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DO NEBULAR FRACTIONATIONS, EVAPORATIVE LOSSES, OR BOTH, INFLUENCE CHONDRULE COMPOSITIONS?

R. H. HEWINS[1], Y. YU[1], B. ZANDA[2] and M. BOUROT-DENISE[2]

[1]*Department of Geological Sciences, Rutgers University,*
Piscataway, NJ 08855, U.S.A.
[2]*Muséum National d'Histoire Naturelle, 61 rue Buffon, 75005 Paris, and*
Institut d'Astrophysique Spatiale, 91405 Orsay, France

Abstract: We have made observations and performed heating experiments to determine the relative importance of several processes which may have influenced the compositions of chondrules. As heating destroys nuclei, the number density of olivine and pyroxene crystals gives an indication of the extent of melting. We determined number densities of Semarkona type I chondrules and converted them to nominal grain size, for use as a measure of intensity of heating. Bulk compositions of the chondrules show correlations with nominal grain size. Na, K, Fe, Ni, P and S decrease as grain size (degree of melting) increases, and we interpret this as evidence of evaporative loss. The evidence is less clear for Mn, Cr and Si. SiO_2/MgO ratios show very large variations even in fine-grained type I chondrules containing FeS, and we interpret those variations as due to nebular fractionations affecting precursors. Experiments show that Na and S losses increase with higher temperatures and lower cooling rates. It is hard to preserve any sulfide at all, without flash heating. Na, however, can be retained at close to chondritic levels (as in type II chondrules) with flash heating and high cooling rate, provided also that the oxygen fugacity is high. Type II chondrules can retain much more Na than type I under identical thermal conditions, because of higher fO_2 (either due to non-nebular gas or possibly internal buffering by FeO content) and melt structure (higher SiO_2/MgO). Gas reduction experiments show that type II compositions can be converted to IB by Fe loss, but evaporative loss of SiO_2 (so as to approach IA composition) is not achieved without prolonged isothermal heating. Precursors of type I and II chondrules were probably close to chondritic in composition, but with higher Fa in the type II case. They consisted of olivine, pyroxene, plagioclase, Fe(Ni)S and carbon compounds, probably with insignificant metal. Sulfur loss generated much chondrule metal in ordinary chondrites. C is a possible alternative to gas reduction to explain dusty relict grains and the lower olivine Fa in the more melted type I chondrules. We agree with J. N. GROSSMAN and J. T. WASSON (Geochim. Cosmochim. Acta, **47**, 759, 1983) that variations in Mg/Si are due to nebular fractionations and with S. HUANG *et al.* (Icarus, **122**, 316, 1996) that variations in Na and Fe in type I chondrules are mainly due to evaporative losses.

1. Introduction

Chondrules are very abundant in undifferentiated meteorites, and therefore appear to document a major melting event in the solar nebula. One of the biggest puzzles about chondrules, apart from the nature of the process that formed them, is that they occur as two major types, I and II (MCSWEEN, 1977a, b). Type I chondrules are enriched in refractory elements and depleted in moderately volatile elements; type II are approximately chondritic in composition. For unequilibrated chondrites, the type I (FeO-poor) or II (FeO-rich) chondrules have each been subdivided by JONES (1994) into A and B (SiO_2-poor or SiO_2-rich; *i.e.*, olivine-rich and pyroxene-rich respectively), with intermediate subtypes called IAB and IIAB. Understanding the origin of the two major chondrule types is essential for understanding early solar system events, but there are several competing models. The chondrule types may have been formed from very similar undifferentiated, virtually solar composition solids, which were subsequently modified during melting to different extents. Alternatively, they may have formed from materials already fractionated by nebular processes. Type I and II chondrules then may either have formed from low temperature material melted under open system conditions, with volatiles much more extensively lost from type I than type II, or they may represent two sets of nebular condensates formed at different temperatures and subsequently melted as closed systems. GROSSMAN and WASSON (1983), GROSSMAN (1988), HEWINS (1991), JONES (1994) and SCOTT *et al.* (1996) have favored closed systems, and HUANG *et al.* (1996), SEARS *et al.* (1996), GROSSMAN (1991), HEWINS *et al.* (1996), JONES (1990) and SCOTT (1994) have presented arguments in favor of open system models. The debate over which alternative is correct has been very heated, perhaps because it would be very satisfying to have a single simple mechanism to explain all chondrule properties. However, we show here that both processes have been important, and in consequence each may differ in detail from what has been proposed previously.

We have made both observations and experiments relevant to the open/closed system problem. The key to our approach is to compare bulk compositions for more and less completely melted natural type I chondrules and experimental charges, to document any open system behavior. In the case of natural chondrules, our interpretations are based on the conclusions from melting experiments on fine-grained material (TSUCHIYAMA and NAGAHARA, 1981; HEWINS and CONNOLLY, 1996) that the more thorough the melting, the more potential nuclei are destroyed, resulting in fewer (coarser) crystals grown during cooling (and in the limit zero crystals, *i.e.* glass). Based on these experiments, many compositional differences between coarse- and fine-grained chondrules can be attributed to more thorough melting and consequent evaporation, though any differences in more refractory elements cannot be explained by open system behavior. In addition, chondrule formation in a nebular setting may lead to reduction as well as evaporation. Several chondrule properties have been duplicated by reduction of silicate charges by internal carbon (CONNOLLY *et al.*, 1994), but reduction by nebular gas is also possible. We therefore examined the extent of gas reduction in our experiments, as well as the potential role of condensed carbon during chondrule melting.

2. Samples and Experimental Methods

We systematically studied all the chondrules (~300) in one thin section of Semarkona (USNM 1805-4), with emphasis on comparing composition to a quantitative measure of the degree of melting experienced by different type I chondrules. In all the finest ones, as well as in a representative set of coarse ones, we determined the number of olivines and inverted protopyroxenes per unit area, including the smallest microphenocrysts but excluding dendrites. This number is a melting indicator, because it reflects the number of relicts or nuclei remaining in the melt when cooling began. The number density can be measured much more precisely than grain size, to which it is directly related, but is simpler than a grain size distribution. It can be converted (by taking the inverse of its square root) to a nominal grain size, a more readily understood parameter. Nominal grain sizes are larger than true mean grain sizes because glass etc. is included in the area counted and, unlike the true grain size, they depend only on the number density of crystals rather than the extent to which they have grown as a result of cooling. A quantitative indicator of melting, even an approximate one like this, is valuable because using textural terms to describe the differences results in rather arbitrary distinctions within an apparent continuum of properties.

Bulk chemical (broad beam electron microprobe) and mineral analyses were obtained for all the finer-grained and the selected coarser grained type I chondrules, using a Cameca SX50 electron microprobe. For bulk analyses, the probe was scanned on a 20×25 micron area, counting first on Na and S for 20 s. Beam current used was 15 nA and acceleration voltage was 15 kV. Phase density corrections, which would increase apparent Ni and S concentrations, have not been applied. Although the broad beam technique has limitations (ALBEE *et al.*, 1977), the order of magnitude differences of concentrations in chondrules in the thin section are clearly greater than the errors involved.

Experiments were performed on several compositions (types IA, I or IAB, and II/III or IIAB) originally used by RADOMSKY and HEWINS (1990) and renamed to be consistent with JONES (1994, 1996a). One IIAB chondrule composition was prepared from glass and type IA, IAB and IIAB analogues were prepared from mixtures of olivine, pyroxene and feldspars (YU and HEWINS, 1997). The minerals were crushed

Table 1. Composition of chondrule analog materials.

