# Chondrules: Their Diversity and the Role of Open-System Processes during Their Formation

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After classification into compositional groups using their cathodoluminescence properties, chondrules were chiseled from sections of the least metamorphosed ordinary chondrites, Semarkona and Krymka. This technique avoided biases due to size and friability and ensured that all classes were adequately sampled. The chondrules were then analyzed by instrumental neutron activation analysis and their major phases (olivine, pyroxene, metal, mesostasis) were analyzed by electron microprobe. Group A1 and A2 chondrules of Semarkona and group A3 chondrules of Krymka have all the properties expected for chondrules which experienced considerable Fe reduction and evaporative loss during their formation (elemental depletions related to volatility, Fe-poor silicates, Ni-poor metal, significant pyroxene, small sizes). This is not the case for group B1, B2, and A5 chondrules (which have unfractionated bulk silicate compositions, FeO-rich silicates, little or no metal, little pyroxene, large sizes). Group A chondrules in Semarkona generally have thicker metal-sulfide-rich rims than group B chondrules, a situation similar to that of the Murchison CM2 chondrite, except that in Murchison aqueous alteration has destroyed the metal and sulfide. Group A chrondrules sometimes show compositional zoning in their mesostases and we suggest that both mesostasis zoning and chondrule rims are the products of recondensation during chondrule formation. Cooling rates differ considerably with chondrule class. Group A1-3 and A5 chondrules cooled relatively slowly and maintained a degree of equilibrium between melt and phenocrysts, while group B1 and B2 chondrules cooled rapidly and underwent considerable supercooling. The chondrule-forming process, whatever it was, was clearly capable of acting with a variety of intensities and produced a range of cooling rates. We suggest that the diversity of chondrules cannot be attributed mainly to variations in the properties and abundances of precursors, although this can sometimes be a factor, but can be derived from a fairly similar precursor of solar composition. © 1996 Academic Press, Inc.

# INTRODUCTION

Chondritic meteorites are especially noteworthy for having bulk compositions and formation ages remarkably similar to the Sun's (Ganapathy and Anders 1974, Hamilton et al. 1979, Evensen et al. 1979, Sears and Dodd 1988). Many have textures indicative of little or no major alteration since their formation. Most notable among the textural features of the chondritic meteorites are the chondrules, dense, usually spherical ~1-mm-sized objects thought to have been made by flash-heating events occurring before final assembly of the meteorite (Cameron 1966, Whipple 1966, Kieffer 1975, King 1982, Wood 1983, 1984, Grossman 1988). Chondrules are an important component of all but one of the chondrite classes. They are thus a unique source of information about conditions in the early solar system, and perhaps even about the origin of the solar system, and they are central to our understanding of chondrites.

Despite decades of intensive research, the origin of chondrules remains unclear in all but the broadest details. It is generally agreed that chondrules were formed by total or incomplete melting followed by rapid cooling (Keil and Fredriksson 1964, Kurat 1967, Van Schmus 1969, Radomsky *et al.* 1986). Subsequent to formation, the chondrules, like the rest of the meteorite, underwent metamorphism

to widely varying degrees (McSween 1977a, Sears et al. 1980, McSween et al. 1988, DeHart et al. 1992). Several authors have suggested that some of this metamorphism occurred during the cooling of the chondrules and before aggregation (Reid and Fredriksson 1967, Fredriksson 1983), while others have argued that it was predominantly a later, post-accretional event (Dodd 1971, Wood 1979). In some cases, metamorphism occurred at low temperatures and involved the passage of aqueous fluids (Alexander et al. 1986, Hutchison et al. 1987, Zolensky and McSween 1988). In any case, a considerable range of chemical and textural modifications among the chondrules occurred as a result of these secondary processes (Van Schmus and Wood 1967, Dodd et al. 1967, Sears and Dodd 1988) and seeing through them is crucial to our efforts to understand the chondrule formation process.

Chondrules may be sorted into the "droplet" and "lithic" forms (Kieffer 1975, Dodd 1981) or, the broadly equivalent, "nonporphyritic" and "porphyritic" varieties (Gooding and Keil 1981). More recently, porphyritic chondrules have been termed type IA when they contain CaOrich, FeO-poor olivine and IB when the olivine is slightly poorer in CaO and richer in FeO and the olivine is sometimes enclosed in pyroxene. Porphyritic olivine chondrules with FeO-rich olivine have been termed type II (McSween 1977a, Scott and Taylor 1983, Jones 1990). Texture alone is used when these classifications are applied to higher pertrologic types (McCoy et al. 1991). Most recently, these definitions have been modified to incorporate mineralogical information, and the FeO constraints relaxed, so that there are now IA, IB, IAB, IIA, IIB, and IIAB types (Jones 1994). Most of the chondrule group definitions are heavily influenced by studies of chondrules in the carbonaceous chondrites and the Semarkona type 3.0 ordinary chondrite. For the purposes of the present paper we will rely on the composition of the two major components in the chondrules, olivine and surrounding mesostasis, to identify eight classes, A1-5 and B1-3 (Sears et al. 1992, DeHart et al. 1992, Sears et al. 1995b). This classification scheme was devised after examining a large suite of ordinary chondrites of all petrologic types, and therefore identifies both primary formation and secondary metamorphism (Table I). Especially important are the A1–3 groups which constitute  $30 \sim 35\%$  of the total chondrule population in ordinary chondrites but whose importance has only recently been realized (Scott and Taylor 1983, Jones and Scott 1989, Sears et al. 1992, DeHart et al. 1992), and the rare group A5 condrules in primitive ordinary chondrites which are not recognized in the other schemes.

There are small but real compositional differences among the chondrites which lead to the definition of the nine major chondrite classes (Urey and Craig 1953, Craig 1964, Sears and Dodd 1988). Each chondrite class has a unique elemental abundance pattern and there are large

differences in the extent of oxidation (Sears and Dodd 1988). The proportion of Fe in the oxidized state increases from essentially zero to 100% along the enstatite, ordinary, and carbonaceous chondrite series. Also, while ordinary and enstatite chondrites display reasonably uniform lithophile element abundances, carbonaceous chondrites are enriched in refractory elements (e.g., Ca, Al, and REE) and depleted in the moderately volatile elements (Mn, Na, and K). The cause of these patterns has proved to be highly contentious but is central to explaining the origin of the chondrite classes and thereby our understanding of important processes in the early solar system. Were these abundance patterns of moderately volatile elements caused by mixing chemically diverse components prior to the formation of chondrules (Wasson and Chou 1974), or were they caused by mixing of different chondrules and other materials in various proportions (Larimer and Anders 1967)? A key point for both theories is whether chondrules lost volatile elements and underwent other elemental changes during chondrule formation or whether they acted as closed systems (Anders 1977, Wai and Wasson 1977).

