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Chondrule formation by repeated evaporative melting and condensation in collisional debris clouds around planetesimals

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Abstract-A synthesis of previous work leads to a model of chondrule formation that involves periodic melting of dispersed dust in debris clouds that were generated by collisions between chondritic planetesimals. I suggest that chondrules formed by the passage of nebular shock waves through these dust clumps, which temporarily surrounded disrupted planetesimals. Type I chondrules formed by more intense evaporative heating of fewer particles in tenuous clumps, or at the edges of dense clumps, and type II chondrules formed by less intense evaporative heating of more particles deeper within dense clumps. Chondrules reaccreted by self-gravity into the planetesimals, mixing with less heated dust and rock. This process of disruption, melting, and reaccretion could have repeated many times. In this way, chondrite components of various origins and thermal histories could remain preserved in planetesimals as a distinctive mix of materials for extended periods of time, while still allowing for a repetitive melting process that converted some of the planetesimal debris into chondrules. I also suggest that during chondrule formation, the inner solar nebula gas was evolving by the gradual incorporation and heating of icy bodies depleted in ¹⁶O, causing a general increase in gaseous Δ^{17} O with time in most places, especially close to the "snow line." In this model, early formed type I chondrules in C chondrites with lower Δ^{17} O values were produced inside the snow line, and later formed type I and type II chondrules in C and O chondrites with higher Δ^{17} O values were created nearer the snow line after it had moved closer to the young Sun.

INTRODUCTION

Probably no other problem in meteoritics has received as much debate as the origin of chondrules. One of the sharpest divides has been whether chondrules originated in "planetary" or "nebular" settings (e.g., Wood 1985; Grossman 1988; Zanda 2004; Sears 2004). A nebular origin for chondrules has been favored among most researchers in the last two decades (e.g., Wood 1985, 2005; Grossman 1988; Wasson 1993; Boss 1996; Hewins 1997; Rubin 2000; Jones et al. 2000; Zanda 2004; Scott and Krot 2005; Krot et al. 2009). More recently, planetary origins involving the formation of chondrules as either splash droplets or melt sheets excavated from molten or partly molten bodies (Sanders 1996; Lugmair and Shukolyukov 2001; Sanders and Taylor 2005; Hutchison et al. 2005; Asphaug et al. 2011) or as objects that contain fragments excavated from differentiated planetesimals (Libourel and Krot 2007; Libourel and Chaussidon 2011; Villeneuve et al. 2011; Faure et al. 2011) have been advocated.

In this paper, I suggest that chondrules formed in a nebular setting closely associated with planetesimals. By a nebular setting, I mean the early dusty and gaseous protoplanetary disk that surrounded the young Sun, with dust consisting mainly of submillimeter particles. By planetesimals, I mean those early formed asteroidal-sized objects, roughly one kilometer to hundreds of kilometers across, which were sufficiently large to avoid transport by gas drag and turbulence in the nebula (e.g., Chambers 2006). The model advocated is a hybrid between planetary and nebular origins for chondrules as it incorporates elements of both. It is shaped by, but not limited to, results obtained by the author on olivine- and olivine-and-pyroxene-rich chondrules (types IA, IIA, IAB, IIAB) and agglomeratic olivine-rich (AO) objects in LL3.1-3.5 meteorites (Ruzicka et al. 2007, 2008, 2012). No attempt is here made to explain the diversity of textural-mineralogical types of chondrules besides that of type I versus II, even though such textural and variations of mineralogical are importance in understanding chondrule formation. Moreover, the model presented is qualitative only. The author's intent is to provide a conceptual framework for the origin of chondrules, to stimulate debate on the nature of chondrule formation and chondrule-forming regions in the protoplanetary disk, and in so doing to perhaps guide further research on these topics. Before describing the model, I discuss some of the inferences upon which it is based.

INFERENCES

Chondrules Formed in a Nebular Setting

Researchers have long agreed that chondrules formed and cooled as independently floating melt objects in space (e.g., Wood 1985; Zanda 2004; Lauretta et al. 2006), which occasionally accreted dust mantles or condensates to form fine-grained rims, or which occasionally collided with one another to form compound chondrules (e.g., Grossman et al. 1988; Rubin 2000; Lauretta et al. 2006). Chondrule melts cooled relatively quickly below the liquidus, within a factor of a couple of approximately 100-1000 °C h⁻¹, based on textures and olivine zoning patterns (e.g., Hewins 1988; Jones and Lofgren 1993; Lofgren 1996; Desch and Connolly 2002; Hewins et al. 2005; Desch et al. 2012), with the higher values more consistent with trace-element data for chondrule olivine (Alexander 1994; Ruzicka et al. 2008). These cooling rates support the idea that chondrules cooled either in a localized dustv environment or in a warm gas (Hewins 1988; Grossman 1988; Hewins and Radomsky 1990).

Parts of type I (magnesian) chondrules in C chondrites known as granoblastic olivine aggregates (GOAs) may be annealed precursors to chondrules (Libourel and Krot 2007; Whattam et al. 2008; Whattam and Hewins 2009), annealed either within a differentiated planetesimal (Libourel and Krot 2007) or within a nebular setting (Whattam et al. 2008). But it is well established that most chondrules did not cool as complete entities in a thermally insulating parent body: they instead crystallized in a space environment.

It is also clear that chondrules must have formed in the protoplanetary disk (solar nebula) that existed at the beginning of the solar system. Ancient ages for chondrules are implied by dating with the Pb-Pb absolute chronometer and with a variety of short-lived chronometers (e.g., Kita et al. 2005; Krot et al. 2009), although others have noted that later I-Xe dates for some chondrules could indicate a more extended period of formation (Hutchison et al. 2005). More recent ages can be attributed to secondary processes (shock heating, thermal metamorphism, or aqueous alteration), but to explain the presence in chondrules of many daughter nuclides produced by the decay of short-lived radionuclides, the initial formation of chondrules must have occurred soon after the birth of the solar system, while a protoplanetary disk was still present (e.g., Kita et al. 2005; Krot et al. 2009; Dauphas and Chaussidon 2011).

Chondrules Formed by the Melting of Dust

Some chondrules formed by the melting of dominantly fine-grained of precursors nearly unfractionated (CI chondrite) composition. The best evidence for this comes from studies of agglomeratic objects in O chondrites that are rich in olivine, so-called agglomeratic olivine (AO) objects (Weisberg and Prinz 1996; Hewins 1997; Hewins et al. 1997; Hewins and Fox 2004; Ruzicka et al. 2012). AO objects often form accretionary structures that rim chondrules, and they show evidence for various degrees of mild heating effects, ranging from sintering, to weak melting, to more significant but still limited melting (Ruzicka et al. 2012).

Figure 1 shows an example of transitional variations in grain size and bulk composition between a weakly melted ferroan AO object and type II chondrules of different grain sizes. The variations are ascribed to progressive heating and evaporative melting. During progressive heating, melting was incomplete and grains were coarsened, producing first fine-grained type II chondrules, and then coarse-grained type II chondrules. Sulfur and sometimes Na were partly lost from AO objects to form the type II chondrules, with S loss occurring at an early stage of the heating. Melting probably occurred more than once to make the coarser grained chondrules. The same kinds of textural-chemical trends have been observed for magnesian AO objects and type I chondrules (Hewins et al. 1997). The observations imply that AO objects with bulk compositions similar to CI chondrites could have been the precursors to some chondrules.