	IA	IAB	IIAB*	IIAB
SiO_2	46.42	47.42	49.10	49.45
TiO_2	0.08	0.06	0.25	0.04
Al_2O_3	3.09	9.70	0.83	4.13
FeO	7.92	5.91	21.30	19.97
MnO	0.12	0.08	0.46	0.06
MgO	38.23	30.84	24.30	22.85
CaO	2.51	3.52	0.86	0.23
Na_2O	1.32	2.09	1.94	2.34
K_2O	0.05	0.07	0.27	0.11
Total	99.74	99.70	99.30	99.17
$T_{(liq)}$	1692°C	1577°C	1509°C	1481°C

Note: $T_{(liq)}$ =liquidus temperature calculated based on HERZBERG (1979). The starting materials are either mixtures of natural olivine, orthopyroxene, albite, and labradorite, or glass (designated by *) made by fusing commercial oxides and carbonates.

but not sieved before mixing, yielding an average grain size of about 50 μm. Table 1 shows bulk compositions of starting materials. These materials were used in experiments to measure independently the extent of Na evaporative loss and Fe reduction. Similar compositions with 5% pyrrhotite added were used to examine S loss. Samples were melted on Pt wire loops in a DelTech vertical muffle tube furnace, with an H_2-CO_2, CO-CO_2 or in some cases H_2-He atmosphere, and with fO_2 generally controlled at 0.5, 2 or 4 log units below the Fe-FeO buffer curve. Pt wires were analyzed for Fe after use, and the charge plus wire were weighed before and after use to estimate evaporative loss. Na loss was also measured in charges with graphite added. Though some isothermal experiments were performed, we report here on flash-heated runs (inserted in furnace, held at peak temperature for 1 min and cooled in steps with successively decreasing cooling rates). The flash-heated runs were cooled over 5 steps to approximate the Stefan-Boltzmann cooling curve appropriate for chondrules (Tsuchiyama *et al.*, 1981). For the steepest curve, initial and final linear steps had 5000 and 500°C/hr cooling rates; for the flattest curve, cooling rates decreased from 480 to 250°/hr.

Experiments were performed in duplicate. One set of charges was analyzed for Na and other major elements by direct current plasma atomic emission spectrometry (DCP-AES), after fluxing and dissolution. A JEOL 8600 electron microprobe was used for imaging the second set of samples, analyzing minerals, confirming glass homogeneity, and checking for the survival of sulfide. Additional details of experimental and analytical techniques are given in Yu and Hewins (1997) and Yu *et al.* (1996).

3. Chondrule Analyses

Type I chondrules in Semarkona are fine grained and described as porphyritic (PO, PP and POP), *e.g.* by Jones and Scott (1989), though technically even coarser grained chondrules (type IIA) should be described as microporphyritic or even vitrophyric. For convenience we set the limit between PO and MPO at 40 μm nominal grain size, about 100 μm average grain size, which makes most IIA chondrules (Jones, 1990) PO and most IA (Jones and Scott, 1989) MPO. We set a lower limit for MPO at 10 μm nominal grain size, for reasons discussed below. An example is shown (Fig. 1a) , with a nominal grain size of 29.6 μm, and a range of actual grain sizes of about 10–80 μm.

Microporphyritic texture can be recognized in the optical microscope as long as the actual grain size is not much smaller than the thickness of the section (30 μm). Otherwise, glass and crystal outlines are hard to see (Dodd, 1971), and the chondrules appear granular (McSween, 1977a), except in BSE images where the very fine porphyritic texture appears clearly (Fig. 1b, c). No adequate terminology exists to describe such very fine grained porphyritic textures. In a significant fraction of them, opaques are abundant as more or less concentric shells or arcs, *e.g.* Fig. 1c at right, leading to the name dark-zoned chondrules (Dodd, 1971; Rubin, 1984; Hewins, 1996). However, this term does not apply to all very fine grained chondrules and does not reflect the actual texture of the silicate portion as seen in BSE. For this reason, we define the texture of chondrules with 5–10 μm nominal grain sizes seen to be porphyritic in BSE

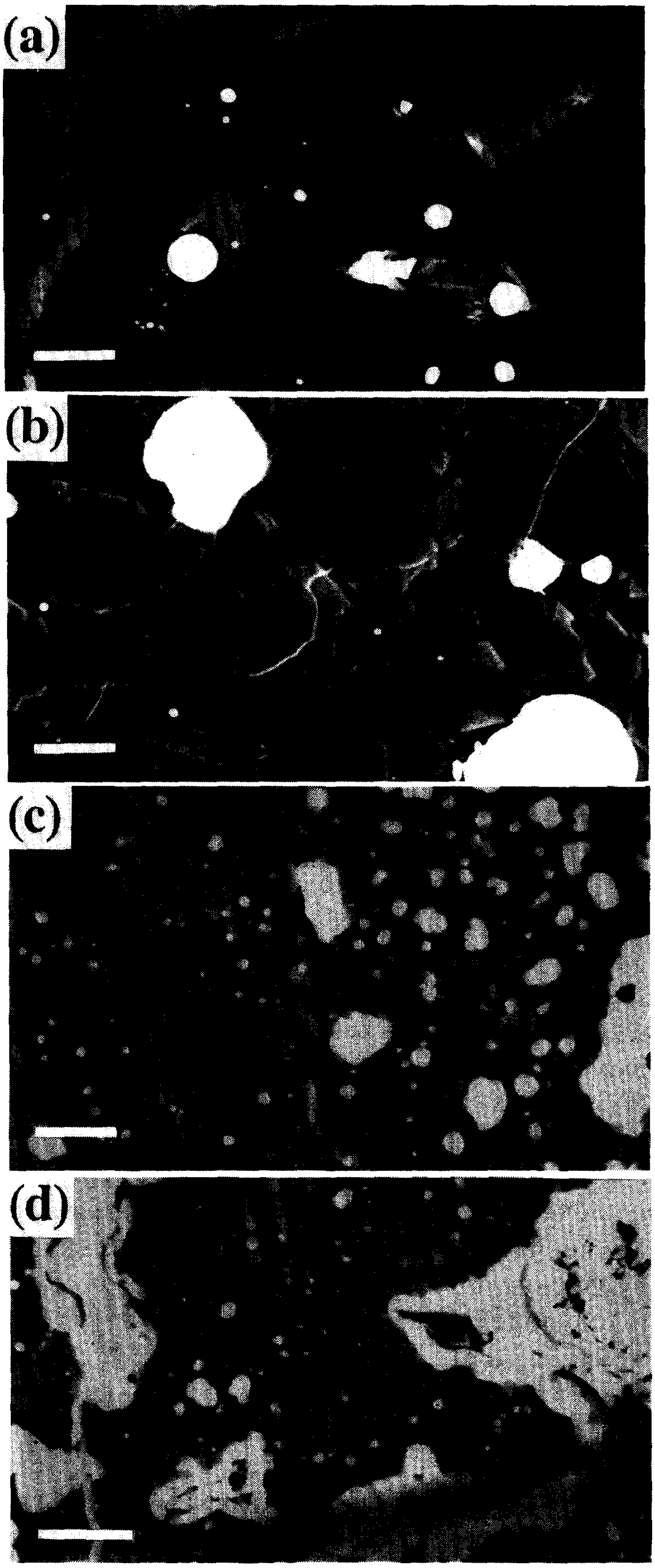

Fig. 1. Semarkona type I chondrule textures, with euhedral olivine and pyroxene in interstitial glass, seen in back-scattered electrons. (a) Microporphyritic, nominal grain size (NGS, calculated from olivine number density: see text) 29.6 μm (b) cryptoporphyritic, NGS 9.9 μm, kamacite droplets (c) cryptoporphyritic, NGS 5.1 μm, dark-zoned with zone rich in troilite-metal blebs at right (d) protoporphyritic, NGS 3.9 μm, abundant troilite-rich masses interstitial to silicate. All pictures at same scale, except (d); (scale bars 10 μm).

as “cryptoporphyritic”. We show two examples of this texture, one close to the upper size limit, with grain size range roughly 1–50 μm and opaques dominated by kamacite (Fig. 1b), and one close to the lower limit, with grains roughly 1–20 μm and opaques dominated by troilite (Fig. 1c).

The finest-grained chondrules have observed crystal sizes ranging from <1 up to ~30 μm (similar to cryptoporphyritic but with smaller mean grain sizes and with calculated nominal sizes in the 3–5 mm range), and they resemble somewhat the aggregational chondrules of Weisberg and Prinz (1996). They too are often zoned, in opaque abundance and/or silicate grain size, and they appear unevenly melted: clear igneous textures are present together with apparently unmelted relict patches. Glass is scarce, mainly interstitial to olivine, and irregularly distributed as small patches (Fig. 1d). In the example shown, the nominal grain size is 3.90 μm. By analogy with terrestrial basalts, we would characterize this texture as “intersertal”, though the chondrules are much finer grained and lack plagioclase laths. To emphasize the similarity to porphyritic chondrules, and the complete gradation of textures from the finest to the coarsest, we use here the term “protoporphyritic”. Opaques tend to form large irregular masses interstitial to the silicate crystals in these protoporphyritic chondrules, rather than forming droplets in glass as in coarser chondrules. The opaque mineralogy of these chondrules is distinctive too: in addition to troilite and scarce Fe-Ni (awaruite+kamacite), pentlandite is present, as well as magnetite and cohenite (Zanda *et al.*, 1996). This indicates the decomposition of a Ni-bearing monosulfide solid solution.

