24: Open-System Behaviour During Chondrule Formation

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ABSTRACT

The question of whether chondrules acted as open or closed systems during formation is important in understanding chondrule history and the differences in bulk composition of the chondrite classes. "Open-system" behaviour assumes that relatively volatile elements (like Fe, Na and K) were lost and the chondrules underwent chemical reactions with species in the environment during formation, while "closed-system" behaviour assumes that the various properties of the chondrules were inherited entirely from the precursors. More than 90% of the chondrules in unmetamorphosed chondrites are either groups A1 and A2, which are low-FeO and refractory chondrules, or group B1 with lithophile element ratios resembling CI proportions and high-FeO silicates. The refractory composition, low-FeO silicates, relatively high metal abundance and low-Ni content of the metal of group A1,2 chondrules are consistent with open-system behaviour. A closed-system scenario would require that chondrule precursors were the products of earlier volatility-oxidation processes. The trend in the olivine to pyroxene ratio (which decreases from group B1 to A2 and then increases again in group A1), the smaller mean size of group A1 and A2 chondrules compared to group B1 chondrules, the relationships between oxygen isotope composition and chondrule size and peak temperature, diffusion of Na into chondrules, and the greater abundance of thick fine-grained rims around group A chondrules relative to group B chondrules are consistent with major evaporative loss, first of FeO and later SiO$_2$, accompanying the formation of groups A1 and A2. These properties are difficult or impossible to understand in terms of closed-system behaviour. It is concluded that while group A1 and A2 chondrules formed by reduction of FeO and major evaporative loss from precursors originally resembling those of CI chondrites, evaporative loss from group B1 chondrules was restricted to only the most highly volatile trace elements like Ga, Sb, Se and Zn. Open-system behaviour was clearly very important during chondrule formation.

INTRODUCTION

Whether or not chondrules formed as open systems has been strongly debated for many decades (*e.g.* Wai and Wasson, 1977; Anders, 1977). The question is of fundamental significance in understanding chondrule formation processes and conditions. The question is also relevant to the bulk compositions and the origin of the chondrite classes, although this topic will not be dealt with here. We will restrict our discussion largely to chondrules from ordinary chondrites, noting only that chondrules in various chondrite classes are qualitatively similar, although the relative abun-

dance of the various chondrule groups may vary (Scott and Taylor, 1983; Dodd, 1981; Sears *et al.*, 1992; 1993), being predominantly FeO-poor olivine in carbonaceous, almost entirely FeO-poor pyroxene in enstatite chondrites and predominantly FeO-rich in ordinary chondrites.

THE DIVERSITY OF CHONDRULE COMPOSITIONS

Before discussing whether or not the system was open during chondrule formation, it is necessary to review the considerable diversity of chondrule properties. Our thesis is that by explaining

some of the differences among chondrule groups, we can understand important aspects of how each of the chondrule groups formed.

Chondrules show a very wide range in composition, mineralogy and texture which has been summarized in the form of a number of classification schemes (Kieffer, 1975; Dodd, 1981; Gooding and Keil, 1981; McSween, 1977; Scott and Taylor, 1983; Jones, 1994). The scheme we prefer is based on the changes in the composition of the two major structural components in the chondrules; the silicate minerals (usually olivine, sometimes pyroxene) and the glassy mesostasis enclosing them (Sears *et al.*, 1992; DeHart *et al.*, 1992). These properties are determined either by electron-microprobe analysis or cathodoluminescence petrography or preferably a combination of these techniques. Unlike virtually all previous classification schemes, texture is not included but treated as an independent variable. (For a discussion of these points see Sears *et al.*, 1995.) The main (and somewhat approximate) technical details of the chondrule groups and some notes on how these groups compare with previously published schemes appear in Table 1.

Some of the chondrule groups thus defined are "primary" in the sense that they only occur in essentially unmetamorphosed meteorites (A1, A2, B1 and a few A5 chondrules), while others are the result of metamorphism (A3, A4, B2, B3 and most of the A5 chondrules). Semarkona (LL3.0) is the only well-known essentially unmetamorphosed (*i.e.* type 3.0) ordinary chondrite observed fall. It is possible that the Yamato 74660 (LL) and Lewis Cliff 86134 (L) chondrites are also type 3.0 (Sears and Hasan, 1987; Sears *et al.*, 1991), but these are weathered finds and data are meagre. Unpublished TEM data suggest that Yamato 74660 resembles the Krymka LL3.1 chondrite (C. Alexander, per. comm, 1995). The percentages (by number) of each chondrule group in Semarkona are given in Table 1. In comparison, chondrules in the primitive CM carbonaceous chondrites are largely (*i.e.* ~70% by number) group A1, while virtually all the chondrules in enstatite chondrites are group A2.

CHONDRULE FORMATION: CLOSED OR OPEN-SYSTEM?

Fig. 1 is an attempt to summarize the two situations for chondrule formation that are discussed here. By "closed-system" we mean that volatiles were not lost during chondrule formation, neither did the chondrule components chemically interact with the ambient gases. This would mean that the chondrule groups are the result of mixing of precursor solids in various combinations. The advocates of chondrule formation as closed (or essentially closed) systems include, Wasson and Chou (1974), Gooding *et al.* (1983), Grossman and Wasson (1983a,b), Ikeda (1983), Rubin and Wasson (1986, 1988), Grossman (1988), Misawa and Nakamura (1988), Jones and Scott (1989), Hewins (1991a), Jones (1994). The term "open-system" refers to cases where volatiles were lost and chemical reactions occurred between chondrule components and the ambient gases. In this case, the chondrule groups are the result of processes occurring during the chondrule-forming events.