AO objects contain fine-grained materials mixed with chondrule debris from both type I and type II chondrules, including larger xenocrystic grains that have compositions identical to those in chondrules, as well as relict chondrules (Fig. 1d) (Ruzicka et al. 2012). Thus, although AO objects can be regarded as protochondrules, they themselves postdated the formation of previous



Fig. 1. Diagram illustrating progression in texture and bulk chemistry between ferroan agglomeratic olivine objects and type II chondrules (Ruzicka et al. 2012). a, d) Bulk composition and BSE image of Beg-2 from NWA 4910 (LL3.1), a weakly melted AO object (AO-WM) that is dominated by ferroan olivine $\leq 5 \mu m$ across and which contains abundant troilite (troi, bright grains). The dashed area outlines a coarse region that appears to be a relict fine type II chondrule. b, e) Bulk composition and BSE image of NWA-21 from NWA 3127 (LL3.1), a fine type IIA chondrule fragment dominated by ferroan olivine phenocrysts approximately 5–60 μm across set in glass. Arrows indicate relict Mg-olivine grains of differing core compositions. c, f) Bulk composition and BSE image of BSE image of Beg-15, a coarse type IIA chondrule from NWA 4910, dominated by olivine phenocrysts approximately 10–250 μm across set in a mesostasis of glass and pyroxene crystallites. Arrows indicate relict Mg-olivine grains of differing core compositions, including a cluster of four small grains at the edge of the chondrule at left. Some phenocrysts show complex zoning, with magnesian olivine in an annulus within the grains, but all olivine grains have ferrous rims.

chondrules. This implies that AO objects formed as part of a recycling process involving the agglomeration of chondrule debris and a fine-dust component. The partly fine-grained, partly coarse-grained character of AO objects matches previous inferences for the precursors of chondrules (Hewins 1997; Rubin 2000).

Besides evaporation, some AO objects provide evidence for condensation. Figure 2 shows an irregularly shaped fine type II chondrule core surrounded by an AO rim, which itself has a troilite-rich periphery. The troilite fills the interstices between silicates (Fig. 2). These S-rich rims probably formed by an influx of S from a surrounding gas that reacted with the objects to form troilite, possibly by condensation of S in a lowtemperature Fe-Ni-S melt phase within the objects (Ruzicka et al. 2012). AO objects demonstrate the operation of both evaporation and condensation, but element mobility was limited to the most volatile elements.

The data for AO objects suggest the operation of melting, evaporation, and condensation phenomena



Fig. 2. BSE images of NWA-11A from NWA 3127 (LL3.1), which has an irregularly shaped fine type IIA core and a surrounding AO rim that is progressively more troilite-rich toward the edge of the object. a) Overview, showing broken edge at bottom indicating that NWA-11A is a fragment. The box outlines the area shown in part (b). b) Close-up of troilite-rich rim showing details of AO object texture. There is no evidence for melting of silicate areas (unmelted AO or AO-U type), which here contain an intimate mixture of unzoned ferroan olivine (Fe-ol), weakly zoned ferroan olivine (zoned ol), and magnesian olivine (Mg-ol). Troilite (troi, white) fills interstices between silicates in a network pattern.

operating on dispersed, fine-grained dust. The characteristics of the objects (evidence for mild heating and limited heating duration, accretionary structures, and occurrence of apparently broken debris) are consistent with heating by nebular shock waves (Ruzicka et al. 2012).

Melting Occurred in a Dusty, Nonsolar Gas Environment

AO objects appear to represent quasi-chondritic dusty chondrule precursors, but the melting events

needed for chondrules occurred in a gas that was far from solar in composition. It has been long recognized that gas in equilibrium with chondrules would have to be far more oxidizing than solar to stabilize FeO in silicates (e.g., Wood 1985; Fedkin and Grossman 2005) and to stabilize volatiles such as Na (e.g., Hewins 1988, 1997). To prevent too much evaporation, the gas would need to be strongly enriched in evaporated dust (D) relative to solar composition gas (G), with D/G approximately 10^4 – 10^6 (Alexander and Ebel 2012). An oxidizing gas is needed also to stabilize melts at relatively low (i.e., nebular) pressures (Ebel and Grossman 2000).

Figure 3 shows how chemical variations among ferroan AO objects and type II chondrules can be explained by evaporation and condensation effects occurring under high D/G (10⁴) values at 10^{-3} bar pressure. Heating of a CI chondrite-like precursor under these conditions causes first S and then Na loss to the gas, with the locus of type II bulk compositions obtained at a temperature of approximately 1600 K (Fig. 3b). Under these conditions, the type II chondrules will be partly molten, and olivine will have a ferroan composition similar to that observed. Sulfur evaporated in the same heating events can condense to form troiliterimmed AO objects, accounting for S/Al values in excess of CI chondrites (Fig. 3a). In contrast, heating under the same oxidizing conditions $(D/G = 10^4)$, but at lower pressure (10^{-6} bar) , misses the locus of type II chondrules, and heating under D/G = 1 does go through the locus of compositions, but at temperatures too low to result in melting (Fig. 3b).

Sulfur and Na mobility requires only mild heating, and this cannot explain variations in less volatile elements or in Si/Al ratios, observed for both AO objects and type II chondrules (Fig. 3a). Such variations must reflect variations in the precursor objects. These precursors could have started as CI chondrite-like dust, but later obtained variable proportions of olivine, pyroxene, and feldspathic components, through the sampling of small parcels of heterogeneous AO object and chondrule materials (Weisberg and Prinz 1996; Ruzicka et al. 2012).

Melting and Mixing Events Occurred Repeatedly

There is good evidence from the presence in chondrules of relict grains (mainly olivine) that chondrules experienced repetitive melting events (e.g., Nagahara 1981; Rambaldi 1981; Kracher et al. 1984; Jones 1996). Relict grain cores represent crystallization from one melting event, and other nonrelict (normal) grains in the chondrules represent a different, later melting event. There are two basic kinds of relict olivine grains, which include (1) Mg-olivine relicts that



Fig. 3. Variation diagrams showing bulk compositions of ferroan AO objects and type II chondrules compared with equilibrium condensate trajectories, shown for systems with "cosmic" and "dust-enriched" $(D/G = 10^4)$ (solar) compositions at two different pressures $(10^{-6} \text{ and } 10^{-3} \text{ bar})$ (Ruzicka et al. 2012). "T" with arrow indicates increasing temperature. AO-U and AO-WM are unmelted and weakly melted AO types, respectively; AO-M are more significantly melted AO objects that contain definite glass regions; Type II chondrules include both fine and coarse varieties. "I" labels represent objects transitional to type I. a) Si/Al versus log S/Al, showing all objects. AO objects with troilite-rich rims have high S/Al, whereas type II chondrules have much lower S/Al. b) Na/Al versus S/Al, objects with S/Al < 10 only. Values close to lines are temperatures in Kelvin. A cluster of type II chondrule and AO object compositions can be matched with the dust-enriched case at a temperature of approximately 1578 K and 10^{-3} bar. The same cluster can be matched for a cosmic composition, but only at subsolidus temperatures.

crystallized from melts more magnesian than the surrounding chondrule and (2) dusty olivine relicts that crystallized from melts more ferroan than surrounding chondrule and which underwent reduction to form finely exsolved (dusty) metal.