For this study, we concentrated on the two least-metamorphosed ordinary chondrites known, Semarkona (LL3.0) and Krymka (LL3.1). Chondrules were selected using CL photographs of thick sections (Sears et al. 1992, DeHart et al. 1992) and then removed by chiseling (Lu et al. 1990). In this way we avoided the possibility of biasing our sample collection against the friable and small group A chondrules. We then performed systematic chemical, mineral, and petrographic studies with a view to characterizing each of the major primary chondrule groups. Here we discuss the processes which may have occurred during chondrule formation, the possible relationships among different chondrule groups, and their relevance to chondrite formation.

## **EXPERIMENTAL**

Cathodoluminescence (CL). CL mosaics of several  $4 \times 4$ -mm slices of Semarkona and Krymka were prepared using our previous methods (DeHart 1989; Lu et al. 1990), except that for the present work we used Kodak EKTAR-1000 35-mm color film with 1- to 1.5-min exposures for the CL photography.

Size. Chondrule sizes were measured from the CL and reflected light mosaics. Although most chondrules were circular in section, a few were elliptical. We measured the diameters of the condrules in two perpendicular directions and then calculated the average of measured diameters of each chondrule. No attempt has been made to correct the data for biases introduced by thin section measurement, so the diameters are "apparent diameters." We noted the

TABLE I
Comparison of Krymka and Semarkona Chondrule Groups in Terms of
Frequency of Occurrence, Cathodoluminescence, and Mineral Compositions\*

	· Me	sostases	Ol	ivine		Frequency <sup>‡</sup>				
	CL	Normative Composition (wt.%) <sup>†</sup>	CL	%FeO	%CaO	Krymka	Semarkona			
	blue	Pl(An>50%) Pl(An>50%) Pl(An>50%) Pl(An>50%) Pl(An>50%) Pl(An<50%)	red none/dull red red none/dull red none	<2 2-4 <4 >4 >4	>0.17 0.1-0.2 >0.2 0.16-0.3 <0.25	3.6 0.0 33.3 7.3 14.5	10.5 25.0 0.0 0.0 5.0			
B1 B2 B3	none none purple	>30% Qtz 30-50% Qtz 15-30% Qtz	none none/dull red none	4-25 10-25 15-20	0.08-0.3 0.08-0.3 <0.08	0.0 36.4 0.0	56.9 0.0 2.6			

<sup>\*</sup> Phase compositions given as a guide, the group fields are not rectangular (see Sears et al. 1992, 1995b, for details). "CL" refers to cathodoluminescence color.

occurrence of rims on the chondrules and measured rim thickness under reflected light.

INAA. Chondrules selected on the basis of their CL colors were chiseled from the sections using stainless steel dental tools while viewed under a low-powered stereomicroscope (Tables I and II). Twenty-one chondrules were removed from Semarkona and 15 were removed from Krymka. Most textural types are fairly well represented in these groups. After removal of the adhering materials by scraping, so as to produce spherical surfaces wherever possible, the Semarkona chondrules were sealed in quartz vials, and the Krymka chondrules were sealed in highdensity polyethylene vials, for INAA. The samples were placed in the nuclear reactor at the University of Missouri, Columbia ( $\phi = 10^{14} \text{ neutrons cm}^{-2} \text{ sec}^{-1}$ ), along with mixed-element standards. Samples and the appropriate standards were individually irradiated for 3 min and counted two or three times (for 2, 3, and 5 min for Semarkona, and two 3-min counts for Krymka) to determine short-lived nuclides (Mg, Al, Ca, Mn, and V). They were then irradiated in a single package for 8 hr (Semarkona) or 1 hr (Krymka) and counted five times for periods of 0.25, 2.5, 4, 8, and 12 hr. Spectrum analyses, decay corrections, and concentration calculations were performed using the new SPECTRA5 interactive computer program (Baedecker and Grossman 1989). Correction for gain and zero drift, pulse pileup, spectral interferences, and interactive manual placement of the baseline are included in the program. Systematic errors in our standard preparations were detected and corrected using secondary standards (i.e., BCR-1 and our internal Allende-H standard).

After irradiation, Semarkona samples were mounted and polished for petrographic and electron microscope study.

Electron microprobe analysis. Olivine, pyroxene, and mesostasis in the Semarkona chondrules were analyzed at the American Museum of Natural History using an ARL-SEMQ electron microprobe. Accelerating voltages of 15-20 kV and sample currents of 10 to 20 nA were used, the exact conditions depending on the excitation level and volatility of the elements being determined. Typical beam diameters were 2-3  $\mu$ m and counting times were 20 sec on the peak and 10 sec on the backgrounds. Typical  $3\sigma$ detection limits (wt%) are TiO<sub>2</sub>, 0.02; MnO, 0.03; SiO<sub>2</sub>, 0.03; CaO, 0.01; Na<sub>2</sub>O, 0.02; K<sub>2</sub>O, 0.01; MgO, 0.03; Al<sub>2</sub>O<sub>3</sub>, 0.03; Cr<sub>2</sub>O<sub>3</sub>, 0.03; and FeO, 0.03. The bulk compositions of the chondrules were also determined using a 50-µm defocused electron beam. All data were corrected using Colby's (1968) alpha factors. Where comparison is possible, most of our compositional and petrologic data are in agreement with previous observations (Osborn 1972, Snellenburg 1978, Gooding 1979, Scott and Taylor 1983, Jones and Scott 1989, Jones 1990). Our mesostasis analyses for group B chondrules differ from those of Jones and Scott (1989) and Jones (1990) because of beam overlap with microlites in the previous studies (Scott et al. 1994). Wherever possible, we use CL as a guide to locating pure mesostasis.

Chondrule classification. After preliminary selection on the basis of CL, removal, and analysis, chondrules were more rigorously assigned to compositional groups using the CL and electron microprobe data for the polished

<sup>†</sup> Pl, plagioclase; An, anorthite; Qtz, quartz.

<sup>‡</sup> The figures in parentheses indicate the number of chondrules on which the statistics are based. Semarkona data from DeHart et al. (1992), and Krymka data are from the present work.

