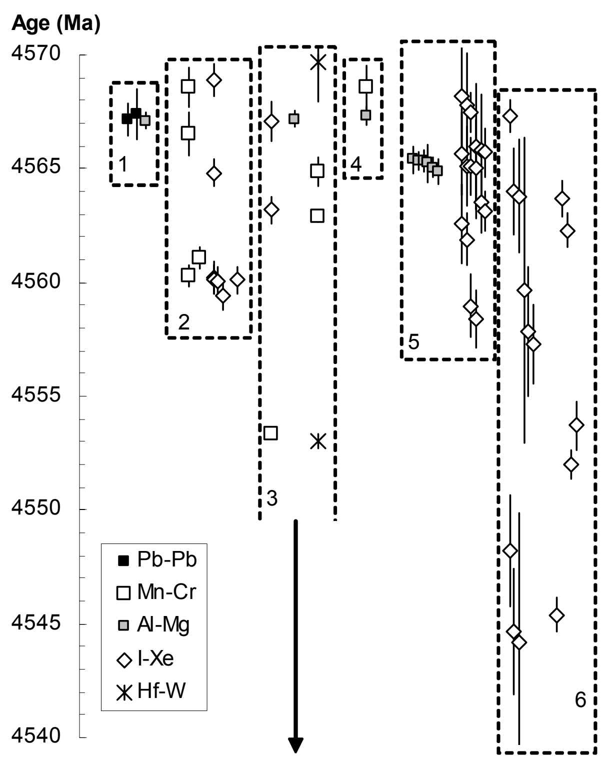

Figure 2. A schematic timescale for early Solar System events, calibrated to a Shallowater I-Xe age of 4563.2±0.6 Ma (see Gilmour et al. 2005 for cross-calibration and references). 1. CAI origin. 2. Aqueous alteration (CI, CM, CR carbonates; Mokoia fayalite; Allende dark inclusions; CI magnetite; secondary minerals in CAIs; Monahans halite. 3. Igneous rocks and differentiation (Semarkona CC-1 by Al-Mg; H chondrite clast, Barwell, L6; Serra de Magé; Mars core formation (Hf-W isotope dating, Kleine et al. 2002); Magmatic iron meteorite formation (Hf-W isotope dating; earliest age plotted; Kleine et al. 2005); LEW 86010; Shallowater pyroxene). 4. Chondrule model ages. 5. Chondrule isochrons, Semarkona (LL3.0). 6. Chondrule isochrons, Chainpur (LL3.4).

The only chronometer that has been applied to suites of individual chondrules and that is capable of resolving small age differences after the earliest ~4 Ma of Solar System history is I-Xe. Swindle (1998) reported I-Xe chondrule ages extending for ~50 Ma, which he interpreted as signifying disturbance by metamorphism or aqueous alteration. However, the I-Xe system has proven to be robust against disturbance by metamorphism at fairly high temperatures. An igneous inclusion in the Barwell (L6) chondrite has 7 times more iodine than the host (Hutchison et al. 1988), yet both retained radiogenic ^{129}Xe from close to the time of CAI formation (Fig. 2). This is taken to be the time of peak metamorphic temperature in Barwell. Barwell whole meteorite and phosphate were open to U-Pb exchange for a further 10 and 30 Ma, respectively (Göpel et al. 1994), without disturbing I-Xe. If, as suggested by Swindle (1998), the chondrules in Chainpur (LL3.4) were open I-Xe systems for ~50 Ma, why is there a spread in ages rather than convergence at 50 Ma? Swindle's interpretation was disputed by Holland et al. (2005), who studied a suite of Chainpur chondrules; 5 were found to have I-Xe isochron ages ranging over ~18 Ma (Fig. 2), and one (the most extreme) apparently pristine chondrule gave an age of ~22 Ma later than CAI formation. The ages of the Chainpur chondrules were interpreted as ages of formation by impact. This is consistent with the Al-Mg data reported by Huss et al. (2001), who argued that Chainpur's peak metamorphic temperature, 450°C, was too low to homogenize Mg isotopes and suggested instead that Chainpur accreted over an extended period, in which "young" chondrules could have formed.