The presence of relict grains implies de facto mixing of chondrule components on a subchondrule scale. The mixing process could have been primarily physical, caused by the collision of xenocrystic grains with independently formed melts. Or it could have been primarily thermochemical, with partial remelting of chondrules occurring under different conditions (e.g., temperature, fO_2 , system composition) than that which produced pre-existing relict olivine grains.

An example of repeated melting is provided in Fig. 4, which shows a type II chondrule that contains typical normal olivine grains, and four different relict olivine grains that crystallized from separate batches of melt. Two olivine grains (#2 and #3) have small relict Mg-olivine cores; an anomalously large grain has a large relict Mg-olivine core (#1); and another grain appears to have been a dusty olivine relict that lost dusty metal by subsequent oxidation (#4). All of these grains are overgrown by ferrous olivine that has a similar composition to other normal igneous olivine grains in the chondrule, which must have crystallized last.

The processes affecting these relict grains were varied. For relict #4, olivine crystallized from an FeOrich melt (stage 1); then, the olivine was FeO-reduced to make fine metal precipitates and more magnesian olivine (stage 2); and finally, the grain was immersed into the host chondrule melt where it was oxidized and grew an overgrowth (stage 3). Thus, relict #4 was affected by three separate events, each of which probably involved a melting episode under different conditions. The large relict #1 in Fig. 1 has anomalously high Mn/Fe compared with other grains, suggesting that it was affected by FeO reduction (see below, and Ruzicka et al. 2008). For relict #1, one can surmise first crystallization from an FeO-rich melt (stage 1); then remelting and FeO reduction of the melt out of which the large olivine crystallized (stage 2); and finally, incorporation of the relict grain inside the current FeO-rich chondrule melt accompanied by formation of an overgrowth (stage 3). Thus, relict #1 was also affected by three separate melting events, possibly the same as for relict #4, but with the grain processed in a different way. Relict #2 crystallized from a separate, refractory and magnesian melt not identical to that of any of the other melts, before being incorporated into the present FeO-rich chondrule melt.

The main point of this example is that repeated, varied melting events affected individual grains in the chondrule. Models of chondrule formation must be able to account for this sort of complexity. Specifically, any viable hypothesis for chondrule origin must take into account repeatable melting or heating, and processes that can result in mixtures of different batches of grains and melt, without destroying the evidence for these.

The assembly of relict grains and host melt must have involved brief heating and subsequent rapid cooling, to allow preservation of the relict grains as discrete entities. Magnesian olivine relicts might be able to persist as physical entities in ferrous melts for a period of time



Fig. 4. Backscattered electron (BSE) images of NWA-8, a type IIA chondrule fragment from NWA 3127 (LL3.1) that contains at least four relict olivine grains. #1 is an unusually coarse relict Mg-olivine grain that has high Mn/Fe compared with other normal olivine grains (Fig. 5c). #2 and #3 are small relict Mg-olivine grains. #4 appears to be a modified dusty olivine that has an unusually ferrous composition for grains of this type (Fig. 5c). a) Overview of chondrule. b) Close-up of relict #2, showing rare dusty metal (tiny bright inclusions) and voids probably created by oxidation of dusty metal. c) Close-up of relict #2, showing a small magnesian core and ferrous overgrowth. Olivine crystals are set in glass.

owing to their higher melting temperatures, but their distinctive compositions would be destroyed by too much diffusional exchange between the grains and surrounding melts. Models of chemical exchange between relict cores and overgrowths suggest that heating and cooling must have occurred over a short timescale of minutes to hours (Greeney and Ruzicka 2004; Hewins et al. 2009). Dusty olivine relicts also must have experienced a limited timescale for heating and cooling to prevent the destruction of their fine metal precipitates. The data imply repeated, brief melting events for chondrules.

Olivine Grains Record Heating and Redox Effects

Trace element data for olivine provide good evidence that chondrules experienced variable degrees of thermal and redox processing (Ruzicka et al. 2007, 2008). The chemical variations in olivine are consistent with suggestions that chondrules behaved as open systems (condensate-gas exchange), and specifically, that type I (magnesian) chondrule melts could have formed by the evaporation and FeO-reduction of type II (ferroan) chondrule melts (Huang et al. 1996; Sears et al. 1996; Cohen et al. 2004; Sears 2004). Olivine shows a continuum in major- and traceelement compositions across a large range of Fa contents, with systematic trends suggestive of vapor fractionation (evaporation or condensation) (Fig. 5). Olivine that is forsteritic is enriched in refractory elements (e.g., Ti, Sc) and depleted in volatile elements (e.g., Mn, Rb) (Fig. 5). These variations are not related to mineral/melt partition coefficients, as forsteritic olivine is depleted in both highly incompatible and semi-incompatible elements (Rb and Mn, respectively), and forsteritic olivine is enriched in both highly incompatible and semi-incompatible elements (Ti and Sc, respectively).

The data suggest that magnesian olivine was more heat-processed than ferroan olivine, either by more extensive evaporation or by condensation at a higher temperature (Ruzicka et al. 2008). Given the evidence that chondrules formed by the melting of pre-existing materials, a difference in evaporation extent is at least part of the explanation, although there is also evidence that condensation was an important process (see below and next section).

The olivine grains are igneous and reflect differences in parental melt composition. Using data for coolinginsensitive elements least susceptible to disequilibrium



Fig. 5. Variation diagrams for olivine composition in chondrules from LL3.1–3.5 chondrites based on SIMS analyses, keyed by grain types (Ruzicka et al. 2008). a) Fe versus Ti. b) Fe versus Sc. c) Fe versus Mn. The dashed line is a regression for all normal olivine grains. r#1 and r#4 refer to the relict grains shown in Fig. 4. d) Fe versus Rb. Grain types: Normal olivine is a nonrelict grain often showing evidence for core-rim igneous zonation; lines connect core-rim values for the same grains (all grain rims are more ferrous). Relict dusty olivine grains and relict Mg-olivine grains have fine dusty metal cores and unusually magnesian compositions compared with other olivine grains in the host chondrule, respectively. Clear olivine is nondusty igneous olivine co-existing with dusty olivine in the same chondrule. Overgrowth olivine refers to ferrous olivine overgrowing Mg-olivine relict grains. Isolated olivine grains are coarse grains existing either as individual grains or with only a small amount of adhering mesostasis.

effects, one finds a systematic difference in the composition of the parental melts calculated for average olivine in type I and type II chondrules, with the former enriched in refractory elements and depleted in volatile elements, and the latter having a less fractionated composition (Fig. 6a). More extensive heating for magnesian type I olivine compared with ferrous type II olivine mirrors the inferences made for bulk type I and type II chondrules, respectively (e.g., Scott and Krot 2005; Lauretta et al. 2006).

To explain the difference in abundances between type I and type II parental melts by a difference in evaporation degree would require substantially more evaporation for type I than type II. The most refractory elements (Al, Sc, Ti, Y) are enriched by a factor of approximately $2-3\times$ in average parental melts for type I suggesting compared with type II (Fig. 6a), approximately 50-66% evaporation of a typical type II melt to make a typical type I melt. Even more evaporation (>90%) would be necessary to make the most Ti- and Sc-enriched forsterite from a type II melt, accompanied by an almost complete loss ($\geq 99\%$) of more volatile elements such as Mn and Rb.