TABLE II
Classification and Petrographic Description of the Semarkona and
Krymka Samples Studied Here

	Mass (mg)	Dia (mm)	CL Ol	CL Mes	Comp Ol	Comp Mes	Sel Class§	Comments*
Semarkon \$C-2-8 \$C-2-12 \$C-2-13 \$C-3-1 \$C-3-3 \$C-3-10 \$C-11-2 \$C-14-1 \$C-20-5 \$C-22-12 \$C-22-12 \$C-22-12 \$C-23-5 \$C-23-6 \$C-23-18 \$C-26-5 \$C-28-12 \$C-30-5 \$C-30-6 \$C-31-1	0.37 0.92 0.157 0.55 0.85 0.85 0.85 0.10 1.25 1.21 1.08 0.65 0.40 0.05 0.25 4.05 0.84 0.36	1.10 1.16 0.61 1.15 0.81 0.88 1.30 2.56 0.41 1.40 0.74 1.175 0.81 0.51 0.29 0.59 0.51 1.33 1.10	Red None Red None None None None None None None None	Yellow Yellow Yellow None Yellow None None None None Yellow	A1 A1 (A1)  A1  A5 A1 (A3) B3 A1 (A5)(B1-2) (A2) A2 A1 B1-2 B1-2 A1 A1	 A1-4 A5  A1-4	A1 A1 A2 B1 A1 A2 B1 B1 A2 B3 A1 A2 B3 A1 A2 B3 A1	POP, Sulf. rim POP, Sulf. rim POP, Sulf. rim POP, Sulf. rim Very fine RP, cryptocryst POP, Sulf. rim PP PO PO PO PO PO PO PO POP POP, opx in ol rimmed with cpx PO large kam. grain, numerous Nifree metal grains. POP PP PP PP PP PO PO PO PO PO PO PO PO
Krymka KC-1 KC-3 KC-4 KC-5 KC-6 KC-7 KC-10 KC-13 KC-15 KC-15 KC-18 KC-20 KC-20 KC-22 KC-23	3.76 2.00 6.65 8.30 0.54 0.61 3.35 0.96 1.02 0.56 0.97 1.01 2.15 0.65	1.18 1.13 0.95 1.20 0.63 0.62 1.08 1.07 1.37 1.02 1.75 0.88 1.26 1.13	None Red None None Red Red None Red Red None Red Red Red Red	None Blue None None Blue Blue None None Blue Blue None Blue None Blue None Blue			B2 A3 B2 B2 B2 A3 B2 A3 B2 A3 B2 A3 B2 A3	is rimmed bý cpx.

<sup>\*</sup> Textural description according to Gooding and Keil (1981): PP, prophyritic pyroxene; PO, porphyritic olivine; POP, porphyritic olivine–pyroxene; BO, barred olivine.

sections of the separated chondrules. As outlined above, the concept behind this scheme is that the chondrules in unmetamorphosed chondrites contain olivines (and pyroxenes) and mesostases with a wide variety of compositions and that during metamorphism these components became uniform in composition. By defining fields on the CaO vs FeO plot for olivine and normative albite–anorthite–quartz plot for mesostasis, both the original diversity and an indication of the changes wrought by metamorphism

can be assessed (Figs. 1 and 2). The chondrules are first assigned to classes to the extent possible by using the mesostasis plot. This discriminates between all chondrule groups except groups A1, A2, A3, and A4. Then each chondrule is classified in terms of its olivine composition. This resolves the A1-A4 groups and may result in the reassignment of a few borderline chondrules. It is important to keep in mind that each analytical data point carries an uncertainty, which may be especially large for

<sup>§</sup> Selected class based on olivine and mesostasis composition and CL. Hyphens indicate no data, either because microprobe analyses were not performed, because the chondrule was plucked from the section, or because the phase was too fine to analyze. Group A1 includes some of the droplet chondrules of Kieffer (1975), some of the nonporphyritic pyroxene chondrules of Gooding and Keil (1981), type I chondrules of McSween (1977a,c), metal-rich microporphyritic chondrules of Dodd (1978), and type IA chondrules of Scott and Taylor (1983). Group A2 includes the type IB chondrules of Scott and Taylor (1983) and many of the type IAB chondrules of Jones (1994). Group A5: there appear to be no previous observations of this chondrule group in unmetamorphosed meteorites. Group B1 includes Dodd's (1981) "lithic" or "clastic" chondrules, Dodd's (1978) metal-poor microporphyritic chondrules, the type II chondrules of McSween (1977a,c) and Scott and Taylor (1983), and radial pyroxene chondrules of Gooding and Keil (1981).

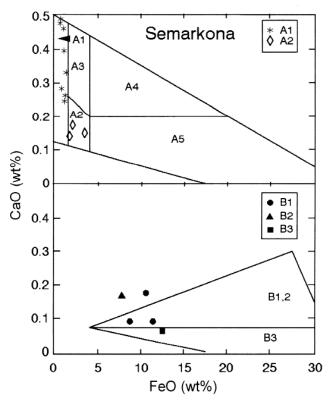


FIG. 1. Plots of CaO against FeO (wt%) for the olivines of the Semarkona chondrules in the present study, compared with the compositional groups of Sears *et al.* (1992) and DeHart *et al.* (1992). The group boundaries have been slightly simplified (Sears *et al.* 1995b). Chondrules show a large range in FeO and CaO, consistent with their assignment to groups A1, A2 and B1, B2, and B3. One B1 and one B2 chondrule plot slightly outside, but within experimental uncertainties, of the group B1,2 field. Olivines were not analyzed in four of the chondrules.

zoned olivines and finely textured mesostases, and that classification is based on both olivine and mesostasis compositions. Thus, the boundaries are not only arbitrary but somewhat diffuse. It is also worth noting that for large structures like chondrules, especially when textures are fine and intergrown, the CL parameters can provide a more reliable indicator of composition than microprobe data. The CL data thus normally resolve any remaining uncertainties. In the absence of microprobe data, the Krymka samples were assigned to classes entirely on the basis of their CL properties. We argue that this is a less modeldependent scheme than earlier chondrule classifications which ignore the effects of metamorphism and brecciation. Although Scott et al. (1994) favor the type IA-IIAB schemes they developed in recent years, we favor the compositional classification scheme because, among several reasons discussed by Sears et al. (1995b) it is simple, comprehensive, and model-independent.