Table 1. *The chondrule groups in terms of cathodoluminescence, mineral compositions and frequency of occurrence in the Semarkona ordinary chondrite**

	Mesostases			Olivine			Freq[‡]
	CL	Composition[†]	CL		%FeO	%CaO	
A1[§]	yellow	Pl(An> 50%)	red		< 2	> 0.17	10.5
A2[#]	yellow	Pl(An> 50%)	none/dull red		2–4	0.1–0.2	25.0
A3**	blue	Pl(An> 50%)	red		< 4	> 0.2	0.0
A4**	blue	Pl(An> 50%)	none/dull red		> 4	0.16–0.3	0.0
A5[@]	blue	Pl(An< 50%)	none		> 4	< 0.25	5.0
B1[+]	none	>30% Qtz	none		7–25	0.08–0.3	56.9
B2**	none	30–50% Qtz	none/dull red		10–25	0.08–0.3	0.0
B3**	purple	15–30% Qtz	none		15–20	< 0.08	2.6

* Phase compositions given as a rough guide since the group fields are not rectangular (see Sears *et al.*, 1995, for details). 'CL' refers to cathodoluminescence color. Electron microprobe data has the advantage of being quantitative and detecting differences missed by CL, while CL data has the advantage of being more rapid and sometimes easier to apply when textures are fine-grained and intergrown.
[†] Normative composition (wt%) of the mesostasis: Pl, plagioclase; An, anorthite; Qtz, quartz.
[‡] Frequency (as percent by number) for 76 chondrules (DeHart *et al.*, 1992).
[§] Includes some of the droplet chondrules of Kieffer (1975), some of the non-porphyritic pyroxene chondrules of Gooding and Keil (1981), the type I chondrules of McSween (1977), metal-rich microporphyritic chondrules of Dodd (1978), and the type IA chondrules of Scott and Taylor (1983).
[#] Includes the poikilitic pyroxene and type IB chondrules of Scott and Taylor (1983) and many of the type IAB chondrules of Jones (1994).
[@] There appear to be no previous observations of this chondrule group in unmetamorphosed meteorites.
[+] Dodd's (1981) "lithic" or "clastic" chondrules and Dodd's (1978) metal-poor microporphyritic chondrules are included in this group, as are the type II chondrules of McSween (1977), Scott and Taylor (1983) and Jones (1990).
** Group A3, A4, B2 and B3 chondrules are only observed in significant amounts in metamorphosed chondrites and are assumed to be the result of metamorphic alteration of the primitive group A1, A2, A5 and B1 chondrules. Common paths of evolution are A1 → A3 → A4 → A5; A2 → A5; A5 → A5; B1 → B2 → B3 → A5.

Advocates of chondrule formation as open-systems in which evaporation occurred include Larimer and Anders (1967), Walter and Dodd (1972), Osborn *et al.* (1974), Kurat *et al.*, (1983), Clayton *et al.* (1985, 1991), Nagahara *et al.* (1989; 1994), Matsuda *et al.* (1990), Lu *et al.* (1990), Huang *et al.* (1993a), Matsunami *et al.* (1993), Nakamura (1993), Scott (1994) and Alexander (this volume). Others have argued for open-system processes involving condensation (*e.g.* McSween, 1977), while Dodd has argued for closed-system behaviour for some chondrules and open-system behaviour for others (Dodd and Walter, 1972; Dodd, 1978).

Throughout the remainder of this paper we will summarize the properties of primitive chondrules, and some of the relevant laboratory experiments that have been performed, in an effort to choose between these options.
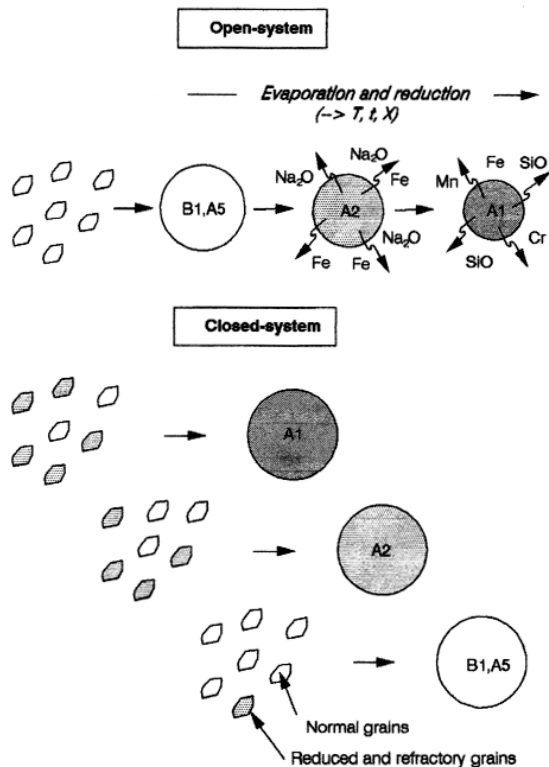
Fig. 1. Schematic representation of the open- and closed-system alternatives for chondrule formation. Open-system theories assume reasonably unfractionated precursor solids that are heated to produce group B1 and A5 chondrules with relatively little mass loss, while group A chondrules lost considerable mass during their formation. During the formation of group B and A5 chondrules only the most highly volatile elements (In, Tl, Bi etc) were lost or suffered modest redistribution. Reduction of FeO followed by the loss of Fe and Na_2O produced group A2 chondrules with about 40 wt % mass-loss. Further loss, this time involving elements slightly less volatile than Fe (like Mn and Si) produced the group A1 chondrules. Closed-system theories assume that all chondrules were the result of closed-system melting but that various properties of the chondrules were the result of mixing various precursors in different proportions. The extent of volatile element loss and FeO reduction would have depended on temperature, heating time and composition of the chondrule and surrounding gases during chondrule formation.