Oxygen isotopic compositions are consistent with the idea that type I and type II chondrules were heated differently. Olivine and pyroxene grains in chondrules from O chondrites mainly lie on a mass fractionation trend, which can be explained by type I chondrules having formed as high temperature condensates after repeated evaporation events, and type II chondrules having formed by melting of precursor dust (Kita et al. 2010).

Besides formation at different temperatures, olivine grains in chondrules show good evidence of having been formed under different fO_2 conditions. Siderophile elements such as Co and Ni are strongly depleted in magnesian olivine grains, indicating that these grains formed under more reducing conditions. Phosphorus appears to have acted as a siderophile element in the most reducing melts, and there is evidence for a change in partitioning behavior of V caused by a decrease in valence state in the most reducing melts (Ruzicka et al. 2008). The high metal contents in type I chondrules compared with type II are thus explained by the formation of type I chondrules under lower fO_2 than for type II chondrules. Redox and thermal processing of chondrules evidently were linked.



Fig. 6. Calculated parental melt compositions for olivine; shown are cooling-rate-insensitive elements arranged according to volatility (50% condensation temperatures, as given by Lodders 2003), using the same dataset as in Fig. 5. a) Average type I chondrule grain cores and average type II chondrule grain cores. b) Average relict Mg-olivine and average relict dusty olivine. Error bars refer to standard deviations of the mean values.

Redox effects are also apparent from Mn/Fe systematics in olivine. During FeO reduction, the Mn/Fe ratios of grains would have increased, so dusty olivine grains, coexisting nondusty ("clear") olivine grains, and some other grains that have elevated Mn/Fe compared with the normal olivine Mn/Fe = 0.017 value in O chondrites probably experienced FeO reduction (Fig. 5c).

Thus, olivine compositions show good evidence for volatility and redox effects, but there is no evidence for igneous differentiation in a large-scale (> chondrule-sized) system. This conclusion agrees with studies of bulk chondrule compositions (e.g., Grossman 1988; Grossman et al. 1988). It should be noted that individual chondrules have bulk compositions that are not always a smooth function of volatility. For example, bulk Ca/Al values are sometimes fractionated, which has been taken to indicate planetary (differentiation) processes (Hutchison et al. 2005). However, such discrepancies do not necessarily

invalidate an important role for volatility, nor indicate igneous differentiation, as chondrule bulk compositions may partly reflect a sampling effect (see above). For instance, more or less sampling of Ca-bearing phases such as Ca-bearing pyroxene compared with Al-rich phases such as glass could potentially explain variations in bulk Ca/Al for chondrules. Variable sampling of condensate precursor phases heated to differing extents (along with the operation of FeO reduction and metal loss) appears to be a promising way to explain the bulk chemical data for chondrules (Alexander 1994, 1996).

Chondrules Formed Under Fluctuating Conditions

There is good evidence that type I and type II chondrules often contain recycled material of the other chondrule type. The importance of this is twofold (1) it proves that varied chondrule components were precursors to later formed chondrules and (2) it indicates that repeated chondrule formation occurred under fluctuating conditions.

Evidence for transformation of type II to type I chondrules is provided by the characteristics of relict dusty olivine grains and coexisting clear olivine grains in chondrules from O chondrites. The average parent melt for relict dusty olivine (Fig. 6b) has a composition similar to that inferred for parental melts in type II chondrules (Fig. 6a). This implies that relict dusty olivine in type I chondrules was derived from ferroan olivine from type II chondrules (Jones 1996; Jones and Danielson 1997; Ruzicka et al. 2008). The metal precipitates in dusty olivine indicate FeO reduction, and as noted above, this is consistent with an elevated Mn/Fe ratio in these grains. Although they lack dusty metal, an elevated Mn/Fe ratio is also observed for coexisting clear olivine in the chondrules (Fig. 5c). These clear grains crystallized from the host chondrule melts, so the melts themselves were evidently affected by FeO reduction. Besides FeO reduction, the transformation of type II to type I also involved evaporation. Clear olivine is enriched in refractory elements compared with ferroan type II grains (Ruzicka et al. 2008). In addition, the O-isotopic compositions of some dusty and clear olivine pairs in type I chondrules are consistent with mass fractionation between the two grain types (Ruzicka et al. 2007; Kita et al. 2010), suggestive of clear olivine having crystallized from evaporated melt involving kinetic isotope mass fractionation (Ruzicka et al. 2007). Using estimated equilibrium isotope partition functions, Kita et al. (2010) modeled the O-isotopic composition of typical olivine and pyroxene grains in type IA chondrules as condensates of vaporized residues, and in type IB chondrules as condensates of evaporated gas, after multiple heating events affecting ordinary chondrite-like dust. Type II



A = FeO reduction & grain immersion in volatile-depleted melt; B = melting + FeO reduction + evaporation; C = grain immersion in oxidized, volatile-rich melt; D = melting + oxidation + volatile addition

Fig. 7. Diagram schematically indicating recycling of type I and type II components. Arrows labeled A, B, C, and D refer to different thermal and redox processes. a) BSE image of Sah98-1, a type IA chondrule fragment from Sahara 98175 (LL3.5), which contains magnesian olivine and low-Ca pyroxene grains (dark) set in glass, a large cluster of relict dusty olivine grains (outlined), and coarse metal (bright grains). b) BSE image of NWA-12, a type IIA chondrule fragment from NWA 3127 (LL3.1), which contains one large relict Mg-olivine grain (circled) and two smaller ones, and more typical ferrous olivine grains, all set in glass.

chondrules were regarded as having formed by the melting of chondritic dust under oxidizing conditions. Thus, the data are consistent with the idea that type II chondrules were transformed to type I chondrules by FeO reduction and evaporation (Huang et al. 1996; Sears et al. 1996; Cohen et al. 2004; Sears 2004), possibly involving one or more condensation steps (Kita et al. 2010), following reheating under lower fO_2 conditions.

Evidence for the reverse process, transformation of type I to type II chondrules, is provided by the characteristics of relict Mg-olivine grains and normal ferroan olivine grains in type II chondrules from both C and O chondrites. The parent melt for average relict Mgolivine (Fig. 6b) is similar to that inferred for the parent melts in type I chondrules (Fig. 6a). This suggests that relict Mg-olivine in type II chondrules was derived from magnesian olivine in type I chondrules (Jones 1996; Ruzicka et al. 2008). As the normal olivine in type II chondrules crystallized from a less refractory melt than the relict Mg-olivine grains (Fig. 6), the last episode of melting occurred under conditions of higher fO_2 and produced a more volatile-rich melt.

It therefore appears that type I and type II chondrules were recycled into one another (Fig. 7). FeOrich melts and ferroan olivine grains from type II chondrules were converted to FeO-poor and volatile-poor melts and grains, by reduction and evaporation. FeO-poor melts and magnesian olivine grains were converted into FeO-rich and volatile-rich melts by oxidation and volatile addition.