## RESULTS

Mineral and Phase Analysis

Olivine. Chondrule olivine analyses are listed in Table III. Group A chondrules show a very steep negative correlation between FeO and CaO in the olivine (Fig. 1), with A1 chondrule olivine being CaO-rich (mean 0.37 wt%) and FeO-poor (mean 0.65 wt%) relative to group A2 chondrule olivine (0.16 wt% CaO, 2.47 wt% FeO). Group B1 chondrules are characterized by FeO-rich olivine relative to group A chondrules (average ~11 wt% FeO, ~0.12 wt% CaO). Similar observations have been made for type IA and type II chondrules in Semarkona (Jones and Scott 1989, Jones 1990). All six group A1 chondrules have the expected CaO contents, as do the three group A2 chondrules. Two of the five group B chondrules plot outside their indicated compositional field, but not beyond the uncertainties in the analytical results.

In contrast to CaO, MnO shows a significant positive correlation with FeO (Fig. 3), with the A groups generally having lower MnO and FeO than the B groups. In terms of chondrule classification on the basis of Fig. 3, to a first approximation FeO boundaries at 2 and 4 wt% and an

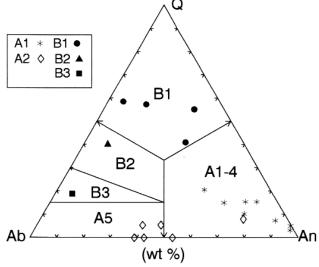


FIG. 2. Compositions of the mesostases of the present Semarkona chondrules, expressed as normative quartz, albite, and anorthite (wt%). The compositional fields for the chondrule classes are from Sears et al. (1992) and DeHart et al. (1992). Mesostasis compositions vary greatly, with the A groups being highly plagioclase-normative while the B groups contain significant quartz in their norms. Quartz-normative mesostases in the presence of olivine implies supercooling. Chondrules have compositions consistent with their compositional groups except that A2 chondrules plot on the boundary of the A1–4 and A5 fields. It is not clear whether this reflects systematic error in the data or the group boundary needs slight modification.

Chondrule	Group	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Total	Fa
SC-2-8 SC-2-12 SC-3-3 SC-22-4 SC-23-5 SC-28-12 SC-30-6 SC-31-1 Mean AI Io Mean AI	A1 A1 A1 A1 A1 A1 A1	41.2 41.5 41.3 41.7 44.1 41.9 40.6 <b>41.4</b> 0.4 42.4	0.07 0.02 0.05     <b>0.05</b> 0.02 0.04	0.15 0.24 0.53    0.31 0.17 0.13	0.20 0.40 0.22 0.14 0.11 0.46 0.21 0.20 <b>0.24</b> 0.12 0.30	0.76 0.60 0.83 0.57 0.46 0.76 0.56 0.66 <b>0.65</b> 0.12	0.01 0.29 0.03  0.37  <b>0.18</b> 0.16 0.08	56.4 56.5 56.4 57.9 57.0 56.1 57.9 57.2 <b>56.9</b> 0.70 55.1	0.46 0.25 0.33 0.48 0.48 0.26 0.28 0.39 0.37 0.09	99.3 99.8 99.7 100.0 99.3 99.8 100.9 99.1 99.8	0.6 0.6 0.9 0.5 0.5 0.8 0.5 0.6 0.6 0.1
SC-2-13 SC-23-18 SC-26-5 Mean A2 1σ Mean A2*	A2 A2 A2	42.1 41.4 41.4 40.7 41.2 0.3 41.6	0.04     0.01	0.14     0.05	0.37 0.61 0.31 0.42 <b>0.45</b> 0.12 0.47	2.01 2.00 3.40 2.47 0.81 4.22	0.09 0.35 0.08 0.21 <b>0.21</b> <b>0.11</b> 0.30	55.7 55.3 55.5 55.4 <b>55.4</b> 0.1 52.7	0.31 0.17 0.14 0.16 0.16 0.01 0.17	99.7 99.8 99.1 100.4 99.7 99.6	2.0 2.0 3.3 2.4 1.3 4.3
SC-11-2 SC-29-11 SC-30-5 Mean B1 Io Mean B1 Mean II <sup>‡</sup>	B1 B1 B1	40.1 40.5 39.5 <b>40.0</b> 0.4 38.8 39.4	    0.01	    0.05	0.48 0.36 0.47 <b>0.44</b> 0.05 0.49 0.43	11.40 9.40 12.20 11.00 1.18 18.8 14.8	0.64 0.29 0.52 <b>0.48</b> 0.15 0.52 0.34	48.1 49.4 46.9 <b>48.1</b> 1.0 41.0 44.4	0.18 0.09 0.09 0.12 0.04 0.15 0.13	101.0 100.0 99.9 100.3 99.8 99.5	12 10 13 12 19 16
SC-23-6 SC-22-12	B2 B3	40.2 39.5			0.61 0.39	8.40 13.50	0.73 0.33	49.9 45.9	0.17 0.06	100.1 99.7	8.3 14

TABLE III Olivine Compositions for Semarkona Chondrules (wt%)

MnO boundary of  $\sim$ 0.3 wt% define the fields corresponding to A1, A2 and B1, B2 chondrules.

Pyroxene. Most pyroxene is of the low-Ca type, with high-Ca pyroxene occasionally rimming other silicates. Analyses are presented in Table IV and Fig. 4. Low-Ca pyroxene shows similar compositional trends to that of coexisting olivine: FeO-poor and CaO-rich in group A1 chondrules (<2 wt% FeO), and FeO-rich and CaO-poor in group B1 chondrules (>2 wt% FeO). Similar observations have been made for type IA, IB, IAB, IIB, and IIAB chondrules in Semarkona (Jones and Scott 1989, Jones 1992). Low-Ca pyroxene compositions also hold a promise for meaningful classification, but data are as yet too few. To a first approximation, though, it appears that >1 wt% CaO and <1 wt% FeO define group A1, <0.5 wt% CaO and 1-3 wt% FeO define group A2, and the B groups are <0.5 wt% CaO and >3 wt% FeO. Low-Ca pyroxenes are of greater value in assigning the higher types, since there is a non-linear positive correlation between CaO and FeO in the low-Ca pyroxene of chondrules in equilibrated chondrites ( $\sim$ 0.5,  $\sim$ 0.7,  $\sim$ 1.0, and  $\sim$ 1.7 wt% CaO for type 4, 5, 6, and 7, respectively.