Average olivine compositions in the Semarkona type I chondrules are $Fo_{99.6\text{-}91.9}$, excluding more ferroan relict grains. This range is more limited than the range in bulk Fe (1.6–29.4%, expressed as FeO) would suggest, reflecting the abundance of Fe as FeS and Fe-Ni. Chondrules with nominal grain size below 10 μm have $Fo_{94.5}$ on average, whereas those with grain size over 100 μm have $Fo_{99.1}$. The correlation between Fa content of olivine and grain size for all chondrules (Fig. 2) is modest ($R=-0.55$), though stronger than between Fa and bulk $\Sigma FeO/MgO$. Both the silicate and non-silicate Fe abundances decrease with increasing grain size. Olivine- and pyroxene-rich varieties occur for all grain sizes. Coarser grained POP chondrules have pyroxene-poor interiors and pyroxene-rich borders or rims, as noted by Jones and Scott (1989), but finer grained ones are homogeneous.

Chondrule bulk composition variations are shown in Fig. 3 where chondrite- and Mg-normalized concentrations for all the elements analyzed are plotted, separating data by nominal grain size. The bins correspond to protoporphyritic (2 samples), cryptoporphyritic (7), microporphyritic (12) and porphyritic (7) chondrules, using these terms as defined above as an indicator of degree of melting. (One barred olivine chondrule is included under PO). Selected standard deviations are shown in Fig. 3. For the more refractory elements, the range of ±1 standard deviation is about the size of the symbol plotted. For the more volatile elements, standard deviations are such that each grain size group tends to overlap the adjacent group(s), a consequence in part of the zoned texture of most of the fine grained chondrules studied.

The finest grained (protoporphyritic) type I chondrules have bulk compositions close to CI (Fig. 3), with most of the Fe present as FeS. One of the two samples is

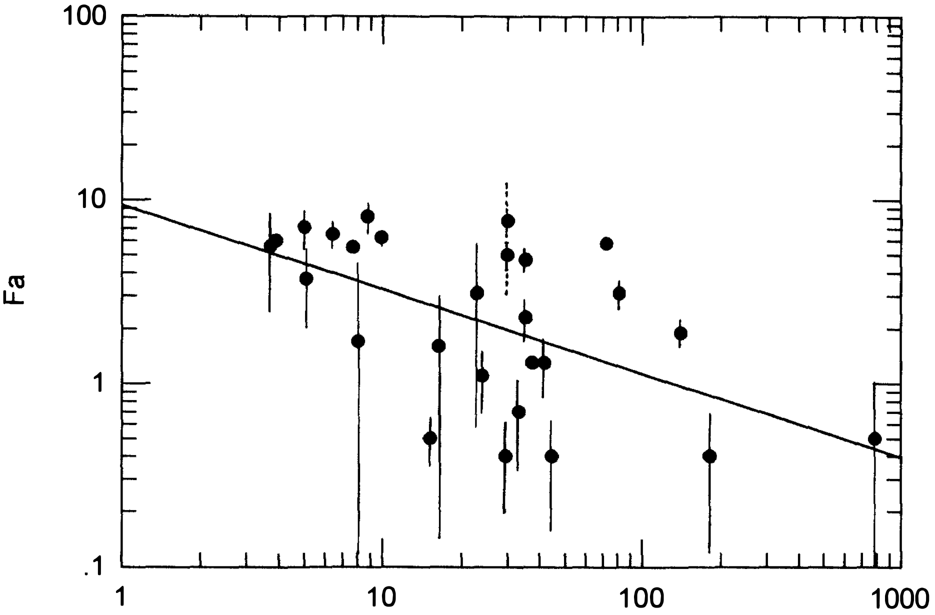

Fig. 2. *Variation of Semarkona type I chondrule olivine Fa (mol%) as a function of chondrule nominal grain size in microns. The least melted (finest grained) chondrules have the most ferroan olivine. The correlation coefficient is −0.55. The error bars indicated are standard deviations.*

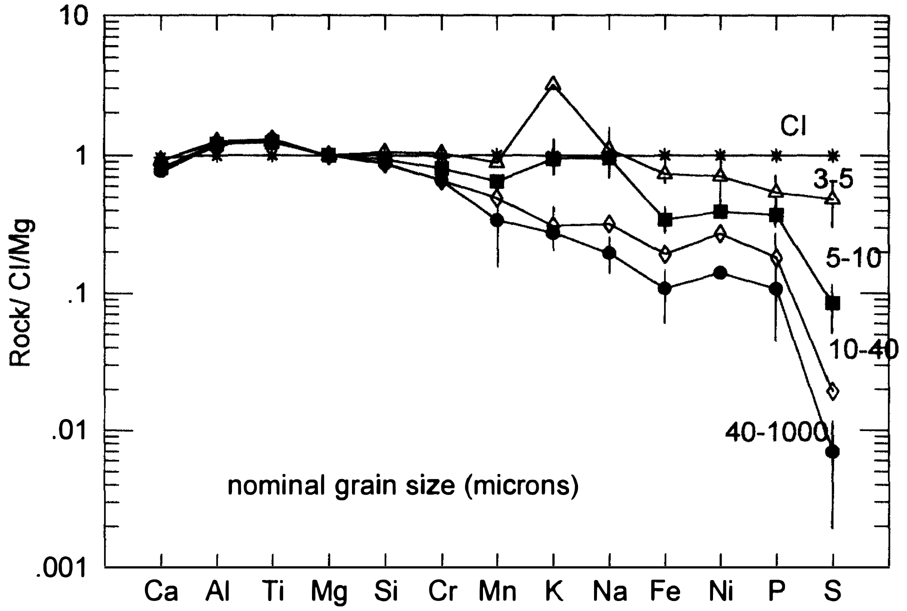

Fig. 3. *Chondrite- and Mg-normalized bulk compositions of Semarkona type I chondrules determined by electron probe broad beam analysis. Depletions in moderately volatile elements correlate with extent of melting. Asterisks represent CI; triangles, protoporphyritic chondrules with nominal grain size (NGS) 3–5 μm; squares, cryptoporphyritic chondrules, NGS 5–10 μm; diamonds, microporphyritic chondrules, NGS 10–40 μm; and circles, porphyritic chondrules (plus one BO), NGS 40–1000 μm. Selected error bars (± 1 standard deviation) are shown.*

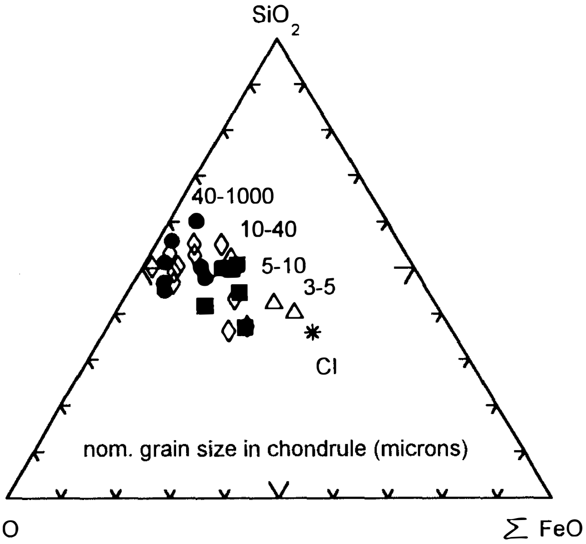

Fig. 4. Chondrule bulk compositions as a function of nominal grain size, with symbols as in Fig. 3. The most extensively melted chondrules have the lowest total Fe concentrations. The biggest variation is seen in the microporphyritic chondrules (diamonds): those with NGS 10–25 μm overlap cryptoporphyritic chondrules, and those with NGS 25–40 μm overlap porphyritic chondrules.

extremely K-rich; the other is normal. Cryptoporphyritic chondrules (5–10 *μm*) are depleted in ΣFe, Ni, P and S and, with grain size coarser than 10 μm, K and Na are also depleted. The moderately volatile elements Na, K, Fe, Ni, P and S decrease systematically as grain size increases, *i.e.* degree of melting increases, (HEWINS *et al.*, 1996). Si concentrations also decrease with grain size, but the differences are not statistically significant.