The extended I-Xe age-range of chondrules is supported by a whole-rock Pb-Pb age of 4480±11 Ma for the Mezö-Madaras (L3) fragmental breccia (Hanan & Tilton 1985). Binns (1968) remarked on the high abundance in this meteorite of chondrules with isotropic glass and interpreted it as "an accumulation of fragments broken from already recrystallized chondritic bodies along with an entirely new generation of chondrules". This was disputed by Scott & Rajan (1981), who suggested that Ni distribution in the metal occurred during metamorphism after the breccia had formed, so the type 3 component and its chondrules were reworked. From its nanodiamond and silicon carbide contents, however, Huss & Lewis (1994; 1995) classified Mezö-Madaras as L3.5 and estimated that it suffered a peak metamorphic temperature of 420°C. This is significantly lower than the peak metamorphic temperature for Allende (CV3.2, 600°C), which did not reset the Pb-Pb age of its chondrules (4566.7±1.0 Ma, Amelin et al. 2004). We conclude that the Pb-Pb age of Mezö-Madaras represents chondrule formation, which therefore continued for 50-80 Ma after CAI formation.

Late formation of chondrules relative to core formation in planetary bodies has also been proposed by Kleine et al. (2005). They used the Hf-W system to determine the formation interval between CAIs and magmatic iron meteorites and compared it with that between CAIs and chondrules, from U-Pb and Al-Mg systematics. The IIAB irons were found to have formed in a core "before or at the same time as chondrules" in two primitive ordinary chondrites. These authors conclude that "chondrule-bearing chondrites ... must represent second generation planetesimals that may be the reaccreted debris produced during collisional disruption of first generation planetesimals."

To conclude, we find no compelling evidence that chondrule formation was limited to the first (4.0±1.5) Ma of Solar System history, as suggested by Kita et al. (this volume). Based on the arguments outlined above, Figure 2 summarizes what we believe is a more reasonable view of early solar system chronology in which chondrule formation took place over an extended time-scale that overlapped such early planetary processes as igneous differentiation and core formation.

3. Discussion

3.1. Ca-Al Fractionation in Chondrules Reflects Planetary Processing

The observation that many type IA and IIA PO chondrules in Semarkona, and radial pyroxene and barred olivine chondrules in H3 chondrites, have significantly non-solar Ca/Al ratios (Fig. 1c) is a problem for nebular models of chondrule origin. Fractionation of Ca from Al in the presence of more volatile Fe, Mg and Si is not achievable by evaporation or classic equilibrium condensation from a high temperature solar gas (Wood & Hashimoto 1993; Wang et al. 2001). Hashimoto (1992) investigated the enhanced volatility of Ca as hydroxide, in order to understand CAI alteration. The reaction kinetics demand a gas that is abnormally water-rich and the conditions militate against a nebular setting; alteration in parent bodies is more likely. We note that Wood & Hashimoto (1993) found that even in a highly oxidizing mixture of solar gas enriched 1000× in dust, tar and ices, no hydroxide has a stability field above ~400 K. It is, therefore, improbable that volatile $Ca(OH)_2$ can be invoked as an agent to produce non-solar Ca/Al fractionation. It is therefore unlikely that the non-solar Ca/Al ratios of ferromagnesian chondrules were inherited from any kind of condensation or evaporation process in a nebula.

Krot & Rubin (1994) proposed an alternative model in which glassy, Al-rich chondrules having low Ca/Al ratios (0.68-0.02; Fig. 1d) were produced by assimilation of partly altered fine-grained CAIs by silicate chondrule melts in a nebular setting. Mass balance calculations, however, indicate that hybridisation with CAIs is unlikely to have achieved the extreme enrichment in Al and impoverishment in Ca. As an example, the composition of one typical glass-rich PO chondrule ("C1") from Chainpur (taken from Krot & Rubin 1994) is given in Table 1. Suppose for the moment that its composition was achieved by addition of altered fine-grained CAI to a ferromagnesian chondrule, as Krot and Rubin suggested. Then the composition of the original (pre-hybridization) ferromagnesian chondrule may be derived by subtracting a putative CAI component and recalculating the remainder to 100 wt%. Of the minerals in altered fine-grained CAIs listed by Krot & Rubin (1994), only nepheline and spinel are consistent with the low CaO and FeO contents of "C1". Subtraction of 20 wt% nepheline and 10 wt% spinel from C1 yields a composition that is abnormally rich in SiO_2 and low in MgO for a low-FeO porphyritic olivine-pyroxene (POP) chondrule (e.g., Jones 1994); moreover the resulting Ca/Al atomic ratio is still less than half the solar value (0.72). Subtraction of a higher proportion of nepheline and/or spinel from "C1" only makes the result worse, driving the calculated composition to even higher values of SiO_2. It thus appears that assimilation of altered fine-grained CAI by ferromagnesian chondrule melts is implausible as a mechanism for producing glass-rich chondrules with low Ca/Al ratios. Using somewhat different chemical arguments, MacPherson & Huss (2000) also concluded that many Ca-Al-rich chondrules cannot be hybrids with CAIs.