Mesostasis. Mesostasis compositions for Semarkona chondrules are given in Table V. All of the group A1 and B chondrules plot is the fields expected; however, only two of the six A2 chondrules plot in the A1–4 field (Fig. 2). The remaining four chondrules, while within experimental error of the A1–4 field, plot in the A5 field. It is possible that the field boundary needs slightly adjusting, but this seems unlikely because A2 chondrules in previous studies were not anomalous (Sears et al. 1992; De Hart et al. 1992). Olivine and CL data clearly indicate an A2 assignment, so we suspect an analytical problem with some of the mesostasis data (for example, overlap with low-Ca pyroxene).

## Petrography

Chondrule diameters and rims. Group B chondrules in both Semarkona and Krymka show an approximately normal distribution of chondrule diameters, whereas group A chondrules show a more skewed distribution with a tail

<sup>\*</sup> DeHart et al. (1992).

<sup>†</sup> Jones and Scott (1989).

<sup>‡</sup> Jones (1990).

<sup>--</sup> Not detected.

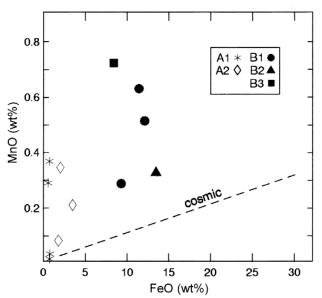


FIG. 3. MnO vs FeO (wt%) in the olivine of Semarkona chondrules. In contrast to CaO, MnO shows a simple correlation with FeO in chondrule olivines, such that group A1.2 chondrules are depleted in Mn, as well as FeO, relative to group B1-3 chondrules. Since Mn has different thermodynamic properties from Fe (never being siderophile, for example), these trends demonstrate that the abundance of an element in a phase is governed by the need for a host site as well as thermodynamic properties. The data plot above the cosmic line (Anders and Grevesse 1989), mainly because Fe was lost preferentially during chondrule formation.

to larger values (Fig. 5). Semarkona chondrule apparent sizes are 267–1976  $\mu$ m, with group A1 and A2 chondrules being generally smaller than B1 (mean diameters are 645  $\pm$  318, 670  $\pm$  313, and 841  $\pm$  335  $\mu$ m for group A1, A2, and B1, respectively). Similarly, Krymka A3 chondrules are smaller than B2 chondrules (mean apparent diameters are 611  $\pm$  239 and 778  $\pm$  293  $\mu$ m, respectively). The Student t test indicates that the difference in diameter between the group A and the group B chondrules is significant at the 0.01 level. Group A5 chondrules (not shown in Table VI or Fig. 5) show a size distribution similar to that of group B1 and B2 chondrules.

Group A1 chondrules are more frequently rimmed than group B1 chondrules ( $\sim$ 70% by number, compared with  $\sim$ 30%) and have higher ratios of rim thickness to chondrule core diameter (Fig. 6). Most A1 chondrule rims contain ultra-fine-grained metal- and sulfide-rich materials (<0.1  $\mu$ m), which are not observed in chondrites of higher petrologic types. B1 chondrule rims, when present, contain fine-grained matrix-like materials with dispersed or massive sulfide and metal, which, in contrast to the ultra-fine sulfide- and metal-rich rims in group A chondrules, are also observed in higher petrologic types (Allen *et al.* 1980).

Similar associations between rim thickness and chondrule group are observed for the Murchison CM chondrite (Sears *et al.* 1993) (Fig. 6).

Bulk compositions. Defocused electron microbeam analyses of the 20 Semarkona chondrules are given in Table VII and plotted as Mg- and CI-normalized ratios in Fig. 7. Analytical sums were excellent and did not require normalizing to 100%. Elements are plotted according to their cosmochemical affinity (lithophiles, siderophiles, and chalcophiles), in the order of increasing volatility (left to right). Because of their small volume abundance, metal and sulfide were not included in the analyses. Groups A1 and A2 chondrules have CI levels but are slightly enriched in Ti, Al, and Ca and depleted in Si, Fe, Mn, Na, and K. In contrast, group B1 chondrules show fairly flat (i.e., CI) elemental abundances with slight depletions of refractory elements and enrichment in Si that are not significant over the "noise" of the overall trend. Iron is depleted in all groups relative to the lithophiles. The data agree fairly well with those in the literature, although earlier data are systematically higher in Na2O and K2O relative to the present data and earlier MnO data. The compositions of group A2 chondrules are intermediate between those of A1 and B1 chondrules except for Si, which is highest in A2 chondrules which are consequently pyroxene-rich.

The INAA data are listed in Table VIII and are shown in Fig. 8, also normalized to CI and Mg. We discuss the lithophile elements, and then the siderophile and chalcophile elements.

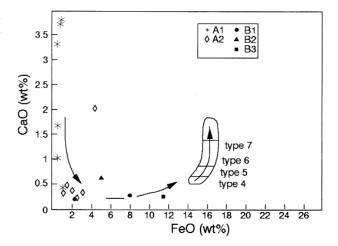


FIG. 4. CaO vs FeO in low-CaO pyroxenes of the Semarkona chondrules. Like the olivines, low-Ca pyroxenes in group A1 chondrules are generally relatively high in Ca, while in group A2 chondrules Ca values are quite low. However, unlike the olivines, low-Ca pyroxenes in all chondrule groups of high petrologic types have high Ca, so that the trend is U-shaped. In some instances, low-Ca pyroxenes may be a better taxonomic phase for chondrule classification than olivine. Type 4, 5, 6, and 7 data are from Gooding (1979) and Heyse (1978).