The largest variation in the major elements is seen in the ΣFe-Si-Mg triangle (Fig. 4) to be in Fe. A small depletion might be inferred for Si, Cr and Mn from Fig. 3, but as SiO_2/MgO varies widely even in the finest-grained type I chondrules (by a factor of 1.6 in those with grain size <10 μm) and independently of Fe, the apparent correlation of SiO_2 with grain size in Fig. 3 is not necessarily significant.

SiO_2/MgO variations are shown in Fig. 5 as a function of Na_2O/MgO, and very similar patterns are seen against Na_2O/Al_2O_3 ratios. The overall trend of positive slope from chondrules near CI composition with high Na and high SiO_2/MgO to chondrules with low Na_2O/MgO and low SiO_2/MgO, though very rough, could suggest that the apparent SiO_2 depletion of Fig. 3 is real and due to Si loss along with Na. However, when the chondrules are broken down into grain size groups, we find the same trends in each group, as indicated by the three separate regression lines in Fig. 5. There is no systematic depletion of both Si and Na as grain size increases. The dashed lines in Fig. 5 represent Fo-En mixtures with 20%, 10%, etc., Ab, and in Section 5.1 we consider an explanation for SiO_2 variations as due to olivine/pyroxene variations in Na-rich precursors.

Figure 6 shows the concentration of S in the Semarkona type I chondrules *vs.*

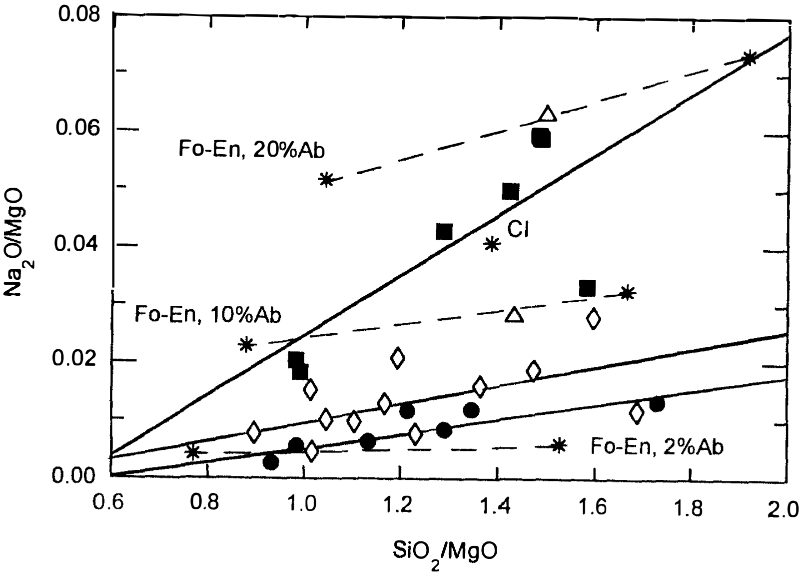

Fig. 5. *Chondrule bulk Na_2O/MgO ratios show a general correlation with SiO_2/MgO. Three regression lines are plotted on the diagram (symbols as in Fig. 3). The upper one (R =.771) is for NGS 5–10 microns (cryptoporphyritic); the middle one (R =.582) is for 10–40 microns (microporphyritic); the bottom one (R =.865) is for 40–1000 microns (porphyritic). The dashed lines are FoEn mixtures with 20%, 10% and 2% Ab. The asterisk is CI composition. Apparently, there is no evaporative loss of Si during chondrule heating, but Na is lost faster from Si-poor compositions.*

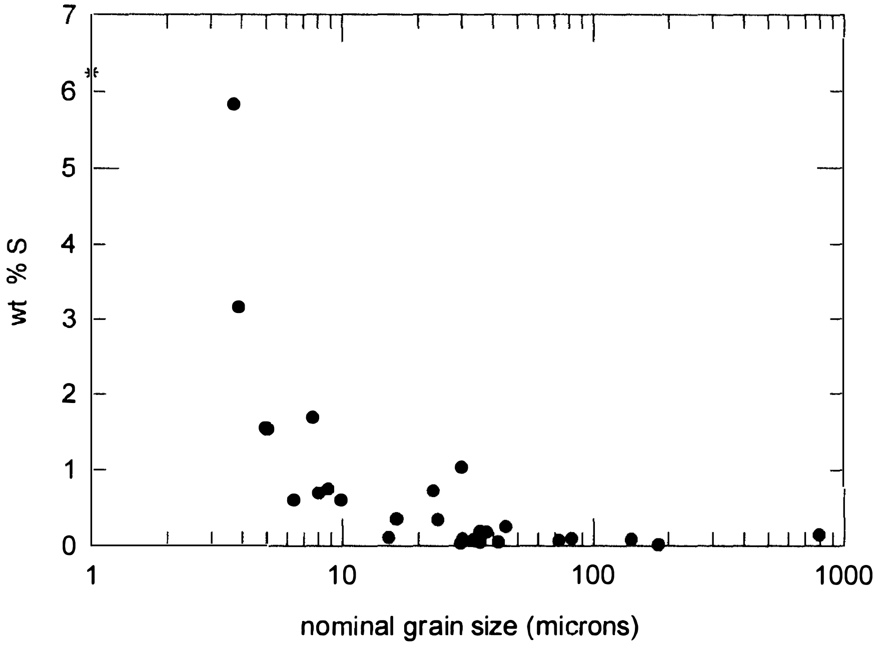

Fig. 6. *Chondrule S concentrations plotted against grain size. Standard deviations are very large, because the distribution of sulfide in the chondrules is very heterogeneous. The asterisk is CI, assigned an arbitrary grain size of 1 micron. The smooth depletion trend as a function of degree of melting suggests evaporative loss.*

nominal grain size. Note that the S depletion is a smooth function of grain size, with no particular concentrations being associated with any of the textural classes distinguished. Similar patterns are observed for Fe, K and Na, though the decrease in concentration as grain size increases is more gradual (HEWINS *et al.*, 1996). Sulfide is totally absent from the most melted type I chondrules (PO, BO) in Semarkona (and Renazzo). On the other hand S is concentrated in opaque veneers around chondrules interior to opaque matrix or silicate rims when present. This veneer or encasement (HAGGERTY and MCMAHON, 1979) is not considered part of the chondrule for analysis purposes. By point counting, we find that the veneers contain about 1/2 of the meteorite's bulk S for Semarkona). As in Allende (HAGGERTY and MCMAHON, 1979), S in veneers is present in troilite associated with pentlandite and awaruite. In the interiors of cryptoporphyritic chondrules, sulfide exhibits clear melt textures (droplets in silicate glass, and eutectic mixes when associated with metal). At even lower grain sizes (protoporphyritic chondrules) the pentlandite assemblage of chondrule veneers is found in the interstitial masses of sulfide, with very little kamacite. Thus the metal-sulfide proportions and phases change systematically as the abundance of S in the bulk chondrule analyses varies.

4. Chondrule Experiments

Various experiments have been performed to examine loss rates of moderately volatile elements from chondrule compositions subjected to short duration heating. Na loss/retention was measured as a function of peak temperature, bulk composition, oxygen fugacity and cooling curve (YU and HEWINS, 1997). Naturally, it is much easier to retain Na with continuous cooling after very brief heating, as may be appropriate for chondrules, than with isothermal heating of superheated liquids as in earlier systematic experiments (TSUCHIYAMA *et al.*, 1981). Na contents of charges correlate with cooling rates, with the strongest effect for the highest peak temperatures, because the longer the charge remains at high temperature, the more Na is lost. The effect of bulk composition on Na loss is shown in Fig. 7, for four compositions whose liquidus temperatures vary from 1481–1692°C heated to initial maximum temperatures of 1470–1620°C. The most MgO-rich composition (type IA) loses up to a factor of two more Na than the least, under identical experimental conditions, despite the fact that (as its liquidus temperature is higher) it is less melted. Though one would expect Mg-rich liquids to lose Na rapidly, because they are very fluid, the partially melted IA charges retain so much solid olivine that the liquids are not that Mg-rich. The strong dependence of Na loss on oxygen fugacity found by TSUCHIYAMA *et al.* (1981) has been confirmed. For type IIAB composition, Na loss can be more than a factor of 2 greater at IW-4 than at IW-0.5, depending on peak temperature (Fig. 8). A similar effect was observed when graphite was added to the charge, instead of lowering the gas oxygen fugacity (YU and HEWINS, 1997).