CHONDRULE PROPERTIES

1. Chondrules display a very wide range of $P(O_2)$

Group A chondrules contain silicates which are low in FeO (McSween *et al.* 1983; Dodd, 1978; Snellenburg, 1978; Scott and Taylor, 1983; Jones and Scott, 1989; Jones, 1994; DeHart *et al.*, 1992), and metal grains which are low in Ni (Snellenburg, 1978; Jones and Scott, 1989; Lu, 1992), relative to group B. Fig. 2 summarizes the ranges observed. (Unfortunately, there are few chondrules for which both metal and silicate compositions have been determined). The interiors of group A chondrules usually contain more metal than group B chondrules (Huang *et al.*, 1993b; Zanda *et al.*, 1995). These data indicate that the group A chondrules are reduced relative to group B chondrules.

The reduced state of group A chondrules compared with group B chondrules is consistent with both open and closed system
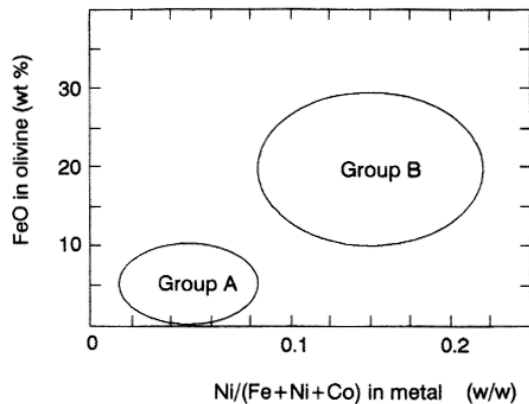

Fig. 2. A schematic summary of the FeO content of the olivine and the Ni content of the metal of group A (A1 and A2) chondrules and group B (essentially B1) chondrules. Original data from Snellenburg (1978), Jones and Scott (1989) and Lu (1992).

behaviour. In the case of an open-system one would argue that group A chondrules were reduced during their formation, while in the case of a closed-system one would argue that the precursors of group A chondrules were more reduced. It is difficult to discuss meaningfully the likelihood of reduced precursors, since very little is known about chondrule precursors. If we use equilibrium thermodynamics as a guide, it seems unlikely that metal as Ni-poor as that observed in the group A chondrules could be the product of nebular processes. Fig. 3, taken from the calculations of Sears (1978), which resemble those of Kelly and Larimer (1977) in their main features, shows while metal is <u>enriched</u> in Ni under all pressure and temperature conditions ($\geq 6\%$, which is the value calculated from cosmic abundances), the Ni-poor metal requires the presence of a phase like schreibersite ($(Fe,Ni)_3P$) which might preferentially remove Ni. This process requires considerably more reducing conditions than cosmic (Sears, 1980; Wood, 1985; Wood and Hashimoto, 1993), whereas chondrules formed in an environment more oxidizing than cosmic (see below). On the other hand, Ni-free metal would inevitably result from the production of metallic Fe by the reduction of silicates which would form low-Ni solid solutions with existing metal.

2. Chondrules display $P(O_2)$-related patterns in their mineralogy

There are some significant, and surprisingly little-discussed, relationships between the mineralogy of chondrules and the composition of their silicate grains. The olivine to pyroxene ratio in group B1 chondrules is high, but is low in group A2 chondrules and intermediate in group A1 chondrules. Fig. 4 shows two histograms of the fayalite contents (Fe-rich olivine, Fe_2SiO_4) for chondrules from Semarkona, one for chondrules with an olivine to pyroxene volume ratio >9 and one where this ratio is <9. The chondrules whose olivine to pyroxene volume ratio is >9 display a bimodal pattern with a broad peak at around a mole fayalite content of 10% (Fa_{10}) and a narrow peak at Fa < 2 mol%, while chondrules with an
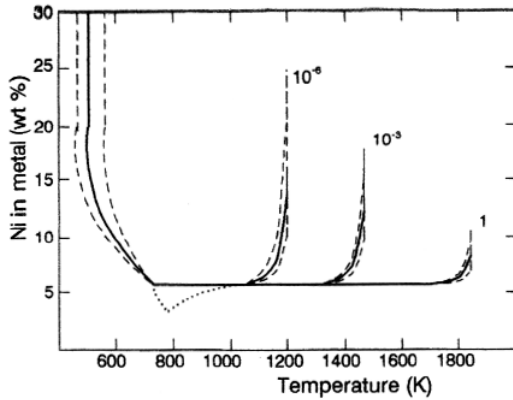
Fig. 3. The weight percent Ni in the metal phase as a function of temperature for a system with cosmic composition for total pressures of 10^{-6}, 10^{-3} and 1 atmosphere. The broken lines indicate the effects of uncertainties in the thermodynamic data. The dotted line shows the trajectory of the path in the presence of schreibersite which can accommodate some of the Ni. Curve from Sears (1978).