Table 1. Silicate component of glass-rich chondrule "C1" calculated by sub tracting 20 wt% nepheline and 10 wt% spinel.

	"C1"	ne	sp	Res.	Sil	10
SiO_2	58.9	42.3	--	50.4	72.3	59.0
TiO_2	0.84	--	--	0.84	1.2	0.05
Al_2O_3	15.3	35.8	71.7	1.1	1.6	1.1
Cr_2O_3	0.37	--	--	0.37	0.5	0.45
FeO	1.7	--	--	1.7	2.4	2.6
MnO	0.05	--	--	0.05	0.07	0.22
MgO	16.0	--	28.3	13.2	18.9	36.1
CaO	0.40	--	--	0.40	0.6	0.5
Na_2O	5.1	21.8	--	0.7	1.0	0.38
K_2O	0.96	--	--	0.96	1.4	0.06
Sum	99.6	100	100	69.72	100.0	100.5*
Ca/Al	0.02	--	--	0.33	0.33	0.41

Chainpur, LL3.4, chondrule C1 comprises glass 75.4, olivine 21.1, Ca-pyroxene 0.4 and Ca-poor pyroxene 3.1, all in vol%. * Sum includes 0.03 wt% FeS. Analysis C1 from (Krot & Rubin 1994,). (ne) = $NaAlSiO_4$. Spinel (sp) = $MgAl_2O_4$. Residue (Res) = C1 - 20 wt% ne and 10 wt% sp. Silicate (Sil) = Residue recalculated to 100 wt%. 10 = type IAB porphyritic olivine-pyroxene chondrule from Semarkona (Jones 1994, Table 5).

We thus arrive at the conclusion that the non-solar Ca/Al chemical fractionation in chondrules most likely arose through planetary processing. Melting experiments aimed at forming eucrites showed that in melts of H, LL, CM and CV chondrites, the Ca/Al ratios and Mg/(Mg + Fe) ratios are related to the proportion of melt (Jurewicz et al. 1995). The Ca/Al ratio in the melt increases with temperature and proportion of liquid, so the range of Ca/Al ratios in chondrules could have been achieved by partial melting or crystal-liquid partitioning in a parent body. We propose that ferromagnesian chondrules formed by the disruption of bodies >10 km in diameter. Some had been metamorphosed, but most of the mass was in larger, partly molten differentiated bodies. Chondrules inherited fractionated chemical compositions from igneous melts or perhaps from mineral assemblages, including carbonate and/or sulfate, that had formed by aqueous alteration on parent bodies. Partial melts are favored because their temperature range overlaps that inferred for chondrule formation. Chondrule precursor bodies may have been disrupted by impact or by gravitational interaction. Impact would have caused additional heating.