Sulfur loss experiments similar to those for Na have been performed in H_2-CO_2 atmosphere, using sulfide in the starting materials (YU *et al.*, 1996). Sulfur loss was always extensive, with only 0–10% of the original amount of FeS remaining in the charge (though about 0.15% S may also be present in the silicate glass). The troilite

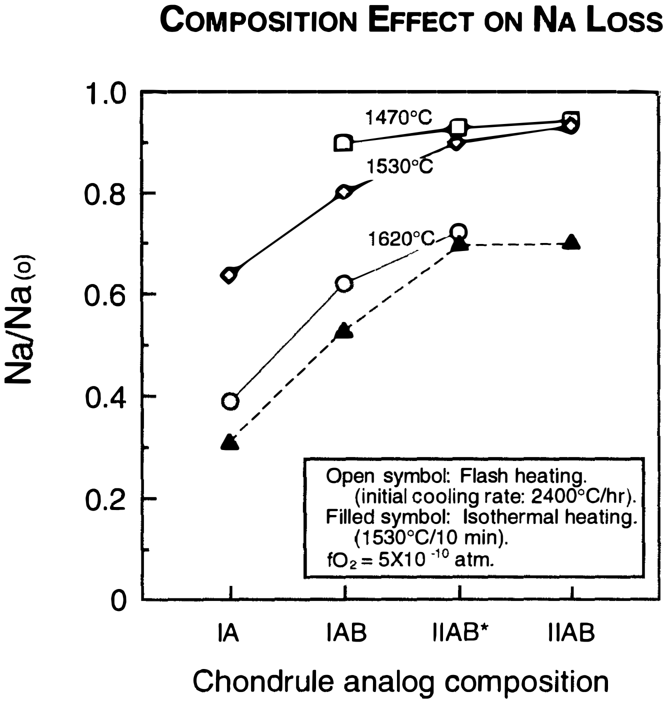

Fig. 7. Heating experiments with different initial temperatures show that Na loss from a magnesian composition (type IA) can be up to twice as much as for a type II composition, for identical conditions, because of the effect of melt structure.

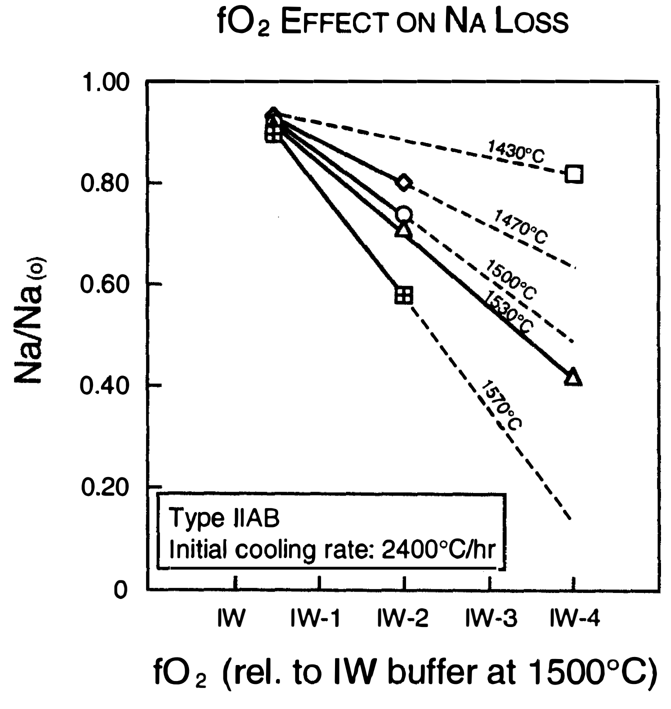

Fig. 8. Lowering the oxygen fugacity can double the amount of Na loss, with all other variables held constant.

occurs as droplets containing kamacite due to reduction caused by S loss, as also observed by Shimaoka and Nakamura (1989). S can be totally lost from chondrules for temperatures near the liquidus, but this depends on total time at high temperature. Some S can survive for lower degrees of heating and S survival is enhanced by higher cooling rates (Yu *et al.*, 1996). Survival is possibly also enhanced by higher oxygen fugacity, but this is not well documented experimentally. We speculate that S is lost more readily at lower oxygen fugacity because more abundant H_2 and CO would promote formation of H_2S and COS.

At the oxygen fugacities which favor extensive Na loss, reduction of Fe silicate by gas is also possible. For runs with type I chondrule compositions, the typical result of gas reduction is the formation of "dusty relict olivines", $Fo_{\sim 90}$ for flash heating conditions. These grains are transformed to $Fo_{98\text{-}99}$ containing Fe metal blebs with longer heating times. Type IIAB chondrule materials, which crystallize more ferroan olivine, would be expected to generate more Fe metal for similar reducing conditions, but even when flash heated at IW-4, they are still similar texturally to those run at IW-0.5, with just a little Fe metal forming on the edge of the charge. They seldom develop dusty olivines except with extremely low fO_2s (run in H_2-He gas). Temperatures higher than the liquidus might favor reduction, but dissolution of the olivine becomes rapid. Longer heating time or slower cooling rate always leads to growth of protopyroxene ($MgFeSiO_4 + H_2 \rightarrow MgSiO_3 + Fe + H_2O$) and poikilitic texture with olivine Fo_{90} to Fo_{92}. About half of the Fe in our experiments is lost to the wire and about half is lost by evaporation, based on analyses of the wires and weight loss of charge plus wire after heating. Type IIAB starting material gradually becomes type IB in composition with 5 to 15 min reduction and Fe loss above the liquidus, similar to evaporative composition changes observed by Hashimoto (1983), and the Na loss is nearly 100%.

5. Discussion

5.1. Chondrule composition trends

Explanations for the occurrence of two major chondrule groups, type I (FeO-poor, enriched in refractory elements and depleted in moderately volatile elements) and type II (FeO-rich and approximately chondritic in composition), involve either open or closed systems. Chondrules may have been formed from closed system melting of material fractionated by nebular processes, *e.g.* medium-low temperature condensates, or from open system melting of undifferentiated, virtually solar composition solids. The main condensation reactions involve reaction of Fo with gas to form En, and of En with Fe to form Fa_{50}. These changes are in the opposite direction to the chondrule reduction reactions we discussed above. In the first case (closed system melting of different condensates), chondrule formation could have continued throughout the condensation sequence. In the second, it would have occurred after condensation, and the range of chondrule compositions might have been largely derived by loss of moderately volatile elements from a single precursor composition.

Huang *et al.* (1996) and Sears *et al.* (1996) proposed that chondrule precursors were FeO-rich, similar to type II (or group B) chondrules: heating in an environment with high oxygen fugacity caused little volatile loss or reduction, giving type II chondrules; heating with lower oxygen fugacities caused extensive Na loss and FeO reduction to Fe metal, giving type IAB chondrule compositions; and in the extreme, Si was also proposed to have been lost by evaporation giving type IA compositions. GROSSMAN (1988, 1996a), however, has argued that chondrule compositions were essentially fixed by prior fractionations and but little modified during melting. The two processes which have been used to explain chondrule compositions, nebular fractionation before chondrule formation and evaporative loss from chondrule melts, were not necessarily mutually exclusive and in this study we consider whether both influenced type I chondrule compositions. We consider firstly variations in the moderately volatile elements and secondly Si.

The continuous negative correlation trend found in Semarkona type I chondrules between grain size and abundance of volatiles suggests a genetic continuity between all type I chondrules from the "orthodox" coarse ones to the finest ones (Fig. 3; HEWINS *et al*, 1996; ZANDA *et al*., 1996). The elements Na, K, Fe, Ni, P and S decrease systematically as grain size of type I chondrules in Semarkona increases. This suggests that the main differences between chondrules in the suite reflect the melting intensity and subsequent degree of volatile loss, and the finest grained chondrules are closest to their precursors. We take this as evidence for open system melting, because if compositions were acquired before melting it is not clear why the most volatile-rich ones should be the finest grained. An alternative interpretation is that fine grained objects, particularly protoporphyritic chondrules, might be similar in age to chondrule rims. They might be derived from dust plus volatiles recondensed after chondrule formation, by melting during the waning of chondrule formation. However, the volatile depletion trends are not restricted to protoporphyritic chondrules (Figs. 2, 5). If the protoporphyritic chondrules are late material, it is not clear why there is a smooth grainsize-composition trend across the data set instead of two distinct chondrule populations, and regardless of the origin of protoporphyritic chondrules, there appears to be volatile loss in the remaining crypto-, micro- and porphyritic chondrules. According to SCOTT (1996, pers. comm.), closed system behavior may still be reconciled with the grainsize-composition correlation we observe if the volatiles condensed more efficiently onto finer grained objects. However, we emphasize that textures of metal-sulfide assemblages in cryptoporphyritic chondrules clearly indicate that S was present in a metal-sulfide liquid and not condensed onto solid metal. It seems implausible that fine-grained condensates or aggregates formed only in the waning phase of chondrule formation. It is easier to suppose that all precursors were similar, and that concentrations of Na, Fe, *etc*., as well as textures, reflect the intensity of heating.