Fig. 4. Histograms of measured Fa contents of olivine for Semarkona chondrules with olivine/pyroxene ratio >9 and <9, as determined by modal analysis. Chondrules with olivine >90% show a bimodal distribution in Fa, with group B1 chondrules forming a broad peak at around Fa_{10} and group A1 chondrules forming a much narrower peak at $Fa_{<2}$. Chondrules with <90% olivine have a very different Fa histogram, with values of Fa between 2 and 4 now being occupied by the group A2 chondrules. The broad Fa_{10} peak of group B1 chondrules is missing. The trends between ol:px and Fa are expected if reduction of the FeO in the olivines during chondrule formation was accompanied first by evaporation of Fe (which lowers the olivine/pyroxene ratio) and then evaporation of Si (which increases the olivine/pyroxene ratio). Data are from Snellenberg (1978).

olivine to pyroxene ratio of <9 show a somewhat broader peak at Fa <2 (mainly due to chondrules with Fa 1–2 mol%) and perhaps a peak at about 5 mol%. The data shown in Fig. 4 are from Snellenburg (1978) but the same features are observed in data from other studies (*e.g.* DeHart *et al.*, 1992; Huang *et al.*, 1995; Sears *et al.*, 1995b). (We have no explanation for the Fa_{17} peaks in Snellenburg's data, except to note that such high values are observed in other data bases only when analysis is made close to the edge of a zoned olivine grain.)

In a closed-system scenario, one would have to propose some *ad hoc* explanation for the data in Fig. 4. For example, one would have to propose that chondrules we see in the meteorites are an incomplete sampling of the true chondrule populations and that olivine-rich chondrules with ~Fa_4 and pyroxene-rich chondrules with Fa_{10} had just been inadequately sampled. In view of the large number of chondrules examined, it would require further *ad hoc* assumptions to explain this fractionation of chondrules. Hewins (1991b) explained the mineralogical variations in terms of complex patterns of condensation, but this does not explain the size differences (that are discussed below), nor the abundant metal and sulfide in group A chondrules. Open-system chondrule formation provides a perfectly straight forward way to explain the trend between mineralogy, Fa content and size. Fig. 5 is a summary of the vaporization experiments of Hashimoto (1983). Many other authors have reported similar data (Gooding and Muenow, 1977; King, 1982; 1983; Mysen and Kushiro, 1988; Nagahara *et al.*, 1989; 1994). Thus, if a mixture of oxides approximately chondritic in composition is heated in the laboratory, loss of Fe first decreases the (Fe+Mg)/Si ratio (and lowers the olivine/pyroxene ratio) and then loss of Si begins to restore the value. A mixture originally fairly rich in normative-olivine (i.e. calculated olivine, (Fe+Mg)/Si ~ 2.0) becomes pyroxene-normative ((Fe+Mg)/Si ~ 1.0) after about 40 wt % of the charge is evaporated in the Hashimoto (1983) experiments (Fig. 5). The relevant reaction is probably of the form:
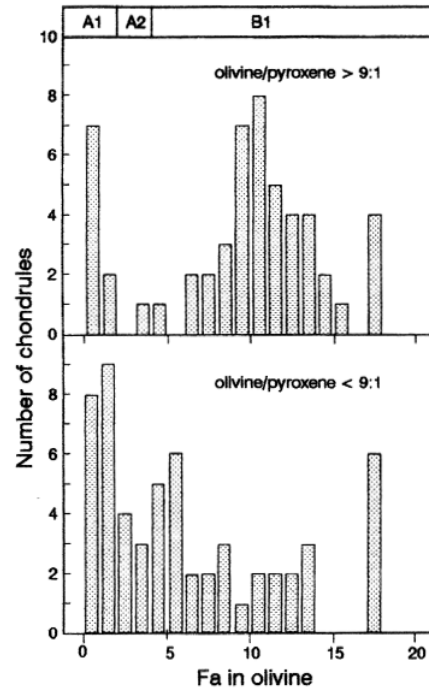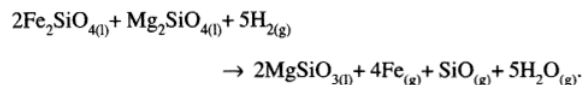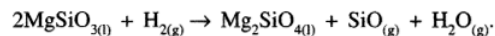
$$2Fe_2SiO_{4(l)} + Mg_2SiO_{4(l)} + 5H_{2(g)}$$
$$\rightarrow 2MgSiO_{3(l)} + 4Fe_{(g)} + SiO_{(g)} + 5H_2O_{(g)}.$$

Continued heating causes further loss of Si by evaporation, with relatively little loss in the less volatile Mg, and as evaporation exceeds about 40 wt% olivine abundances begin to increase again. This reaction is of the form:

$$2MgSiO_{3(l)} + H_{2(g)} \rightarrow Mg_2SiO_{4(l)} + SiO_{(g)} + H_2O_{(g)}.$$

The data of Hashimoto (1983) were obtained in a non-cosmic $P(O_2)$ but it seems clear from thermodynamic calculations (Larimer, 1967; Grossman, 1972; Sears, 1980; Wood and Hashimoto, 1993) that qualitatively similar results would be observed in cosmic and a wide variety of non-cosmic conditions. One would therefore expect the olivine to pyroxene ratio to vary as a function of Fa content if chondrules formed by a process involving various degrees of reduction and evaporation of material of approximately similar starting compositions. We have assumed that the reducing agent might be nebular H_2, but carbon is another
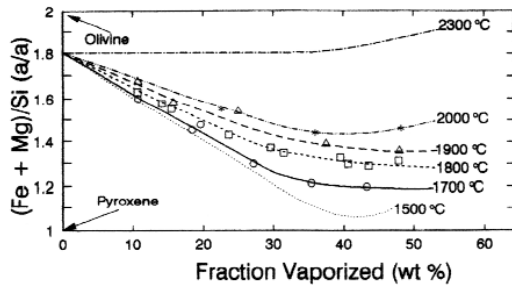
Fig. 5. The normative olivine/pyroxene ratio of solids of initially chondritic composition as a function of mass evaporated during laboratory heating experiments. Loss of Fe and partial loss of Si as the total mass evaporated approaches 30–40 wt % causes the residues to assume pyroxene compositions. Thereafter, loss of Si would cause the residues to become more olivine-like in composition. Data from Hashimoto (1983). If the starting compositions were more similar to group B chondrules than the chondritic compositions used by Hashimoto, then the starting value of (Fe + Mg)/Si would be lower and the initial straight portion of the curve would be shorter. Hashimoto (1983) obtained the curves at 1500 and 2200°C by extrapolation.

possibility, as recently discussed by Connolly *et al.* (1994).