Volatile addition to create type II chondrules from type I precursors could have occurred by gas-to-melt condensation, involving an influx of volatile elements into chondrule melts (Ruzicka et al. 2008). For example, Si addition to chondrule melts from a SiO gas has been proposed to explain pyroxene-rich igneous rims in type I chondrules, SiO₂-rich igneous rims on chondrules, and Si enrichments in glass (Tissandier et al. 2002; Krot et al. 2004; Hewins et al. 2005; Libourel et al. 2006; Libourel and Krot 2007; Nagahara et al. 2009). Besides Si, there is evidence that more volatile elements (Na, K, FeO) could have entered melt droplets (Ruzicka 1988; Georges et al. 2000; Nagahara et al. 2009), although Grossman et al. (2002) argued that common alkali metasomatism of type I chondrules in Semarkona (LL3.0) was probably produced by light aqueous alteration. Conversion of type I to type II chondrules also could have occurred indirectly, by the accretion of volatile-rich fine-grained materials (e.g., AO object rims) onto type I chondrules or their fragments, which were then remelted to create type II chondrules (Ruzicka et al. 2012).

Chondrules From Magmaspheres?

Recent ideas call for chondrule components to have been derived from the magmaspheres of heated planetesimals. There are two variants of this hypothesis: Either the olivine grains themselves crystallized from large-scale magma bodies (e.g., Libourel and Krot 2007; Libourel and Chaussidon 2011; Villeneuve et al. 2011) or the melt from these bodies was dispersed into space by collisions (e.g., Sanders and Taylor 2005; Asphaug et al. 2011). In both cases, the decay of 26 Al (or some other short-lived radionuclide) within planetesimals is the main heat source for chondrule formation.

The olivine data shown in Fig. 5 cannot be easily accommodated by the specific model put forward by Libourel and Chaussidon (2011) for type I chondrule olivine in C chondrites. This model involves correlated FeO reduction and olivine crystallization on a large scale (magma ocean). Thus, enrichments in refractory incompatible trace elements for magnesian olivine are ascribed to the combined effect of (a) FeO reduction to remove Fe from the system, and (b) crystal-liquid fractionation to enrich later formed olivine in incompatible elements.

There are problems with applying this model to chondrules in O chondrites. (1) Rb is more highly incompatible than any of the other elements shown in Fig. 5, so according to this model it should be the most enriched in magnesian olivine, but, in fact, it is highly depleted. (2) It is unclear why magnesian olivine would be strongly depleted in Mn, which is a semi-incompatible element that should approximately maintain a uniform abundance in melt during FeO reduction. (3) The reason for progressive FeO reduction in a crystallizing magma ocean is not apparent, whereas it is easier to understand if chondrules were heated in gases of differing compositions. (4) Trace element compositions of olivine grains including relict and nonrelict types suggest disequilibrium during crystallization, most likely caused by rapid cooling (Ruzicka et al. 2008). This is not what one would expect for cooling within a magma ocean.

The Mg-isotope data presented by Villeneuve et al. (2011) imply crystallization of olivine from melt systems with different ²⁶Al contents. Such different melt systems potentially could be established by vapor fractionation processes occurring over time, so one is not forced to choose between only (1) a differentiating magma ocean or (2) an evolving chondritic system of one composition, the alternatives presented by Villeneuve and coworkers.

One might invoke efficient degassing of the melted interior of a planetesimal to explain the observed vapor fractionation effects, but such efficient degassing of a molten planetesimal, especially if capped by a substantial unmelted lid, would not be expected (Sanders and Taylor 2005; Asphaug et al. 2011).

Removal of melt from within a molten planetesimal to crystallize as chondrules in space does not face the same set of problems, provided that this leads to no record of differentiation either in the olivine grains (see above) or in the bulk chondrules (Grossman 1988; Grossman et al. 1988). This seems unlikely, although if no significant differentiation occurred, there would be no record of it. However, the molten planetesimal model has difficulty in plausibly explaining the detailed observations for relict grains and chondrule formation under fluctuating conditions, as explained below.

With molten planetesimals, one has to explain type I and type II chondrules, as these are fundamental varieties of chondrules. Sanders (2011) and Sanders and Scott (2011, 2012) proposed that type I chondrules formed by melt ejection from refractory, reduced planetesimals closer to the sun, and that type II chondrules formed by melt ejection from more oxidized. volatile-rich planetesimals farther from the sun. This implies the inheritance of planetesimal compositions from a preaccretionary era, in which planetesimals accreted from grains (presumably condensates), which reflect an overall temperature gradient throughout the nebula, much in the way that different planets in the solar system reflect their different formation locations (e.g., Lewis 1995).

To account for the observations presented here and elsewhere, type I and type II chondrules or their components would have to become mixed after their formation, so that they could become precursors to each other. Although this would be possible in a nebular environment, the chondrules could not be remelted by ²⁶Al unless they reaccreted inside a planetesimal. Grains could not be completely remelted without destroying the evidence for relict grains, nor could the grains be soaked indefinitely in the hot interior of a planetesimal without erasing the chemical-petrographic features of the grains. Thus, while ²⁶Al decay might work once for melting, it is more difficult to explain the evidence that chondrule grains were repeatedly heated or melted under rapid heating and cooling conditions, and that the grains preserved the signatures of these different events.

The only recourse seemingly would be to deliver grains to a cool lid within a hot planetesimal, and to mix these grains with melt from the interior of the planetesimal upon collisional ejection (Sanders and Taylor 2005). This might work, except it seems problematic to cycle between type I and type II host melts if these compositions were derived from different melted planetesimals separated in space. The chondrule particles of one type (e.g., type I) would have to be transported to the cool lids of planetesimals of the different type (e.g., type II), partly melted, and moved back and forth between type I and type II planetesimals repeatedly in some cases. If type I and type II planetesimals did not form in different regions of the nebula, this might ease the transport problem. But if the planetesimals formed close to one another, it would not explain why some planetesimals were type I and others were type II. In any case, with this model, chondrite components would seemingly become thoroughly scrambled between planetesimals. With so much mixing,

however, it might be a problem to maintain discrete batches of chondrite planetesimals (Jones 2012).

Based on currently available data, most of the chemical and petrographic features of chondrules evidently have little to do with large-scale melt zones within planetesimals. I suggest instead that chondrule attributes were largely established by processes operating on melt droplets dispersed in space. Still, the observations do not preclude the possibility that some components in chondrules were derived from hot or even molten planetesimals (Libourel and Krot 2007).

Chondrules Formed in Varied Oxygen Isotope Reservoirs

In the last decade, much O-isotope data were obtained for chondrule phases (e.g., Krot et al. 2009; Kita et al. 2010; Libourel and Chaussidon 2011), and the self-shielding hypothesis has been developed, which explains nonmass-dependent oxygen isotope variations in chondrites in terms of mixing between C¹⁶O-rich gas and H_2^{17} O-rich and H_2^{18} O-rich ice components (e.g., Clayton 2002; Yurimoto and Kuramoto 2004; Lyons and Young 2005: Lyons et al. 2009). Oxygen isotope diffusion in olivine is extremely slow (Ryerson et al. 1989) compared with that in melt (Lyons et al. 2009), so that in brief heating and cooling events, the O-isotope composition of chondrule olivine will reflect the composition of the melt from which it crystallized (Ruzicka et al. 2007). If chondrules formed in a nebular environment as believed, the melt composition should largely reflect the composition of coexisting gas at time of melting (Ruzicka et al. 2007; Kita et al. 2010; Nagahara and Ozawa 2012). If instead the olivine crystallized from magma in planetesimals, the O-isotope composition would reflect the composition of the planetesimal (Libourel and Chaussidon 2011). In either case, the O-isotopic composition of olivine reflects the composition of the reservoir in which it formed. It appears that this reservoir varied in space and time, which provides important evidence for the formation and evolution of chondrules.