3.2. Oxygen Isotopic Ratios in Chondrules are not the Result of Nebular Exchange

An estimate of the solar oxygen isotopic ratio has been obtained from the oxygen of Solar Energetic Particles (SEP) implanted into metal grains in lunar soil (Hashizume & Chaussidon 2005). The solar oxygen is enriched in ^{16}O, ($\Delta^{17}O$ ~-20‰) relative to terrestrial oxygen. Most CAIs are equally rich in ^{16}O (MacPherson et al. this volume), so they presumably formed from oxygen with bulk solar isotopic ratios. As predicted by one of us, it thus seems that it is the ferromagnesian chondrules, chondrites, differentiated asteroids, Earth, Moon and Mars that formed from oxygen that had been isotopically enriched in ^{17}O and ^{18}O by mass-independent fractionation (Hutchison 2002 p. 123). Lyons & Young (2005) propose that ^{17}O- and ^{18}O-enrichment was achieved by preferential dissociation of $C^{17}O$ and $C^{18}O$ gas at the edge of the presolar accretion disk by far ultraviolet photons. The "heavy" oxygen ions thus liberated combined with hydrogen to form water-ice, which was carried to the midplane of the disk and migrated inwards as ice-rich, meter-sized lumps. Here, the gas would have retained its original isotopic composition, somewhat diluted by evaporated ice. Had hot ferromagnesian chondrules been immersed in the gas, they would have become ^{16}O-enriched by isotopic exchange. We conclude that the gas had gone when the ferromagnesian chondrules in ordinary chondrites formed, suggesting that nebular formation mechanisms are not consistent with the oxygen isotopic data.

In the CR group of carbonaceous chondrites some chondrules that include relict CAIs are enriched in ^{16}O (Krot et al. 2005). Others less enriched in ^{16}O do not have relict CAIs. Krot et al. (2005) suggest that these chondrules formed in nebular gas while its oxygen isotopic ratios were evolving to "heavier" values. Some early formed Al-rich chondrules may have equilibrated with nebular gas, but Al-rich chondrules in ordinary chondrites probably formed independently of CAIs (MacPherson & Huss 2000) and gas. The proposal of Lyons & Young (2005) that water became the carrier of "heavy" oxygen seems incompatible with the enstatite chondrites. These have terrestrial oxygen isotopic ratios (Clayton 1993) and highly reduced mineral assemblages with water-soluble sulfides (Keil 1968). Enstatite chondrites appear to have been completely dry (Grossman et al. 2000). Perhaps all disk solids, including silicates, carried excess ^{17}O and ^{18}O, inherited from the parent molecular cloud (Yurimoto & Kuramoto 2004).

3.3. A Model for Early Solar System History, Leading to Chondrule Formation by Giant Impacts

The means of "storing" CAIs for ~1.5 Ma until the earliest ferromagnesian chondrules formed and accreted is a serious problem. In addition, presolar dust must also have been available. The suggestion of Cuzzi et al. (this volume) that CAIs and dust could have been redistributed and held in a turbulent nebula until the formation of ferromagnesian chondrules is inconsistent with their near terrestrial oxygen isotopic ratios, if the gas was of solar composition. We argued above that ferromagnesian chondrules formed after the gas had been lost, which means that the dust must have been stored to avoid expulsion with the gas. We propose that CAIs and presolar grains were stored together in early formed bodies that were small enough to escape severe heating by ^{26}Al decay, but big enough, ~10 km (see Shu et al. 1997), to withstand inward drift to the protosun. After the gas had gone, some of the bodies fragmented to yield portions <10 km in size that were stable against orbital drift. We use "planetary" for bodies larger than a few km, but cannot set an upper limit to the size, which may have been larger than Mars.

The isotopic signatures, ages, mineralogy, textures and chemical compositions of the components of chondrites testify to the existence of diverse planetary objects when chondrite parent bodies accreted. Samples of such objects include: an olivine-plagioclase pebble, with H chondrite oxygen isotopic ratios, in Barwell, L6 (Hutchison et al. 1988); a Mn-rich microgabbro in Parnallee, LL3.6 (Kennedy et al. 1992); also in Parnallee, silica-bearing inclusions with strongly zoned pyroxenes and "heavy" oxygen (Bridges et al. 1995); an igneous clast in Semarkona, LL3.0 (see Hutchison 2004, Fig. 12.6); Ca-plagioclase glass with a Eu anomaly of +33, in Bovedy, L3.7 (Hutchison & Graham 1975). The pebble in Barwell and the CC-1 clast in Semarkona were "dated" by I-Xe and Al-Mg, respectively (Fig. 2). They formed at the same time as chondrules. Matrix in highly unequilibrated chondrites includes presolar grains with primordial noble gases that were not heated above 600°C (Huss & Lewis 1994). This matrix must have been held in small, unmelted bodies or in cool, near surface layers in larger bodies. Similar storage over ~1.5 Ma is required for CAIs, but many were partially altered, which implies that they were more strongly heated.

Table 2. Bodies contemporary with chondrule formation and accretion.