The composition of the mesostasis surrounding the silicate grains also shows significant variations, some related to evaporative loss (DeHart *et al.*, 1992). The group A chondrules, being depleted in volatile elements, contain mesostases which are refractory in nature being low in K and Na and high in Ca. Group B chondrules contain mesostasis which is not only enriched in Na and K compared to group A, but higher in SiO_2. However, the high SiO_2 reflects the history of the chondrule immediately following its formation because olivine, the first silicate to crystallize from the melt, was somehow prevented from reacting with the SiO_2 in the glass to produce pyroxene, as required by equilibrium. Apparently, group B chondrules cooled more rapidly than group A chondrules and underwent considerable supercooling (DeHart, 1989; Jones, 1990).

3. Chondrules display a range of CI-normalized abundance trends

The bulk compositions of chondrules are notoriously difficult to determine. Defocussed beam electron microprobe methods are intrinsically difficult because of the complex textures of chondrules and the two-dimensional nature of the method. Whole-chondrule bulk analyses are fairly straight forward (using neutron activation, isotope dilution or other methods) but freeing the chondrules from the meteorite is not a simple procedure. Disaggregating a sample and physically removing the fragile chondrules from their tough host material produces biases towards large strong chondrules, while chiselling the chondrules from polished surfaces avoids this bias but may result in sampling large amounts of rim material. There is no ideal way of physically separating chondrules. Nevertheless, despite differences (mainly in the relative abundance of the various chondrule populations represented and the tendency for electron-microprobe analysis towards high Na

and K values) there is reasonable agreement in the results of the various methods. Fig. 6 shows the results that were obtained by INAA. Group B1 (and A5) chondrules have flat lithophile elemental abundance patterns when normalized to CI chondrites, "lithophile" elements being those normally associated with silicates. On the other hand, groups A1 and A2 show significant depletions in volatile and moderately volatile lithophile elements like Si (not shown in Fig. 6 but accurately determined by electron microprobe), Mg, Cr, Mn, Na and K. The siderophiles and chalcophiles (elements normally associated with the metallic and sulfide phases, respectively) behave similarly in both groups A and B, showing major volatility-related depletions.

Since chondrules are mixtures of discrete phases, each with characteristic properties (volatile-rich or -poor, reduced or oxidized etc), it is possible to mathematically reproduce these compositional trends by mixing components of the requisite properties. Components of the requisite properties, to a good approximation, are also the products of the theoretical condensation sequence thermodynamically predicted for a gas of cosmic composition. However, such exercises are not particularly instructive because, as pointed out by several authors, condensation and evaporation are thermodynamically equivalent processes.

Fig. 7 summarizes the Tsuchiyama *et al.* (1981) data for evaporative loss of Na from chondritic material. Tsuchiyama *et al.* (1981) and Hashimoto (1983; Fig. 5) used different conditions for their experiments so direct comparison should be made with caution, but the results should be qualitatively applicable to a wide variety of conditions. Sodium- and Fe-loss is fairly rapid, followed by Si-loss. Sodium-loss is also dependent on oxygen fugacity, with
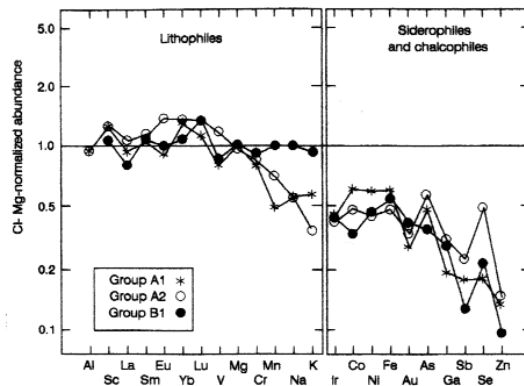

Fig. 6. The composition of chondrules from the Semarkona ordinary chondrite as determined by instrumental neutron activation analysis plotted as abundances ratioed to CI and Mg. The elements are divided into two groups on the basis of their chemical properties and are plotted in order of increasing volatility. Huang *et al.* (1995) data are shown, but the Grossman and Wasson (1983b; 1985) and Swindle *et al.* (1991) INAA data yield very similar results, as do defocussed beam electron microprobe analyses (Scott and Taylor, 1983; Jones and Scott, 1989; Jones, 1990; 1994a). Group A1 and A2 chondrules show volatility-controlled elemental abundance patterns for lithophile and siderophile/chalcophile elements, while group B1 chondrules show flat elemental abundance patterns for lithophile elements. The siderophile and chalcophile elements are depleted in both groups A and B also display volatility-related depletion patterns.
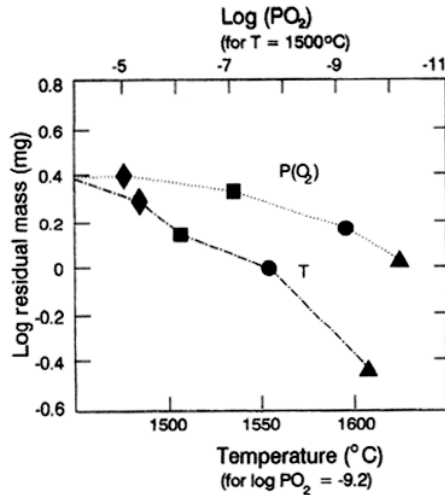
Fig. 7. The loss of Na from charges of initially chondritic composition (about 2.5 wt %) as a function of temperature and oxygen fugacity for 100-minute heating experiments. The vertical axis refers to the logarithm of the mass of Na (as wt % oxide) remaining in the charge after heating. The Na sometimes shows more than an order of magnitude loss, depending on temperature and oxygen fugacity. Data from Tsuchiyama *et al.* (1981) from which further details can be obtained.

higher $P(O_2)$ values favoring retention of Na.