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Chon.	Group	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O	3Cr2O3	FeO	MnO	MgO	CaO	Total	Wo	En	Fs
SC-2-8	A1	59.9	0.30	2.20	0.49	0.52	0.09	35.6	1.01	100.1	2.0	97.2	0.8
SC-2-12	A1	58.3	0.07	0.74	0.63	1.50	0.30	37.2	0.47	99.3	0.9	96.9	2.2
SC-3-3	A1	57.3	0.26	4.50	0.69	0.78	0.38	31.9	3.70	99.6	7.6	91.2	1.2
SC-28-12	A1	56.6	0.24	1.85	0.62	0.56	0.16	37.4	1.67	99.1	3.2	96.0	0.8
SC-30-6	A1	56.9	0.25	1.70	0.95	0.51	0.43	35.6	3.30	99.6	6.1	93.1	0.8
SC-31-1	A1	56.4	0.40	2.88	1.00	0.90	0.40	34.3	3.80	99.8	7.2	91.2	1.4
Mean A1		57.6	0.25	2.31	0.73	0.80	0.29	35.3	2.32	99.6	4.5	94.3	1.2
$I\sigma$		1.2	0.10	1.17	0.18	0.35	0.13	1.9	1.33		2.6	2.5	0.5
SC-2-13	A2	58.3	0.14	0.82	0.75	1.09	0.28	38.2	0.28	100.0	0.8	97.6	1.6
SC-3-10	A2	58.6	0.08	0.76	0.46	1.19	0.06	37.9	0.06	99.3	0.6	97.4	2.0
SC-20-5	A2	57.4	0.04	0.42	0.69	2.58	0.34	37.9	0.34	99.5	0.4	95.9	3.7
SC-22-10	A2	57.6	0.15	1.82	1.23	4.40	1.32	32.1	1.32	100.9	8.3	87.7	4.0
SC-23-18	A2	58.2	0.05	0.41	0.74	2.09	0.37	38.3	0.37	100.6	0.6	96.6	2.8
SC-26-5	A2	57.6	0.08	0.56	0.87	3.20	0.42	37.2	0.42	100.2	0.6	94.8	4.6
Mean A2		58.0	0.09	0.80	0.79	2.43	0.47	36.9	0.47	100.1	1.9	95.0	3.1
$1\sigma$		0.4	0.04	0.48	0.23	1.15	0.40	2.2	0.64		2.9	3.4	1.1
SC-14-1	B1	58.7	0.03	0.24	0.49	2.34	0.26	36.4	0.26	98.8	0.4	96.1	3.5
SC-30-5	B1	56.9		0.18	0.65	7.90	0.44	32.9	0.44	99.3	0.5	87.7	11.8
Mean B1		57.8	0.03	0.21	0.57	5.12	0.35	34.7	0.35	99.1	0.45	91.9	7.65
Ισ		0.9	0.02	0.03	0.08	2.78	0.09	1.8	0.03		0.05	4.2	4.2
SC-23-6	B2	57.1	0.05	0.43	0.79	5.00	0.61	35.1	0.66	99.8	1.2	90.7	8.1

11.50 0.51 30.6 0.51 99.9 0.5

TABLE IV Low-Ca Pyroxene Compositions for Semarkona Chondrules (wt%)

56.1

0.09 0.77

SC-22-12 B3

Lithophile elements. In both Semarkona and Krymka, groups A and B chondrules show distinctive lithophile element abundance patterns. In general, group A1 and A2 chondrules in Semarkona, and group A3 chondrules in Krymka, show flat refractory lithophile element patterns from Ca to V, but are depleted in the moderately volatile

lithophile elements (with depletions increasing with volatility) from Mg to K. Most significantly, it is not just Na and K that are depleted, but Cr and Mn as well. In contrast to group A chondrules, the lithophile elements in group B chondrules of both Semarkona and Krymka show flat abundance patterns. Aluminum data in Semarkona are not

82.2 17.3

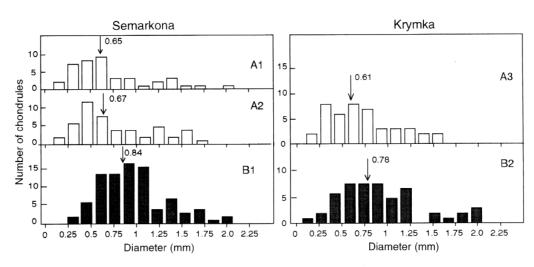


FIG. 5. Histogram of chondrule sizes as a function of chondrule group (data from Table VI). Chondrule diameters are the averages of two perpendicular measurements on the CL mosaics. The mean diameters for group A chondrules are smaller than those of group B chondrules by an amount which is significant at the 0.01 level, the difference being 20–23% (in diameter) for both Semarkona and Krymka. Arrows represent the mean of each group.

<sup>--</sup> Not detected.

TABLE V
Mesostasis Compositions for Semarkona Chondrules (wt%)

Chondrule	Group	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O	<sub>3</sub> FeO	MgO	CaO	Na <sub>2</sub> O	К2О	Total
SC-2-8	A1	54.9	0.38	22.6	0.68	5.40	14.0	1.88	0.06	99.9
SC-2-12	A1	49.6	0.35	23.7	1.89	6.00	16.6	0.40	0.04	98.6
SC-3-3	A1	53.8	0.76	21.3	1.80	7.90	13.7	1.29	0.60	100.6
SC-22-4	A1	45.3	1.09	24.6	3.70	5.30	18.9	0.00	0.00	98.9
SC-23-5	<b>A</b> 1	48.3	1.14	24.7	0.63	5.60	20.0	0.07	0.00	100.4
SC-28-12	A1	55.2	0.58	21.6	0.53	4.80	17.0	1.03	0.04	100.8
SC-30-6	A1	57.7	0.88	19.5	0.48	3.70	15.8	2.29	0.14	100.5
SC-31-1	A1	54.5	1.01	22.9	0.48	5.10	16.5	0.68	0.03	101.2
Mean	AI	52.4	0.77	22.6	1.27	5.48	16.6	0.96	0.03	101.2
<b>1</b> σ		3.9	0.27	3.1	0.95	1.25	2.0	0.87	0.14	
SC-2-13	A2	45.8	0.36	24.5	2.80	4.20	7.2	3.70	0.19	88.8
SC-3-10	A2	50.9	0.42	22.4	3.10	6.80	10.5	1.26	0.09	95.5
SC-20-5	A2	54.5	0.56	18.8	2.48	4.20	12.5	5.20	0.14	98.4
SC-22-10	A2	58.4	0.55	17.3	2.70	7.70	8.9	4.40	0.25	100.2
SC-23-18	A2	57.6	0.59	20.4	2.57	4.10	10.8	4.40	0.20	100.7
SC-26-5	A2	55.9	0.51	19.2	4.50	5.10	9.3	5.20	0.19	99.9
Mean	A2	53.4	0.50	20.4	3.03	5.35	9.9	4.03	0.18	97.3
$I\sigma$		5.2	0.10	2.6	0.75	1.54	1.8	1.47	0.06	
SC-11-2	B1	70.4	0.46	12.1	5.40	2.33	4.7	0.69	0.69	96.8
SC-14-1	B1	63.4	0.48	14.4	3.90	2.82	10.9	2.29	0.40	98.6
SC-29-11	B1	72.3	0.56	13.5	8.40	0.89	0.8	3.00	0.94	100.4
SC-30-5	B1	71.3	0.63	15.9	5.50	1.13	2.3	2.45	0.94	100.1
Mean	<b>B1</b>	69.4	0.53	14.0	5.80	1.79	4.68	2.11	0.74	99.0
$1\sigma$		3.5	0.07	1.4	1.63	0.81	3.9	0.86	0.22	
SC-23-6	B2	61.4	0.54	15.8	2.81	1.88	1.6	4.10	0.92	89.1
SC-22-12	B3	69.6	0.40	15.4	5.50	0.87	1.1	7.60	0.39	100.8

obtained due to the interference of  ${}^{28}Si(n,p){}^{28}Al$ , as a result of using quartz vials for irradiation.