Diameter (km)	Composition and Thermal History
~10-70	1. Porous "matrix" with presolar grains, ices (and CAIs?). Heated and disrupted. The outer 1-4 km stayed cold (Wilson et al. 1999).
~1-6	2. Fragments of disrupted bodies, no longer heated. Stable against drift into protosun after dissipation of disk gas.
~30-150	3. Dehydrated centrally, followed by aqueously altered layer (after Young 2001) with CAIs; near surface composed of unaltered "matrix" with presolar grains and CAIs. Reassembled after early break-up?
~150-250	4. Compact, layered metamorphosed bodies; metamorphism decreases outwards to an aqueously altered subsurface layer? (after Bennett & McSween 1996).
>250	5. Differentiated, partly molten bodies; central metal-rich cores, partly molten mantles (Vesta, Mars?) then thin metamorphosed layers and aqueously altered subsurface?

As pointed out by Sanders & Taylor (this volume), rapid decay of ^{26}Al would have melted bodies >10 km in diameter, but they would have cooled by radiation and largely solidified within ~4 Ma. If, as we propose, chondrules formed by disruption of partly molten bodies over 50 Ma or more, larger bodies are needed to sustain the melts. An example of a younger, partly molten object is the eucrite parent body, which differentiated into core and mantle ~4 Ma after CAI formation and still contained melt ~10 Ma later, when the Serra de Magé basaltic meteorite formed. Eucrites are probably from the 500 km diameter asteroid, 4 Vesta (Gaffey 1997), so bodies of similar size existed during much of the time when chondrules were forming. Indeed, if chondrules formed intermittently over only 50 Ma, Mars-sized and Earth-sized bodies existed. Mars' core formed ~14 Ma after CAI formation (Fig. 2) and Earth's core was completed ~20 Ma later (Kleine et al. 2002).

In addition to igneous rocks, metamorphosed chondrites existed when chondrules formed. Bennett & McSween (1996) attempted to determine the size and history of ordinary chondrite parent bodies. Estimates of peak temperature and body radius depend on many variables, including initial temperature, degree of compaction, presence or absence of ices and initial $^{26}Al/^{27}Al$ ratio, which decayed with time. We know that the CC-1 clast in Semarkona had crystallised, its rare earth elements had cleanly partitioned between Ca-plagioclase and pyroxene and it had been excavated and cooled to Al-Mg closure temperature when the $^{26}Al/^{27}Al$ ratio was $(0.77\pm0.21)\times10^{-5}$ (see Hutchison 2004, Fig. 12.6). A higher ratio must have obtained when the parent body of CC-1 melted. We conclude that metamorphosed (Bennett & McSween 1996) and differentiated bodies of radii >85 km existed when the earliest chondrules in UOCs formed, ~1.5 Ma after CAIs (Fig. 2).

If melts were not sustained in 500 km asteroids for 50-80 Ma, some chondrule formation may have required larger bodies. Selective remelting and disruption by impact of olivine and/or Ca-poor pyroxene phenocrysts and solid mesostases in a planetary body might have produced chondrules. But without pre-existing melt there could have been no temperature control; the internal temperature of a convecting body is self-regulated (Tozer 1978). The products of impact or gravitational disruption of a convecting body would include solid debris, melts and vapour. If peak temperatures had a restricted range (Hewins et al. this volume) controlled by the formation mechanism rather than chondrule size, convection is implicated.

We tabulate (Table 2) the sizes and types of body whose disruption contributed chondrules and other material to accreting chondrite parent bodies.

The sequence of events that physically produces chondrule-sized objects and concentrates them on chondrite parent bodies is admittedly unclear. Here we briefly review some investigations that demonstrate that chondrules can form by impact. For the future, detailed modeling of the products of impact and disruption of planetary bodies is needed.