Concurrent with evaporation, these experiments and thermodynamic calculations also predict reduction of Fe during chondrule formation in an open system. Fig. 8 compares the Na-loss predicted by the Tsuchiyama *et al.* data with the Fa content of the olivine predicted by thermodynamic equilibrium (Lu, 1992; Huang *et al.*, 1995). The compositions of the group A and group B chondrules seem reasonably consistent with small differences in formation temperature and the temperatures suggested seem consistent with liquidus temperatures calculated from the bulk compositions of the chondrules in the way described by Herzberg (1979) of ~1710, ~1550 and ~1630°C for groups A1, A2 and B1, respectively. However, time as well as temperature at peak temperature affects composition, so these estimates might be low if higher temperatures were experienced for too a short time to affect compositions. Yu *et al.* (1994) have suggested that Na loss (and presumably FeO reduction) could also be minimized by flash heating. The presence of relict grains in chondrules indicates that some of these chondrules were not completely melted during formation (Jones, this volume), either because temperatures were too low for complete fusion or because times spent at peak temperature were very short. In view of the facility with which Na is lost from experimental melts under a wide variety of conditions, we think it most likely that group A and B chondrules were formed in environments in which oxygen fugacities were several orders of magnitude higher than predicted by cosmic compositions (Wood, 1985).

Cooling rates differ considerably with chondrule class. Group A chondrules cooled relatively slowly and maintained a degree of equilibrium between melt and phenocrysts, while group B chondrules cooled rapidly and underwent considerable supercooling

(Huang *et al.*, 1995). Cooling rates seem to generally vary from ~100°C/h for porphyritic (e.g. Lofgren, 1989) to ~1000°C/h for non-porphyritic chondrules (e.g. Hewins, 1988; Lofgren, 1989). It has also been argued that some chondrules experienced multi-stage cooling, ~300°C/h above 1300°C and ~3000°C/h below 1300°C (Planner and Keil, 1982). That the chondrules with the highest peak temperatures during formation also have the slowest post-formation cooling rates is consistent with group A chondrules being surrounded by warm gas and dust during their formation and subsequent cooling.

There is no *a priori* reason to suspect that volatile alkali elements should directly correlate with Fa since the thermodynamics and kinetics of the two processes are very different. However, there is evidence that the barred-olivine chondrules (which arguably suffered highest temperatures during chondrule formation) do show such a correlation. Matsuda *et al.* (1990) found that Allende BO chondrules showed a positive correlation between FeO and potassium which they interpreted as being due to simultaneous loss of volatiles and reduction of FeO.

4. The chondrule groups show statistically significant differences in size.

In Fig. 9 we show histograms of chondrule sizes for the Semarkona and Krymka chondrites. Group A3 and B2 chondrules from Krymka are also included since the small level of metamorphism suffered by Krymka should not have significantly affected these data. For both chondrites, the group A chondrules are significantly
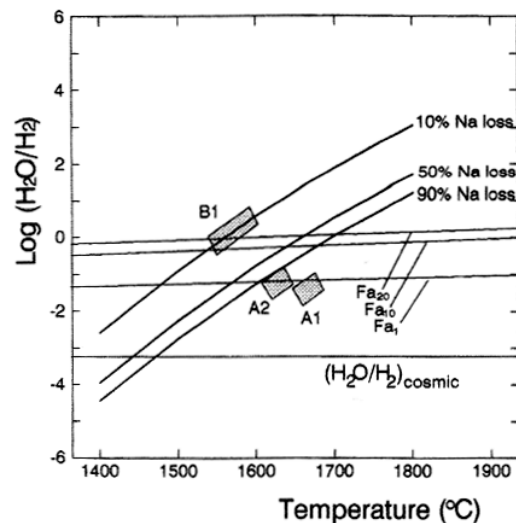

Fig. 8. Evaporation temperatures of Na-bearing phases and Fe reduction/oxidation lines for olivine (for fayalite values of 1, 10 and 20 mol%) as a function of oxygen fugacity (expressed as H_2O/H_2 ratio). The cosmic H_2O/H_2 ratio is shown for reference. Under cosmic conditions there would be considerable loss of Na and reduction of FeO. The boxes show the fields in which conditions are suitable for the formation of group A1, A2 and B1 chondrules. Na data are from Tsuchiyama *et al.* (1981), thermodynamic data for the fayalite calculation are from Robie *et al.* (1979) and the JANAF tables, and the cosmic abundance data are from Anders and Grevesse (1989).
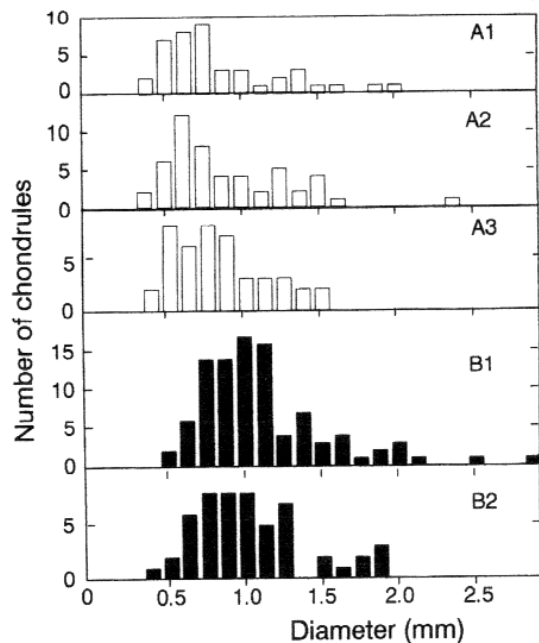
Fig. 9. Histogram of chondrule sizes as a function of chondrule group for Semarkona and Krymka. The small amount of metamorphism suffered by Krymka is not expected to affect these data. Chondrule diameters (averages of two perpendicular measurements) have been corrected for thin section-ing effects which tend to systematically underestimate diameters (Hughes, 1978). The mean diameter for group A chondrules is less than that of group B chondrules by 15–20% for both Semarkona and Krymka. Data from Huang *et al.* (1995).