The two group A5 chondrules analyzed, one each from Semarkona and Krymka, whose data are not shown in the plots, have bulk compositions with flat abundance patterns, perhaps with slight volatile element enrichments.

Siderophile and chalcophile elements. Both group A and B chondrules in Semarkona and Krymka show very large depletions in siderophile and chalcophile relative to CI, although A1 and A3 chondrules may be less depleted in refractory siderophile elements (such as Ir, Co, and Ni) relative to B1 and B2 chondrules. There is a slight indication that the abundances of siderophile and chalcophile elements decrease with increasing volatility with exception of group B2 chondrules in Krymka.

Figure 9 summarizes these bulk compositional trends in the form of CI- and Mg-normalized averages for the chondrule groups. We prepared similar plots to Fig. 9, using Grossman and Wasson's (1983a, 1985) data, and assuming that three of their chondrules with Fa <2 mol% were group A1, that two with Fa 2–4 mol% were group A2, and that the remaining 22 chondrules were group B1. These earlier data show very similar results to the present

Semarkona data, with their group A1 showing comparable volatility-related depletions to those we observe, although Mg appears to be systematically high by about 20% relative to other elements with comparable volatility (Grossman, personal communication, 1995), and there is considerable scatter in the earlier data for Ti, Cr, Au, and Ge. Our INAA data Semarkona differs from our electron microprobe data, and Grossman and Wasson's data, in a manner which suggests that our chondrule samples contained a considerable amount of rim material. The lithophile elements in our INAA data are about 40% lower, and the siderophile and chalcophile element data are about 40% higher, than Grossman and Wasson's INAA data and the electron microprobe data. This is consistent with the presence of rim material, which contains abundant sulfides and metal (see "Recondensation" below), on the sections of the present chondrules which were prepared after analysis. This has been taken into account in interpreting the data.

# DISCUSSION

There have been a bewildering array of theories for the origin of chondrules and these have been reviewed many

TABLE VI
Apparent Diameters of Chondrules in the Semarkona and Krymka and Thicknesses of Chondrule Rims in Semarkona ( $\mu$ m)

Group Chon.	A1 dia <sup>†</sup> rim	Group A2 Chon. dia <sup>†</sup> rim	Group A3 Chon. dia	Group B1 Chon. dia <sup>†</sup> rim	Group B1 (cont.) Chon. dia	Group B2 Chon. dia
Semark	cona	Semarkona	Krymka	Semarkona	A74 672	Krymka
Rimme	ed	Rimmed	C1 423	Rimmed	A75 625	C2 635
A22	1128 75	A2 834 20	C5 905	A10 566 25	A76 531	C3 729
A24	362 30	A3 1187 30	C6 423	A20 389 6	A82 954	C4 729
A28	551 40	A4 503 30	C11 582	A23 802 25	A92 636	C7 1434
A50	1482 115	A11 692 21	C12 646	A31 766 10	A97 683	C10 776
A60	999 70	A38 1105 42	C13 541	A32 625 30	A102 1247	C16 852
A63	1025 55	A43 381 18	C14 329	A36 578 22	A103 625	C18 1293
A78	586 44	A53 727 45	C15 388	A39 542 28	A105 566	C25 1152
A79	374 22	A69 963 80	C17 658	A54 825 40	A111 942	C26 917
A80	397 14	A93 444 23	C22 952	A55 413 26	A112 754	C29 1469
A90	822 55	A101 1234 15	C24 323	A59 1297 59	A114 860	C34 1340
A109	1258 145	A104 362 37	C27 605	A47 861 55	C2 1012	C39 693
B18	273 12	B3 1081 24	C28 664	A73 483 35	C4 1036	C40 823
B28	327 12	B6 928 39	C30 470	A85 660 22	C5 1576	C41 564
B43	929 60	B7 527 18	C31 611	A86 554 20	C12 701	C42 455 C43 341
B48	529 63	B14 645 33	C32 294	A87 755 41	C16 801 C23 1976	C43 341 C44 467
B53	586 48 1576 90	B21 657 21 B25 987 30	C33 729 D1-3 635	A95 1509 125 A96 1038 37	C23 1976 C31 707	C44 467
B63 B64	1576 90 680 48	B25 987 30 B27 409 21	D1-3 635 D1-8 402	A110 1438 50	C40 801	C45 299
B70	727 54	B32 444 36	D1-8 402 D3-7 940	A116 755 45	C40 801 C41 1541	C47 550
B71	527 36	B35 951 21	D3-10 1081	B8 825 45	C41 1341 C45 542	C47 536
B73	562 42	B36 1010 29	D3-18 517	B11 1651 69	C46 566	C49 658
B80	444 9	B38 562 24	D3-23 682	B24 766 42	C49 531	C50 646
B91	729 42	B47 350 21	D3-25 752	B30 2264 65	C54 850	C51 1149
B99	1092 90	B52 468 30	D4-11 270	B39 1038 33	C55 672	D1-1 470
B101	1033 90	B56 928 48	D4-21 588	B51 814 33	C58 848	D1-6 846
B120	456 51	B74 574 21	D5-3 423	B59 1120 30	C65 460	D3-1 1481
		B83 586 30	D5-7 394	B60 1532 55	C68 595	D3-3 588
Unrim	med	B93 1128 57	D5-12 1175	B61 1238 45	C75 813	D3-6 687
A6	337	B96 456 45	D5-15 306	B66 778 18	C77 1059	D3-8 588
A45	422	B104 751 27	D5-16 364	B69 590 24	C85 1153	D3-12 1398
A48	502	B113 244 27	D5-17 752	B90 601 18	C94 888	D3-22 576
A49	494		D5-20 834	B92 802 48	C97 719	D4-4 799
A61	414	Unrimmed	D5-24 329	B98 495 54	C100 1335	D4-8 564
A70	572	A1 502	D6-5 341	B107 849 45	C106 1001	D4-20 975
A98	731	A21 437	D6-8 1069	B117 696 30	C108 484	D4-22 717
B15	690	A34 402	D6-10 494	B118 920 54	C109 730	D4-23 588
B19	431	A42 408	D6-14 823	B122 825 42	C112 653	D5-4 964 D5-10 846
B34	267	A51 396	D6-16 846	B124 943 45 B125 1038 39		D5-10 646 D5-18 635
B42 B84	452 678	A62 373 A77 690	D6-21 505 D6-24 523	B125 1036 39		D5-18 033
B87	326	A83 1806	D6-24 525 D6-25 576	Unrimmed		D5-14 905
B88	349	A44 1195	D6-30 1105	A5 695	4	D6-3 917
B89	561	A113 702	D6-33 599	A7 883		D6-7 376
B110	408	A117 519	1 2033 333	A8 589		D6-11 470
2110	100	B13 561		A9 789		D6-13 752
		B22 373		A12 531		D6-18 776
		B37 796		A13 719		D6-22 529
		B44 260		A14 566		D6-28 447
		B57 433		A15 484		D6-34 423
		B62 455		A17 707		D6-35 952
		B79 472	1	A19 801		D6-36 893
		B102 878		A27 672		D6-24 928
		B119 402	1	A29 860		
			1	A33 601		
			1	A35 777		
			1	A37 1294		
			1	A46 754		
	C45	M (50	M (11	A58 1106	Man 941	Mean 778
Mean	645 318	Mean 670 1σ 313	Mean 611 1σ 239	A68 648 A72 480	<b>Mean 841</b> 1σ 335	Mean 778 1σ 293
$1\sigma$	310	1σ 313	1σ 239	A/2 400	10 333	10 473