Measurements of Δ^{17} O for olivine from chondrules imply that there are at least two overarching O-isotope populations, one with low Δ^{17} O (<-4%) and one with high Δ^{17} O (>-4%) (Ruzicka et al. 2007) (Fig. 8). Smaller subgroups have been proposed for type I chondrule olivine (Libourel and Chaussidon 2011), but Fig. 8 emphasizes the bigger picture. In a broad sense, most olivine from both type I and type II chondrules in O chondrites belongs to the high Δ^{17} O group (e.g., Kita et al. 2010), whereas most olivine from type I chondrules in C chondrites belongs to the low Δ^{17} O olivine group (e.g., Krot et al. 2009; Libourel and Chaussidon 2011; Rudraswami et al. 2011; Ushikubo et al. 2012) (Fig. 8). Thus, there is a systematic difference



Fig. 8. Chemical and O-isotopic compositions of olivine in chondrules from LL3.2-3.4 chondrites, keyed by grain type (using the same nomenclature as in Fig. 1) (Ruzicka et al. 2007). A dashed line separates data into low Δ^{17} O and high Δ^{17} O groups. The low Δ^{17} O group contains magnesian olivine only, including some relict Mg-olivine grains from type II chondrules, as well as isolated olivine fragments. These grains generally have compositions which resemble the composition of Mg olivine from the predominant type I chondrules in C chondrites (box labeled "C, type I ol") (Libourel and Chaussidon 2011; Rudraswami et al. 2011; Ushikubo et al. 2012). Relict Mg-olivine grains in this group that lie at lower Fo values probably reflect partial Fe-Mg equilibration with more ferrous olivine melts during chondrule formation. The high Δ^{17} O group includes olivine of widely varying Fo content from both type I and type II chondrules in O chondrites, including both normal igneous olivine and dusty olivine relicts. Average compositions of olivine and pyroxene in chondrules from O chondrites are shown (box labeled "O, avg type I & II ol & px") (Kita et al. 2010). The high Δ^{17} O group also includes some olivine from type I and type II chondrules in C chondrites (Libourel and Chaussidon 2011; Rudraswami et al. 2011; Tenner et al. 2011, 2012; Ushikubo et al. 2011, 2012).

in oxygen isotope reservoir compositions between the two chondrite classes.

However, in detail, olivine O-isotope compositions overlap between the classes. Some (not all) Mg-olivine relict grains in type II O chondrules crystallized in a similar oxygen reservoir to that for typical type I chondrules in C chondrites (Ruzicka et al. 2007; Kita et al. 2010), and some isolated Mg-olivine grains (probably derived from fragmented type I chondrules) in the O chondrites also crystallized from this same reservoir (Fig. 8). Moreover, the less common type II olivine in C chondrites crystallized in the relatively high Δ^{17} O group, although often with lower Δ^{17} O than typical for olivine in O chondrites (Ushikubo et al. 2011, 2012; Rudraswami et al. 2011; Tenner et al. 2011, 2012). To summarize, type II chondrule olivine mainly formed in a high Δ^{17} O reservoir, whereas there were at least two different reservoirs for type I chondrule olivine, one with low Δ^{17} O and the other with high Δ^{17} O.

These reservoir compositions are partially decoupled from the intensity of heating events inferred for chondrules (Ruzicka et al. 2007). Thus, chondrules from the high Δ^{17} O reservoir consist of both type I (more heat-affected) and type II (less heat-affected) chondrules, although the low Δ^{17} O group appears to consist only of the more heat-affected type I chondrules.

A mostly one-way change to higher Δ^{17} O with time has been repeatedly inferred for chondritic materials (e.g., Clayton 1993; Bridges et al. 1998; Wasson et al. 2004; Krot et al. 2005b, 2006; Ruzicka et al. 2007), based in part on inclusion relationships. That is, relict grains had to form before the surrounding host chondrule melts, and relict CAIs and AOAs in chondrules (which almost always have Δ^{17} O much lower than chondrules—e.g., see summary by Krot et al. 2009) had to form prior to the host chondrules. One can confidently conclude from these data that the reservoir(s) generally evolved to higher Δ^{17} O with time. This conclusion does not depend strongly on the choice of models, nor on the identity of the reservoir(s). Although a general trend to higher Δ^{17} O with time is well established, relative ²⁶Al dating does not support a simple time progression as the only explanation for changes in Δ^{17} O, implying instead that formation location was also important (Kita et al. 2005, 2010; Krot et al. 2009; Tenner et al. 2011; Kita and Ushikubo 2011). Thus, the data suggest two causes for changes in $\Delta^{17}O$, one reflecting differences in formation time, and the other reflecting differences in formation location.

Planetesimals Were Present

Although heating and processing of chondrules appear to have occurred in a nebular setting, I suggest that chondrules formed in the vicinity of planetesimals and that these planetesimals played an important role in the storing and mixing of chondrules and other chondrite components.

The main reason for asserting the presence of planetesimals is the very high D/G values that are inferred for chondrule formation, especially for type II chondrules. For such chondrules, I have suggested D/G up to approximately 10^4 – 10^5 (Ruzicka et al. 2012), which appears to require a gas that was formed almost entirely by the vaporization of O-bearing dust. Gas enriched in such vaporized dust requires a concentrated dusty environment to begin with. A gas with high values of

D/G (approximately 10^4 – 10^6 or higher) for both type I and type II chondrule melts was implied by Alexander and Ebel (2012) to prevent excessive evaporation of Na, FeO, and Fe in chondrule melts. A high number density of melted chondrules is needed to explain compound chondrules formed by collisions of melt droplets (Alexander and Ebel [2012]; and references therein). Finally, an environment containing numerous melt droplets generating their own gas by evaporation is favorable for preventing kinetic isotopic mass fractionation effects, which mainly are not observed in chondrules (e.g., Cuzzi and Alexander 2006). All of these considerations suggest a dusty formation environment for chondrules, which implies proximity to а planetesimal (Alexander et al. 2008; Hewins et al. 2012).

For nebular regions enriched in dust, self-gravitation to form planetesimals is possible. For D/G approximately 10–100, accretion to form planetesimals can occur, although the time for complete collapse under these conditions is long, approximately 3 Ma (Chambers 2010). The collapse timescale is shorter for denser dust accumulations, perhaps approximately 300–30 orbits for D/G approximately 10^4 – 10^6 , respectively (Cuzzi et al. 2008). These collapse times correspond to dust clumps experiencing nebular gas headwinds, but do not include the possible effects of other processes such as shock waves or already-formed planetesimals.

A key advantage to forming chondrules in selfgravitating lumps that can produce planetesimals is that it provides a means of storing and preserving components. Clumps that have not yet accreted could be "leaky," but those that have already accreted into a planetesimal will be less so. With the accretion of chondrite components (chondrules, matrix, CAIs, metal, etc.) into planetesimals, the components will not be easily redistributed by nebular gas drag or turbulence, potentially allowing them to be maintained in their formation regions for millions of years or more. Different batches of chondritic materials, each corresponding to a different chondrite group, can be preserved in a substantially closed system, if accretion is sufficiently rapid (Wood 2005).

THE MODEL

The model proposed here involves nebular shock waves (e.g., Connolly and Love 1998; Desch and Connolly 2002; Desch et al. 2005) acting on collisional debris clouds produced by impacts between planetesimals (Fig. 9). Debris clouds that were highly enriched in dust would probably be self-gravitating, and would undergo reaccretion. However, if a nebular shock wave passed through the cloud before reaccretion was complete, some particles could melt to form chondrules.