The general trends, in particular Fe loss, expected for open system melting follow the average compositions of some of the main chondrule types (IIA-IB). However, the observed Si losses in evaporation experiments (HASHIMOTO, 1983; NAGAHARA, 1996) suggest that very high temperatures or very long times would be required to generate type IA chondrules from IB by the Si loss mechanism suggested by SEARS *et al*. (1996). If chondrules formed by flash heating, extreme temperatures would be required. Conceivably type II chondrules formed by flash melting, but type IA experienced long heating times at similar temperatures (LIBOUREL and CHAUSSIDON, 1995; NAGAHARA, 1996). Extended heating times are hard to reconcile with possible chondrule formation mechanisms (BOSS, 1966) so that appealing to more intense temperatures (HUANG *et al.*, 1996) would be the more conservative position, if Si evaporation could be demonstrated.

In the ΣFe-Si-Mg triangle (Fig. 4), the data lie predominantly on the Si-poor side of a simple Fe loss trend from CI composition, suggesting possible evaporative Si loss accompanying Fe loss. However, they also lie mainly within a polygon bounded by forsterite, enstatite, troilite and fayalite, showing that the Si/Mg variations could equally well have been caused by precursor effects (condensation). SiO_2/MgO variations are shown in Fig. 5, as a function of Na_2O/MgO ratios, with the data broken down into three grain size groups. For each group there is a similar trend, as indicated by the three separate regression lines in Fig. 5. It is hard to believe that the more refractory Si was being lost along with Na from the 5–10 μm grouping, where sulfide was partially preserved. The data are more easily explained as resulting from mixing of a Na-rich phase like albite with forsterite-enstatite mixtures, *i.e.* precursor effects, with subsequent modification by Na loss almost exclusively. If we take the upper dashed line in Fig. 5 ($Fo_{80}Ab_{20}-En_{80}Ab_{20}$) as representing a possible range of precursor compositions, we could postulate that the different grain size groups of chondrules correspond simply to different levels of Na loss, except that the slopes of the regression lines for the chondrule groups are steeper than the dashed Fo-En tie lines. Assuming initial Na near (or above) CI levels for all the chondrules would require greater Na loss from those with lower SiO_2/MgO, and exactly that effect is observed in melting experiments described above: Na losses are higher from Mg-rich, Si-poor compositions (Fig. 7). While the most melted chondrules have conceivably lost a little Si, it is likely that most of the variation arises from Na-rich precursors with very different SiO_2/MgO and pyroxene/olivine ratios. Large scale SiO_2/MgO variations throughout the Semarkona type I chondrule suite are uncorrelated with grain size and therefore do not appear to be related to degree of heating and Si volatile loss, as predicted by SEARS *et al.* (1996). Similarly, in the Semarkona chondrules of JONES and SCOTT (1989) and JONES (1990, 1994, 1996a) there is a pattern consistent with Na and Fe loss in the sequence IIA-IIB-IB-IA, but Si reaches highest values in the type IIB chondrules (Fig. 9). Different olivine/pyroxene ratios in chondrule precursors, assuming they were crystalline, presumably could be due to condensation/agglomeration processes, either systematic differences in condensation location or conceivably just random differences during agglomeration (HEWINS, 1989; HEWINS *et al.*, 1996), or random differences in chondrule debris, etc., to be recycled (ALEXANDER, 1996). If this explanation, instead of Si loss, should prove correct, it would indicate limits to the intensity of the melting event.

Grossman (1996b) has found that type I chondrule glasses in Semarkona are enriched in Na near the chondrule margins, and are particularly low in Na when enclosed in olivine crystals. He concluded that there was pervasive Na metasomatism of chondrules in Semarkona. As in the case of S (below), this might be linked somehow to a recondensation process, with Na lost during chondrule melting subsequently diffusing back into chondrule glass. The smoothness of the trends we see makes us believe that the secondary modification has a relatively minor effect on chondrule bulk compositions.

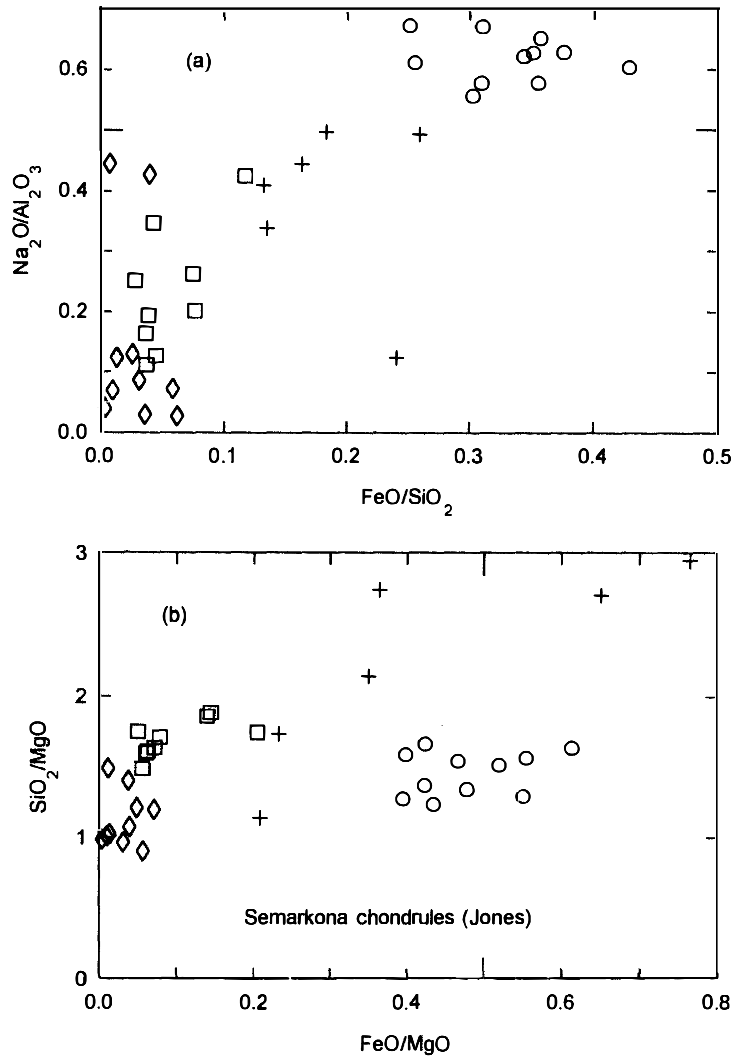

Fig. 9. Semarkona chondrules analyzed by Jones *and* Scott *(1989) and* Jones *(1990, 1994, 1996a). Diamonds - type IA; squares - IAB,IB; circles - IIA; plusses - IIAB,IIB. There is a pattern consistent with evaporative loss for Na and Fe in the sequence IIA-IIB-IB-IA (top). This is not true for Si, where IIA are out of sequence such that Si would have to be acquired to reach IIB, and another mechanism (precursor effect?) is required.*

We have made some preliminary analyses of some of the type II chondrules in Semarkona and note that the difference in olivine composition on which the classification as type I or II is based, is maintained down to the finest grain size. This suggests that there were pre-chondrule differences as well as modifications during chondrule formation (Hewins *et al.*, 1996). These differences might be simply different initial olivine compositions or alternatively different C contents (as above reflecting condensation kinetics or agglomeration efficiency) with reduction forming more Mg-rich olivine in the latter case. The possible role of carbon is discussed more fully below.