Geological materials shocked to high pressure approach the liquid-vapour phase boundary from the liquid side as they decompress, breaking up into an expanding spray of liquid droplets (Melosh & Vickery 1991). This model was applied to tektite formation, but probably applies also to chondrules. Benoit et al. (1999) found that droplets of chondrule size may be produced by impactors <10 km in diameter with a collisional velocity of 5 km/s. They also suggested that log-normal size distributions characteristic of chondrules may result from their formation rather than from later size-sorting. Separation of melt-rich "chondrules" from the huge volume of coeval fragmented rocks led Melosh et al. (2004) to consider impacts between lunar-sized or larger bodies. They suggest that such chondrules formed late, because of the time taken to grow the bodies. Against this, Chambers & Wetherill (2001) suggested that <200 bodies of 0.02 - 0.33 Earth mass formed within ~10^5 years of Solar System origin and that most of the mass within the early asteroid belt was vested in large bodies. The eucrite parent body and Mars differentiated early (Fig. 2), so batches of chondrules may have formed by impact on similar bodies. Tidal disruption of a small body during an approach to a large object may have liberated melt-rich droplets without the need for impact.

Crystalline Lunar Spherules (CLS) in Apollo 14 regolith breccias were modelled by Symes et al. (1998) in terms of impact processes. They demonstrated that glassy spherules and agglutinates were associated with small impacts, but formation of chondrule-like CLS required the largest impacts, such as the Imbrian event. It was noted that the proportion of CLS in the regolith is similar to that of chondrules in some carbonaceous chondrites.

There may be a paradox in models which suggest that high energy impacts are required to form chondrules: preservation and mixing of chondrules demand a less destructive regime (Holland et al. 2005). Early accreted large asteroidal bodies tended to rotate faster than coeval smaller bodies, so it seems that at one stage of Solar System evolution the difference in velocity (ΔV) between colliding bodies tended to increase. Collisions of small (~1 km) bodies with larger ones, however, act to reduce the angular momentum of the larger body, which reduces (ΔV) for subsequent impacts (see Lewis 2004). Early collisions between numerous small bodies and planetesimals would have been more frequent than collisions between larger bodies, so high (ΔV) collisions possibly were rare enough for the survival of chondrules on large planetesimals.

3.4. Hypervelocity Impacts in the Early Solar System

Excavation of igneous and metamorphic lithic clasts from their parent bodies and transport of fragments between orbital zones requires hypervelocity impact from ~1.5 Ma after CAI formation (Hutchison et al. 2001). Impact and redistribution of molten, differentiated material have been invoked in forming the Shallowater enstatite achondrite (Keil et al. 1989) ~4 Ma after CAI formation. Even earlier (Fig. 2), impact apparently stripped silicate from the metallic cores that were parental to 5 groups of magmatic iron meteorites (Kleine et al. 2005). Removal of silicate, containing Hf, from cores occurred before significant radiogenic ^{182}W had been produced by ^{182}Hf decay.

Early hypervelocity impacts are consistent with several evolutionary models of the zone between Mars and Jupiter. Here, many bodies apparently formed, some being Mars-sized or larger (Hughes 1991; Chambers & Wetherill 2001). Formation of the Moon by a giant impact on the early Earth (Hartmann & Davis 1975) is part of this scenario. High relative velocities of bodies require the presence of a large, gravitationally perturbing mass. Mars-sized bodies formed within ~10^5 years of Solar System origin may have been massive enough (Chambers & Wetherill 2001), but to us, a protojupiter seems more likely. The evidence that chondrules, eucrite parent body, Earth and Mars did not equilibrate with oxygen of bulk solar isotopic composition indicates that the accretion disk had lost its gas within ~1.5 Ma after CAI formation. Jupiter was, therefore, captured or had formed by gravitational collapse when gas was still abundant. In contrast, the "standard model" of giant planet origin by the formation of rocky cores and capture of gas takes ~10^7 years (see Chambers & Wetherill 2001).

4. Conclusions

Observations on chondrules and their contemporary materials strongly support a planetary origin for ferromagnesian chondrules. There is no evidence that chondrules formed from unreprocessed dust. We challenge the concept that ferromagnesian chondrules were rapidly heated and cite evidence that some large PO chondrules were derived from semi-molten igneous masses. Chemical variability, co-existence with igneous and metamorphic rocks and age and isotopic systematics militate against a nebular origin of most, if not all, chondrules. For the future, questions to be investigated include: What size of body was wholly or partly disintegrated to produce chondrules and igneous rock fragments? Can we numerically model the break-up of partly molten asteroids or larger bodies? Would an abundance of mm-sized, partly melted objects have resulted and, if not, how were chondrules size-sorted?

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