Table 2. *Reduction and evaporation of major elements (wt%) to give the observed size difference between group A and B chondrules**

	B1¶ Obs.	Step 1† Calc.	Step 2‡ Calc.	A1§ Calc.	A1¶ Obs.
SiO_2	50	50	25	49	45
MgO	34	34	29	47	43
FeO	12	0.6	0.6	1.0	2.1
Al_2O_3	1.5	1.5	1.5	2.4	5.3
CaO	1.1	1.1	1.1	1.8	3.3
Fe (metal)	0.0	0.44	0.44	0.71	3.4
Diameter (mm)	1.05	—	—	0.89	0.81
Mass loss (wt%)	—	11	27	38	—

* Relative losses are estimated from the experimental data of Hashimoto (1983) assuming 1700°C heating and 54% total mass loss, which is sufficient to partially restore the olivine/pyroxene ratio. A 54% mass loss in Hashimoto's (1983) experiments corresponds to about a 40% in chondritic material because of the lower bulk FeO in the latter.
† Step 1: 95% of FeO is reduced, then 95% of the reduced Fe is evaporated.
‡ Step 2: 40% of SiO_2, and 15% of MgO, is evaporated.
§ Previous column recalculated to 100% being the calculated group A1 composition.
¶ Observed average composition.

smaller than group B chondrules by 15–20 percent. This translates to a difference in mass of about ~50 wt%. The mean sizes (in mil-limeters) we calculate for the Semarkona chondrules in the figure are group A1, 0.81±0.40; A2, 0.84±0.40; A3, 0.76±0.30; B1, 1.05±0.42; B2, 0.97±0.37. (Because the distributions are not nor-mal, these standard deviations are misleadingly large).

Open-system behaviour predicts that the group A chondrules would be smaller than group B chondrules, while it is difficult to understand how closed-system behaviour would have produced such a size difference. Why would chondrule formation involving reduced and volatile-poor precursors preferentially produce smaller chondrules? In fact, making reasonable assumptions about the evaporation of major elements from the chondrules during for-mation the size difference is also in quantitative agreement with the compositional differences (Table 2). This is despite considerable departures from equilibrium and the possibility of recondensation of lost volatiles. We also think the calculation may be conservative; the low Al_2O_3 and CaO, high SiO_2 and MgO, and large size relative to observed group A chondrules indicates that we have underesti-mated the amount of evaporative loss.

5. Chondrules <u>did</u> behave as open-systems with respect to O isotope exchange, but the details are unclear.

One of the potentially most informative properties of chondrules is

their oxygen isotopic composition (Fig. 10). Unfortunately, these properties are very poorly understood. Among the Allende chon-drules, those whose texture suggests complete melting (the non-por-phyritic chondrules) contain isotopically heavier oxygen than those which may not have been completely melted (the porphyritic chon-drules). This seems to suggest that the surrounding environment contained heavier oxygen than the chondrules. Conversely, among chondrules from ordinary chondrites there is a correlation between the abundance of isotopically light oxygen and chondrule size. Since smaller chondrules would exchange more completely with environ-mental gases during formation than large chondrules, it would seem that the environment contained lighter oxygen than the chondrules. (We suspect that the clustering of data for the Chainpur chondrules reflects metamorphic equilibration within this type 3.4 chondrite.) Thus it would appear that the ordinary and carbonaceous chondrule precursors were originally on opposite sides of the terrestrial line but that during chondrule formation they exchanged oxygen with a com-mon gas plotting close to the terrestrial fractionation line. This inter-pretation was first offered by Clayton *et al.* (1983). More recently, a glass fragment in the ordinary chondrite Mezö-Madaras has been located which contains very heavy oxygen, leading to the suggestion that both carbonaceous chondrites and ordinary chondrites exchanged oxygen with two different reservoirs of isotopically heavier oxygen (Mayeda *et al.*, 1989; Clayton *et al.*, 1991). Silica-rich chondrules and clasts also contain isotopically heavy oxygen (Olsen *et al.*, 1981; Bridges *et al.*, 1993; 1994). Rates of exchange with silicate melts have been measured at 1 atmosphere by Yu *et al.* (1994). Thiemens (1994) has suggested that these trends are the result of chemical fractionation processes accompanying chondrule formation, rather than exchange with environmental gases.
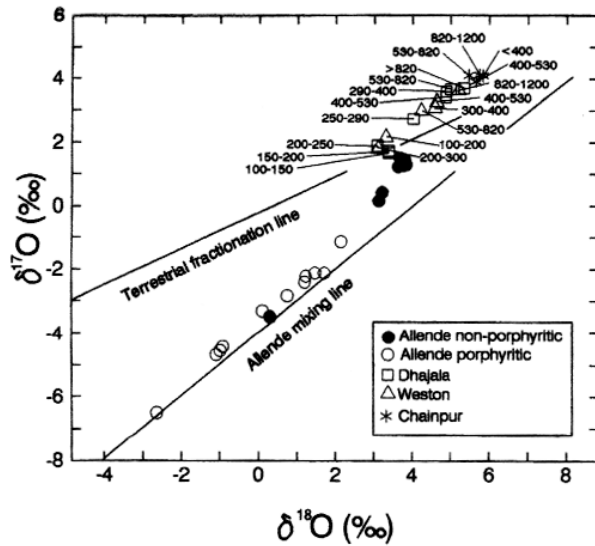
Fig. 10. Three-isotope plot for Dhajala, Weston, Chainpur and Allende chondrules. The values alongside the chondrule data refer to diameters in micrometers. Smaller chondrules from ordinary chondrites (which includes the non-porphyritic chondrules) show a tendency towards lighter oxygen while non-porphyritic chondrules from Allende show a tendency towards heavier oxygen. The two trends seem to be converging near the terrestrial line. Data from Clayton *et al.* (1983, 1991).