5.2. Evaporation and reduction experiments

We have observed the behavior of some of the moderately volatile elements in melting experiments. It is hard to retain all of the least volatile of these elements (Na) or any of the most volatile (S) in our charges. In order to retain chondritic levels of Na, as in type II chondrules, we require flash heating, peak temperature not much above the liquidus, initial cooling rates in the thousands of degrees per hour and, relative to the solar nebula, very high oxygen fugacity. Type IA chondrules may lose more Na than type IIAB chondrules under identical conditions because they are less oxidised and because the melt has lower Si/Mg, is much less polymerized and the Na-O bond is weaker. Figure 7 appears to show such bulk composition effects on Na, when other variables including gas oxygen fugacity, are constant. However, the more MgO-rich charges in Fig. 7 are not completely melted, which should limit the efficiency of this melt structure effect. In Semarkona chondrules (YU and HEWINS, 1967), bulk Na concentrations correlate with oxygen fugacity (calculated from the composition of olivine coexisting with Fe-Ni and pyroxene or glass, as in ZANDA *et al.*, 1994) but also negatively with Mg/(Si+Al). It may be that their Na losses result in part from initial differences in bulk liquid composition. However, the different Na contents of type I and II chondrules could be derived from an identical precursor concentration, conceivably with bulk composition influence after evaporation has started, provided that very different heating times or oxygen fugacities were involved. The lower S content of type I than type II chondrules (ZANDA *et al.*, 1996) could be explained by different heating conditions for the same bulk composition.

The absence of K isotopic mass fractionation has been interpreted as showing that chondrule melts suffered no evaporative losses (HUMAYUN and CLAYTON, 1995). However, chondrule melt experiments with Zn losses up to 90% show virtually no Zn isotope mass fractionation (XUE *et al*, 1996). Clearly the mechanisms of evaporative loss from melts need more study. According to ESAT (1996), the absence of Rayleigh-type isotopic fractionation effects cannot exclude evaporation, but only the special conditions required for Rayleigh fractionation, e.g. the absence of a gaseous envelope. The presence of a reactive gas like hydrogen would tend to permit loss but inhibit isotope fractionation, while abundant high pressure gas would be in accord with the relatively high Na contents of some chondrules.

CONNOLLY *et al.* (1994) heated type I compositions with added carbon and reproduced a number of features of type I chondrules (ZANDA *et al.*, 1994), including Mg-rich and dusty olivines, Cr and Si dissolved in metal and silica inclusions inside metal. They argued that carbon inside chondrules would be a much more effective reducing agent than low pressure nebular hydrogen and that chondrule oxidation states were controlled by internal reactions. Chondrules may have been internally buffered by Fe-bearing phases after the exhaustion of C. However, reduction of chondrule materials by ambient gas could possibly also be effective. In our gas reduction experiments described above, we also produced abundant Mg-rich and dusty olivines from a type I composition. We used much shorter heating time than DANIELSON and JONES (1995) and LIBOUREL and CHAUSSIDON (1995), but produced similar results. Dusty olivine, however, occurs only in a small fraction of natural type I chondrules, which typically have Mg-rich olivine grains without inclusions. To reduce our relatively Fe-rich initial olivine to uniformly forsteritic olivine requires either hours of heating at moderate temperatures in reduced gases, or else extreme volatile loss at higher temperatures. We therefore do not believe that all highly magnesian type I chondrules were formed by gas reduction during the recycling of more ferroan type I chondrules by flash reheating. Long heating times and gas reduction are possible for type IA chondrules (NAGAHARA, 1996; LIBOUREL and CHAUSSIDON, 1995) but are not favored by the absence of Si evaporative loss trends or by the survival of sulfide in fine-grained chondrules.

More FeO-rich compositions, *e.g.* type II chondrules (SEARS *et al.*, 1996), or FeO- and FeS-rich CI-like compositions (HEWINS *et al.*, 1996), tend to be more popular choices than type I initial compositions for production of type I chondrules by reduction coupled with evaporation. In general, if open system behavior is considered to have been demonstrated, *e.g.* for Na, Fe and S, as above, we are required by Occam's razor to try to do without fractionation effects and FeO-poor precursors. Specifically, however, the choice of FeO-rich compositions is consistent with the estimates of highly ferroan original composition of the dusty relict grains before reduction (JONES, 1996b), though reduction of ferroan material does not necessarily lead to appropriate chondrule bulk compositions. Forming charges resembling highly magnesian type IA chondrules from type II chondrule compositions through gas reduction (and evaporation) is an even more difficult process than from relatively ferroan type IA. Reduction of olivine enhances the SiO_2 content of the melt and the pyroxene content of the charge. We have produced type IB compositions from IIAB by Fe-loss with prolonged isothermal heating: Na loss was almost complete, as in some glasses in natural chondrules (GROSSMAN, 1996b). There was no SiO_2 loss as required to generate Type IA compositions in these 1 atm gas reduction experiments in which peak temperatures were relatively low. Conceivably evaporative losses at low (nebular) pressures could produce chondrules close to IA compositions.

HASHIMOTO (1983) showed that significant SiO_2 loss relative to MgO is achieved with 3 min heating in vacuum at 2000°C, though some Si and Mg are both lost with less extreme heating. NAGAHARA (1996) showed significant SiO_2 loss relative to MgO at temperatures more reasonable for chondrule formation (1700°C), but only after heating for about half an hour. With the kind of thermal history generally favored for chondrules (flash heating and rapid cooling), formation of type IA from type IIA via type IB is difficult. It would require extremely high temperatures, and/or long heating times, unless reactions with nebular gas accelerate Si loss, and both conditions are unfavorable to the survival of relict grains. Though SiO_2 loss from chondrule melts is certainly possible (NAGAHARA, 1996), we argue above that there is an absence in natural chondrules of clear proof of evaporative loss of SiO_2. Therefore, though some of the compositional characteristics of chondrules, *e.g.* Na concentrations, were clearly established by volatile loss during their formation, other characteristics, *e.g.* SiO_2/MgO ratios, seem more probably produced by pre-chondrule fractionations. Demonstration of Si loss from chondrules would certainly pose a problem for the flash heating model.

5.3. *Metal and sulfide*

Metallic Fe-Ni, especially as kamacite droplets, is common in type I chondrules and its composition was fixed by equilibration with silicates during chondrule formation (ZANDA *et al.*, 1994). Reduction was responsible for Fe-rich metal grains in dusty olivine, and Si, Cr and P dissolved in chondrule metal (ZANDA *et al.*, 1994) but the large metal droplets may have another origin. Condensate Fe-Ni has been suggested in the past, but kamacite is a high to moderate temperature condensate mineral replaced by fayalite and troilite (and/or magnetite) in equilibrium condensation calculations (WOOD and HASHIMOTO, 1993). The presence of troilite in chondrules has been interpreted to show that their precursors aggregated at low ambient temperatures (GROSSMAN *et al.*, 1988; WASSON, 1993), but according to our observations in Semarkona, the sulfide they observed in coarse type I chondrules must have been secondary. If the finest (protoporphyritic) type I chondrules differ from the "orthodox" coarse ones only by the intensity of melting experienced and degree of subsequent volatile loss, they are the chondrules closest to their precursors. In Semarkona they contain a troilite-pentlandite assemblage, with very little kamacite, which suggests that Fe and Ni were present in the precursors extensively as sulfide. This is consistent with the experimental results of LAURETTA *et al.* (1995), showing that S condensation on Fe-Ni would produce a Ni-bearing monosulfide solid solution. It also indicates that sulfide is a better candidate for a precursor mineral than kamacite. As a consequence, sulfur loss contributes materially to the formation of metal in chondrules in ordinary chondrites (SHIMAOKA and NAKAMURA, 1989; HEWINS *et al.*, 1996; YU *et al.*, 1996; ZANDA *et al.*, 1996).

The concentration of sulfide in opaque veneers around chondrules suggests recondensation of S lost from chondrules onto the metal blebs decorating chondrule surfaces (ZANDA *et al.*, 1995). This is perhaps analogous to the Na metasomatism (GROSSMAN, 1996) discussed above, though the site of Na condensation is uncertain. The assemblage troilite-pentlandite-awaruite in veneers also results from the breakup of an initial Ni-bearing monosulfide phase, the presence of which is consistent with a condensation origin as shown by the experiments by LAURETTA *et al.* (1995).

Both the extent of evaporation measured in experiments and the observed composition changes as a function of degree of melting in the chondrules strongly suggest that there was evaporative loss during chondrule melting. The material lost must have recondensed somewhere and, after such an intense heating event, chondrules may have been the principal available substrate, especially for S where an Fe-Ni substrate was required. The sulfur loss rates, presence of Fe-Ni sulfide in the least melted chondrules, the disappearance of sulfide during melting, and the veneers of secondary sulfide around chondrules all suggest that there was loss of primary sulfur during melting but that some of the sulfur recondensed onto chondrules.