Fig. 9. Cartoon of model proposed in this paper. a) Early type I Chondrule era. b) Late type I and type II chondrule era. YSO = young stellar object, our forming sun. Snow line = H_2O gas condensation front.

Not all of any given planetesimal would need to be heated to the same extent—only particles lofted sufficiently far from the center of the disrupted planetesimal and not reaccreted by the time of nebular shock wave passage would undergo chondrule formation. Following reaccretion, the process of collisional disruption, with or without shock wave melting, could occur again, with debris clouds consisting of both recycled chondrule debris and finer-grained dust, the necessary precursors to later formed chondrules.

A version of this model was proposed by Weidenschilling et al. (1998) and Weidenschilling and Cuzzi (2006), who suggested that an early generation of planetesimals was destroyed by collisions, after planetesimals were gravitationally excited following the formation of Jupiter. Nebular shock waves generated by planetesimals or planetary embryos then acted upon the debris to produce chondrules. Weidenschilling and Cuzzi (2006) suggested that the first generation of planetesimals were composed of early formed refractory components such as CAIs and possibly AOAs. However, the specific model proposed here envisions a repetitive process operating on multigenerational chondritic planetesimals that could contain other constituents such as previously formed chondrules, matrix, and agglomeratic objects.

Type I and type II chondrules could have formed in different environments within the clouds. I suggest that type I chondrules formed in smaller, lower pressure clouds with fewer dust particles, or at the edges of larger clouds where gas pressures and particle densities were not as high. Type II chondrules would have formed deeper within the clouds, where particle densities and gas pressures were higher. AO objects could have formed in either denser or more tenuous clumps, and could have become ferroan or magnesian, respectively.

The idea of different formation environments for type I and type II chondrules in a given dust-rich region of the nebula is similar to one previously proposed (Cohen et al. 2004). For the type I chondrules, lower pressures would promote more evaporative loss of volatiles, and lower dust loading could have enabled particles to cool more slowly (Desch and Connolly 2002), which would also promote more loss of volatiles, thereby explaining the more refractory compositions of type I chondrules. Fewer heated particles would produce less O-bearing gas, accounting for the more reducing conditions under which type I chondrules formed. To make type II chondrules, it would seem that larger debris clouds with relatively large numbers of particles would be needed, with more particles being heated, but not so intensely, resulting in high gas pressures, but less evaporative loss, per given chondrule melt.

It is important to emphasize that this model, which calls for a nebular setting for chondrule formation, involves formation in clouds that were very different from the surrounding less dusty, lower pressure, more Hrich ambient nebular gas. Clouds were sufficiently dense to allow significant back reaction between gas and melt, hindering complete evaporative loss of volatile elements, preventing kinetic isotope mass fractionation effects, and allowing re-entry of volatiles into chondrule melts upon cooling. A "canonical" low pressure, H-rich gas was not relevant for chondrule formation.

A recurrent cycle of disruption and shock wave processing would allow for the recycling of chondrule materials. Thus, one could get type I chondrule debris mixed into type II chondrules, and vice versa, as required for chondrule recycling. One could also have melting of fine-grained materials that either avoided earlier chondrule formation or that contained chondrule debris, consistent with the evidence provided by AO objects. Although not all planetesimal material would need to be heated, the repetitive action of collisions, melting of dust in debris clouds, and reaccretion would tend to produce a higher proportion of chondrules with time in a given planetesimal. Thus, O chondrites with their high proportion of chondrules might indicate a larger number of chondrule formation episodes, whereas C chondrites with lower proportions of chondrules could indicate fewer episodes of chondrule formation.

After melting, chondrules reaccreted to offspring planetesimals that could have been similar to the parent planetesimals except for containing a higher proportion of melted material. This can explain the "complementary compositions" of chondrules and matrix in a given chondrite (e.g., Wood 1985; Bland et al. 2005; Hezel and Palme 2008, 2010), as both components would move together in and out of the same chondritic planetesimal. Each debris cloud would have a distinctive mix of materials that would correspond to the particular planetesimal that was disrupted. Thus, distinct chondrite reservoirs could be preserved over time (Jones 2012), by repeated reaccretion. Rapid accretion especially would favor preservation of distinct chondrite reservoirs. although collisional mixing could merge initially distinct reservoirs to form new reservoirs.

If reaccretion occurred while chondrules were still warm, "warm accretion" and "cluster chondrite" textures for chondrites could be explained (Metzler 2011). Repeated disruption and accretion could explain the tendency for chondrites to be composed of distinct clasts with different accretion textures (Metzler 2011b), each of which might correspond to a particular accretion episode. Having multiple episodes of disruption, heating, and reaccretion would appear to solve the dilemma (Chambers 2006) of having chondrule ages spanning > 1 Ma preserved within distinct chondrite groups.

It would be possible for some chondrites (e.g., CI chondrites) to avoid much or any chondrule formation. if they did not experience as much collisional disruption or did not experience passage of a shock wave after formation of a debris cloud. On the other extreme, CB chondrites may have experienced a particularly energetic, late collision that vaporized much of the target after most nebular gas had been removed, with constituents representing various types of condensates in the collisional cloud (Krot et al. 2001, 2005a). The CB chondrite chondrules are unusually small and may have formed by a different process than for other "normal" chondrules. With a particularly late collision, there might be no opportunity to reprocess chondrite components-that is, no way to make chondrules with nebular shock waves-and evidence for a single, unusual event might be preserved. Viewed in the context of this model, CI and CB chondrites would be end members of a continuum in the processing of chondrites, with both largely lacking evidence for the type of chondrule formation proposed here.

According to the ideas presented above, the same debris clouds would be able to generate type I and type II chondrules simultaneously, if they were sufficiently large and dense, or only type I chondrules, if they were small. Debris cloud size would depend on (1) the size of disrupted body—larger later, after planetesimals had grown by accretion, and on (2) the relative collisional velocity—larger later, if planetary embryos (and Jupiter?) had grown and pumped up orbital eccentricities. Thus, one would tend to get larger debris clouds later, where both type I and type II chondrules could have been generated, in what I term the "late type I and type II chondrule era." Earlier chondrule production produced only type I chondrules, in the "early type I chondrule era."

I propose that the early era (Fig. 9a) is recorded by type I chondrules in C chondrites and by some fragments of type I chondrules in O chondrites, including relict Mgolivine grains and isolated Mg-olivine grains. These olivine grains crystallized from the most heated melts under reducing conditions, resulting in magnesian and refractory olivine compositions. Olivine in the early era had $\Delta^{17}O \leq -4^{\circ}_{00}$ because that is what the prevailing gas composition was at the time. This gas composition could correspond to the addition of some water ice, assumed to be ¹⁷O-rich and ¹⁸O-rich, compared with the ¹⁶O-rich gas in which CAIs and AOAs formed (e.g., Krot et al. 2009). I suggest that the formation of early type I chondrules occurred well inside the "snow line" where water ice was stable, but not so far from the snow line that ice boulders from beyond the snow line could drift (Fig. 9). Evaporation of the migrating ice boulders would enrich the nebular gas in water vapor and cause a shift to higher Δ^{17} O compared with CAIs and AOAs if there was no cold sink for the water vapor (regime 2 of Cuzzi and Weidenschilling 2006). Figure 9b shows type I chondrules forming in debris clouds generated around both O and C chondrite planetesimals. Although I make the traditional assumption in Fig. 9 that O chondrite planetesimals formed closer to nascent sun (YSO) than C chondrite planetesimals (e.g., Wood [2005] and many others), the data permit both types of planetesimals to form at the same time. Indeed, ²⁶Al relative chronology suggests overlapping formation times for chondrules in O and C chondrites (Kurahashi et al. 2008; Kita and Ushikubo 2012).