While the details are disputed, it seems clear from oxygen isotope properties that the chondrules were open systems during their formation.

6. Recondensation

Several chondrules in Semarkona (LL3.0) show evidence for the recondensation of volatiles prior to aggregation in the meteorite, probably during or immediately following chondrule formation. Compositional zoning in the mesostasis of certain group A chondrules can be measured directly with the electron-microprobe or observed indirectly in cathodoluminescence and thermoluminescence images. Such chondrule mesostasis zoning has been observed in ordinary chondrites (Matsunami *et al.*, 1993) and carbonaceous chondrites (Ikeda and Kimura, 1985). The possible causes of this zoning were discussed at some length by Matsunami *et al.* (1993) who concluded that it was the recondensation of volatiles lost from the chondrule during formation. Certainly, the zoning implies that the hot chondrule was in an environment enriched in the volatile elements like Na. Lewis *et al.* (1993) have demonstrated experimentally that Na can re-enter the heated chondrules very rapidly under conditions where P(Na) is considerably enhanced over cosmic.

Grossman and Wasson (1985), Huang *et al.* (1993b) and Zanda *et al.* (1995) have pointed out that sulfides are less abundant in the interiors of group A chondrules than group B chondrules. Sulfides often occur near the outer edges of group A chondrules or in their rims, suggesting major redistribution of sulfur during chondrule formation rather than complete loss. Sears and Lipschutz (1994) have discussed trace element data for highly labile elements in

chondrules which they also interpret in terms of redistribution, possibly involving recondensation, during chondrule formation.

Hewins (1989) and Huang *et al.* (1993b) have suggested that the fine-grained metal- and sulfide-rich silicate rims around chondrules, described by King and King (1981) and Allen *et al.* (1980), are the product of recondensation of major volatiles (like Si and Fe) lost during chondrule formation on the outside of the chondrule prior to aggregation in the meteorite. This seems to be consistent with the observation of Huang *et al.* (1995) that rims are more common around group A chondrules than group B chondrules. Sears *et al.* (1993) made a similar observation for the chondrules in the Murchison CM chondrite.

SUMMARY AND CONCLUSIONS

At the risk of oversimplifying a number of complex arguments, Table 3 summarizes the major properties of chondrules and whether these are best interpreted as evidence for open or closed system chondrule formation. Precursor mixing requires components which are members of a reduction-volatility sequence perhaps analogous to a condensation/evaporation sequence. It is possible, but not proven, that nebular condensation could have produced such precursors, although not the low-Ni metal observed in group A chondrules. A major problem for the precursor mixing theory is that it does not explain the size and mineralogical differences between group A and group B chondrules.

Open-system behaviour during chondrule formation explains why reduced and volatile-poor chondrules are smaller and why the mineralogy varies as a function of olivine composition. It involves a process known to have occurred (chondrule formation), and associated processes which are to be expected on the basis of laboratory and theoretical data. Open-system behaviour is also consistent with the O isotope data, the compositional zoning sometimes observed in the mesostases and the preferential occurrence of rims on group A chondrules.

Chondrule formation was a very heterogeneous process. While evaporative loss of major elements and reduction of FeO during chondrule formation were the major factors in determining the diversity in chondrule properties, the processes went to varying degrees of completion and there was considerable random heterogeneity in the precursors. It seems clear from the presence of relict grains in chondrules (Rambaldi, 1981; Nagahara, 1981; Jones,

Table 3. *Chondrule properties and open- and closed-system behavior*

Major chondrule properties	Open	Closed
1. Range of P(O$_2$)	Yes	Yes
2. P(O$_2$)-related patterns in mineralogy	Yes	No
3. Elemental abundance trends	Yes	Possibly
4. Differences in size	Yes	Doubtful
5. O isotope trends	Yes	No
6. Recondensation of volatiles	Yes	No

1995) and the restricted range of oxygen isotope compositions (Clayton *et al.*, 1991), that recycling of chondrule fragments also occurred during chondrule formation (Alexander, 1995). While significant progress has been made in identifying the many factors driving chondrule properties, and it is possible to sort some of these factors in order of importance, some of the details will be difficult or impossible to determine because of the complexity of the process. Indeed, because of the stochastic and heterogeneous nature of the processes it may not be possible to even meaningfully address some details. This is the second major aspect of chondrule formation; the process was stochastic, and the precursors heterogeneous, and this surely eliminates some of the many mechanisms for chondrule formation that have been proposed.

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