5.4. *Carbon and chondrule precursors*

Both graphite (MOSTEFAOUI and PERRON, 1994) and organic compounds (HANON *et al.*, 1996) have been found in chondrules and suggested as precursor materials. MOSTEFAOUI and PERRON (1994) found that most of the graphite occurs with the least reduced (Co-rich, Cr-poor) metal grains which are outside chondrules. These are interpreted as grains mechanically lost from chondrules (separation of immiscible liquids of different density while spinning) relatively quickly so that the reduction reaction could not go to completion. HANON *et al* (1996) found that C, probably as organic compounds, is an order of magnitude more abundant in type I than the FeO-rich type II chondrules. Both observations support the idea that solid carbon was present in chondrule precursors and acted as a reducing agent on the fayalite component. Probably the earliest chondrules were made from fine-grained aggregates composed mainly of olivine, pyroxene, albite, troilite and carbon in the form of organics and/or graphite.

The modest negative correlation we observe between olivine Fa and chondrule grain size (Fig. 2) is consistent with more extensive Fe loss from the melt with stronger heating. The correlation might be explained in several ways. We see no reason that it should be due to precursor condensation differences, as the negative correlation would be too much of a coincidence. It could be due to greater evaporative loss of Fe from the silicate melt with more extensive heating, and/or a correspondingly more efficient C reduction. The decrease in Fa content corresponds very closely to a decrease from Fa_6 to $Fa_{0.6}$ observed in experimental charges when 5% C is added to the starting materials (CONNOLLY *et al.*, 1994). It is therefore natural to consider what type of precursor modified by C reduction could produce the spectrum of type I chondrule compositions.

C reduction and Fe loss from a single composition such as CI would produce a linear array on the SiO_2-MgO-FeO triangular plot (Fig. 4) and SiO_2/MgO ratios should be constant. This is clearly not the case in Fig. 5, and there is wide scatter even at high (close to "initial") FeO contents. When SiO_2/MgO ratios are plotted against olivine Fa, chondrule grain size or bulk FeO corrected for FeS, there is no linear trend. SiO_2/MgO ratios vary by a factor of 2 for the entire data set, and by 1.6 for all chondrules with nominal grain size <10 μm. Though C reduction (and/or subsequent enhanced Fe evaporation) may explain the range of olivine compositions and some dusty olivine grains in the chondrules, it clearly is not the only process controlling the chondrule compositions, as we show below.

We have suggested above that chondrule MgO-SiO_2-FeO variations could be due to condensation reactions between Fo-En-Fa. A much more complex scenario may be considered if C was abundant in at least some of the precursors and caused Fe reduction followed by evaporation and/or mechanical loss of Fe (droplet separation). The initial silicate composition, graphite/organic abundance and heating intensity all could have played roles in determining the final chondrule bulk compositions. Two distinct possibilities are that the initial silicate was mainly olivine with a wide range of Fe/Mg ratios (and/or with varying amounts of troilite) or mainly Fe-rich olivine-pyroxene mixtures with a wide range of SiO_2/MgO ratios. In either case, Fe loss produced a dispersion of compositions for the type I chondrules. More pyroxene-rich final compositions would reflect more reduction of precursor fayalite component for pyroxene-poor precursors. The observed dispersion in Fig. 4 could be reproduced from either starting assemblage, provided that a rather extreme range of precursors was available. This would require such Fe-rich material in the case of pyroxene-free precursors or such Si-poor material for olivine-pyroxene precursors that neither case is especially plausible. Furthermore, Fe-loss independently of reduction would be more plausible than following major C reduction, given the correlation of Fe concentrations and textures, unless the finest grained chondrules are shown to be the most C-rich (and can thus be considered to be "loaded guns"). Even if such a role for C should ever be demonstrated, the dispersion of type I chondrule compositions requires differences in precursors. The simplest explanation is major differences in olivine and pyroxene compositions and abundances due to condensation (GROSSMAN, 1988); another involves recycling of chondrule debris (ALEXANDER, 1996).

5.5. Chondrule formation

Na, Fe and S evaporative losses are seen both in Semarkona type I chondrules and experiments, but conditions were not extreme enough for significant Si loss relative to Mg. The very high Na concentrations of type II chondrules remain an enigma that cannot be easily explained. Experiments suggest that the very different Na contents of type I and II chondrules require very different fO_2 and/or very different heating times, unless their initial bulk compositions were already different in Na or were otherwise sufficiently different (Fig. 7) to control loss rates. A heating mechanism of variable duration would explain variations in Na contents, but then one would expect total loss of S and partial loss of Si. With currently favored heating mechanisms such as shock waves (BOSS, 1996) heating time cannot vary significantly. Whatever the heating time, the gas conditions were non-nebular with sufficient total pressure, pNa and fO_2 to retain significant Na, especially for type II but with the type I environment approaching a classical nebula more. The greater Na loss from type I chondrules could also be explicable in part by the lower fayalite and/or higher C contents of their precursors relative to type IIs. However, gas oxygen fugacity much higher than the nebular value is inescapable, as suggested by the results of TSUCHIYAMA *et al.* (1981) and GROSSMAN (1988), and may be responsible for the high oxygen fugacities recorded (ZANDA *et al.*, 1994) by chondrules. Such results give comfort to those who propose a non-nebular origin for chondrules. If type II chondrules formed in the nebula, the gas might be enhanced in oxygen by water ice or dust evaporation.

The difference in olivine composition on which the classification as type I or II is based, maintained down to the finest grain size, suggests that their precursors were different, though not as different as the chondrules themselves. The precursors of type I and II chondrules appear to have been relatively similar and near-chondritic, though with variations in Al/Mg/Si ratios which may be attributable to prior nebular fractionations. There are higher fayalite and troilite contents in general in the type II chondrules than the type Is, which might correspond to small differences in the precursors, *e.g.* final temperature of condensation, or nebular segregation time. There could conceivably have been higher contents of other low temperature materials, such as magnetite and water ice, which would have contributed to the more oxidised nature of type II chondrules. However, the greater abundance of organics in the more reduced (type I) chondrules (HANON *et al.*, 1996) is hard to understand in the context of precursor condensation temperatures. If we make the usual assumption that type I were derived from higher temperature condensates, we would expect the organics to accompany the lower temperature condensates, i.e. to be more abundant in the type II chondrule precursors. Conceivably the organics formed by Fischer-Tropsch-type reactions on Fe grain surfaces (FEGLEY, 1993). If this catalysis was inhibited by reaction of the Fe to FeS, the organics must have formed above the S condensation temperature. This implies that they would have been available for incorporation into precursor aggregates at relatively high temperature and, if the II had more FeS, the I could have had more C. Alternatively, one might postulate extreme heterogeneities of C in the nebula.

Both nebular fractionations and evaporative losses influenced chondrule compositions, and carbon may have been involved in both steps. More abundant C in type I precursors would have imposed a lower oxygen fugacity on the chondrule, therefore allowing greater Na and S loss, as we have shown experimentally (YU *et al.*, 1996) than for the type IIs, even in the least melted type I chondrules. Both type I and II chondrules lost volatiles during melting, as a function of extent of heating, but partially reacquired volatiles later by recondensation, etc. Though type Is experienced some reduction of FeO, as clearly attested by the presence of dusty relict olivines, breakdown of FeS followed by both evaporation and mechanical loss of Fe was more important in controlling the final abundance of metal in the chondrule. Given the problems discussed above and the real complexities of chondrules, *e.g.* recycling and relict grains (JONES, 1996b), it is not surprising that some people have abandoned hope of a simple model to explain chondrules and instead depend entirely on secondary processes (remelting of chondrule debris) to generate their compositions (ALEXANDER, 1996).

6. Conclusions

Type I chondrules in Semarkona have lower Na, K, Fe, and S content when the textures indicate extensive melting: they lost volatiles during melting, as a function of extent of heating. There is, however, no clear evidence that the large Si variations in chondrules are due to evaporative loss. Melting experiments suggest that Type I chondrules lost more Na than type II primarily because of different oxygen fugacities, but also possibly because of bulk composition effects on bond strengths. Longer heating times for type I than type II chondrules could also explain lower Na, but then one would expect clearer signs of Si loss. Type Is experienced a small amount of reduction of FeO, probably because of the presence of C, but metal abundance has been essentially controlled by breakdown of FeS followed by both evaporative and mechanical loss of Fe. The precursors of type I and II chondrules in Semarkona were similar and near-chondritic, but with higher fayalite and perhaps troilite contents in the type IIs. Both nebular fractionations and evaporative losses influenced chondrule compositions.

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