I propose that the late era (Fig. 9b) is recorded by both type I and type II chondrules in O chondrites as well as by type II chondrules and some type I chondrules in C chondrites. Many chondrules were processed in the O chondrite formation region during the late era, perhaps owing to late, large collisions that affected O planetesimals. This late processing meant that virtually no chondrules from the early type I era were left intact in O planetesimals; most were broken and recycled as grain fragments. Type I and type II chondrules, which formed in the late era, would have inherited $\Delta^{17}O > -4\%$ from gas, which had evolved to heavier O as a result of more addition to vapor of ¹⁶O-poor water ice. This implies that chondrule formation in the late era occurred closer to "snow line." Cooling of the nebula would move the snow line closer to the forming sun, so a higher Δ^{17} O value at the later stage is consistent with this overall cooling trend. Melting of chondrules in higher $\Delta^{17}O$ gas affected chondrules in both O and C chondrites. However, most type II chondrule olivine grains in O chondrites have somewhat higher Δ^{17} O than in many type II chondrules in various C chondrites (compare Kita et al. [2010] and Tenner et al. [2011, 2012]), so it is possible that more water ice was heated in the formation location for O chondrites than for C chondrites. Addition of water vapor could have made the gas more oxidizing (e.g., Grossman et al. 2012) as well as changed the O-isotope composition of the gas (Tenner et al. 2012). On the other hand, generally similar Fa values for olivine in type II chondrules from C and O chondrites could imply that the main reason for ferrous olivine compositions in type II chondrules from various chondrite groups was a high proportion of silicate dust vaporized, not necessarily a high proportion of water ice vaporized. Vaporization of different amounts of silicate and ice dust would be expected to lead to different combinations of elevated oxidation state and Δ^{17} O value, so the two parameters would not be necessarily exactly correlated.

One can also ask how chondrules in other groups, such as the E chondrites with their highly reduced mineralogy, fit into this picture. Although these meteorites are highly reducing and dominated by type I chondrules, chondrule olivine and pyroxene grains mostly have values of $\Delta^{17}O \sim 0$ (Weisberg et al. 2011). This implies formation of these chondrules in the late type I and type II era. E chondrites may have formed inwards of the snow line in a dry region where gas was depleted in H₂O vapor and had high C/O values (e.g., Hutson and Ruzicka 2000). Depletion of H₂O vapor could correspond to a situation in which water vapor was condensing into larger bodies outwards of the snow line, with these bodies too large to be affected by inward drift as a result of gas drag, and thus acting as a cold sink for water (regime 3 of Cuzzi and Weidenschilling 2006). This would imply that chondrule formation in E chondrites occurred relatively late within the late type I and type II chondrule era.

Although this model for chondrite formation appears to be consistent with a large body of meteoritic

evidence, it is not clear whether the required heating and dynamical processes can occur. Effective heating by shock waves in dense particle clumps has not been proven (Alexander and Ebel 2012). In addition, it is not known how the accretion of dense particle clumps would be affected by either shock waves or the presence of already-formed planetesimals. The distinct batches of materials in chondrite groups imply that cloud collapse must have been relatively rapid, and hot accretion implies collapse timescales of hours after chondrule formation. Possibly, shock waves or the presence of pre-existing planetesimals or planetesimal remnants can help speed the collapse of already self-gravitating clouds. A related aspect of this model that needs to be evaluated is the longevity of transient gas clouds produced by vaporization relative to chondrule cooling and accretion timescales. More modeling of these processes is needed.

Some predictions of this model may be made, which can help guide further research:

- There should be evidence for more thermal processing of type I compared with type II chondrules across chondrite groups. Any measurement capable of serving as a geothermometer would be helpful. Further chemical studies of various chondrule phases and of bulk chondrules, coupled with comparisons with thermodynamic models, could be fruitful.
- 2) There should be evidence of higher fO_2 during the formation of type II compared with type I chondrules across chondrule groups. Measurements of Fa distributions in olivine and Fs contents in pyroxene; quantitative measurements of valence states or trace element contents for multivalent elements (e.g., Cr, V, Ti, Co, Ni) in phases; and detailed studies of phase assemblages, coupled with experimental data and thermodynamic models, could be useful in further constraining fO_2 conditions during chondrule formation.
- 3) Some type I chondrules as well as some Mg-olivine relict grains should have formed earlier than other type I and type II chondrules. In contrast, dusty olivine relict grains should have formed at about the same time as type II chondrules. Most type I chondrules in C chondrites should be slightly older than most type I and type II chondrules in Ochondrites. However, some older type I chondrules in O-chondrites might be found, whose ages were not reset during later episodes of chondrule formation. Type I chondrules in E chondrites might have formed even later than most chondrules in O chondrites. High-precision chronometry is needed to evaluate these possibilities. In situ measurements of short-lived nuclides within multiple phases and positions within chondrules would be especially helpful to evaluate

isotopic homogeneity and the possibility of multiple stages of formation and resetting.

- 4) There should be evidence for the evolution of Δ^{17} O to higher values with time. This would require measurement of oxygen isotope composition and high-precision chronometry of the same objects in the same chondrite group. To the extent that Δ^{17} O variations are caused by vaporization of ¹⁶O-poor ice, a correlation should exist between Δ^{17} O and time of melting. The possibility that each chondrite group could be on a somewhat separate evolution path should be considered.
- 5) Type II chondrules might show various petrographic or isotopic evidence of having formed in a higherparticle-density, higher-pressure cloud than type I chondrules. For instance, the number of compound chondrules formed by collision might be higher for type II than type I chondrules, corrected for possible differences in relative collisional velocities, sizes, and cooling rates between chondrules. If back-reaction between molten chondrules and a transient gas cloud is partially obliterating evidence for kinetic mass fractionation during evaporation, one might expect that type II chondrules would show less evidence of such fractionation than type I chondrules, although possible variations in diffusion rates caused by variations in exchange temperature would need to be evaluated.
- 6) Type II chondrules might show evidence for more rapid cooling than type I chondrules, if it is true that higher particle densities result in faster cooling. Mineral zoning patterns, microstructures, or textures might reflect such differences. However, with mineral zoning patterns, the possibility of open-system fluxes for chondrules would need to be considered as well as crystal fractionation during cooling.

The inference that collisions could have been important in initiating chondrule formation allows the possibility of a dual origin for chondrules—partly through the melting of suspended particles in collisional debris clouds by nebular shock waves as proposed here, and partly through impact heating induced by the collisions of planetesimals themselves. Thus, two origins for chondrules in the same meteorites are possible, with the proportions and kinds of chondrules formed by each process depending on the characteristics of the collisions (e.g., collisional velocity, sizes of impacting bodies, trajectory of ejecta), the clouds generated (size and particle density), and the nebular shock waves (e.g., timing, speed, size, ambient gas pressure).

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