Note. Chondrule numbers prefixed by A and B refer to Semarkona thin sections 4728-1 and 549 in the American Museum of Natural History, New York, and University of New Mexico, Albuqerque, collections, respectively. Prefix C refers to thin section 1729-1 of Krymka from the Smithsonian Institution, Washington, DC, and prefix D refers to thick sections of Krymka made in our laboratory.

<sup>†</sup> Apparent diameters (including the means) refer to those of the core chondrules. No corrections have been made for biases caused by taking the measurements from thin sections.

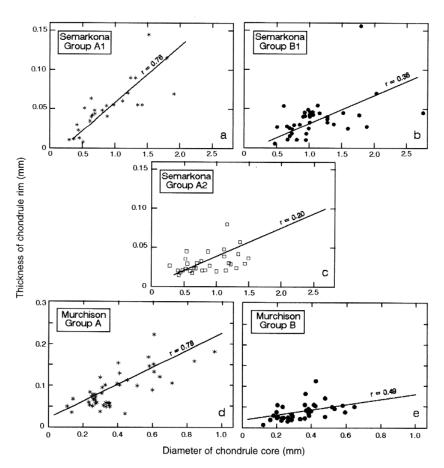


FIG. 6. Thicknesses of chondrule rim vs the diameters of chondrule core, for chondrules in Semarkona (Table VI) and Murchison (Sears et al. 1993). The correlation coefficients for the regression lines are indicated. Group A chondrule rims in both Semarkona and Murchison are thicker than group B chondrule rims and define better correlations with chondrule cores. Similar processes may govern the rim thicknesses in both cases. An association between the presence and thickness of chondrule rims and the compositional group of the core chondrule suggests that rim formation and chondrule formation may be related processes. The rims may be the recondensation products of the material evaporated from the chondrules during their formation; group A rims are thicker because they have evaporated and recondensed a larger quantity of material.

times (e.g., Dodd 1981, Grossman 1988, Hewins 1991). Part of the reason for so many theories is that some of these, perhaps most, are based on a few or even individual chondrules and there are a great variety of chondrules. A great many factors were clearly involved in chondrule formation and it is essential to fully describe the range of materials present and only then to discuss the processes involved in their formation. After summarizing the range of chondrules found in primitive ordinary chondrites, we then discuss formation mechanisms for chondrules, dividing the theories into (1) open-system theories, involving evaporation and other chemical interactions with the ambient gases during chondrule formation (Walter and Dodd 1972, Kurat et al. 1983, Lu et al. 1990); and (2) closed-system theories, assuming that the compositional properties of the chondrules were mostly inherited from the precursor solids and few interactions with the ambient gas took place (Grossman and Wasson 1982, 1983b, Ikeda 1983, Rubin and Wasson 1987, 1988, Hewins 1991). Once popular theories involving the formation of chondrules by direct condensation from the solar nebula (Wood 1962, Blander and Katz 1967, Wood and McSween 1976, Herndon and Suess 1977, Blander 1983) are here considered a subset of the first category.

# The Diversity of Chondrule Compositions and Textures

The diversity in primary chondrule properties is fully represented by the groups A1, A2, B1, and A5 observed in Semarkona (Table II). We summarized the properties of these chondrules in Table IX. All textural types are represented in these groups.

Group A1 chondrules are listed as having a "low" redox state, reflecting their FeO-poor silicates (Fig. 1), relatively

TABLE VII
Bulk Compositions of Semarkona Chondrules as Determined by Defocused Electron
Beam Microanalysis

Chondrule	Grp	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Total
SC-2-8 SC-2-12 SC-3-3 SC-22-4 SC-23-5 SC-28-12 SC-30-6 SC-31-1 Mean A1	A1 A1 A1 A1 A1 A1 A1	43.9 55.8 44.9 40.0 39.3 51.5 42.1 43.0 <b>45.1</b> 5.7	0.18 0.09 0.14 0.26 0.11 0.34 0.30 0.08 <b>0.19</b>	6.30 2.84 5.60 5.90 1.42 10.50 7.90 2.22 5.34 3.07	0.24 0.57 0.30 0.56 0.26 0.64 0.34 0.41 <b>0.42</b> 0.16	0.75 2.44 4.40 2.40 4.60 0.61 0.77 1.17 <b>2.14</b> 1.62	0.05 0.33 0.10 0.07 0.02 0.40 0.17 0.17 <b>0.16</b> 0.14	44.2 36.0 41.8 47.0 53.6 28.5 37.8 52.1 42.6 8.4	3.90 1.54 2.38 3.50 1.05 7.10 5.60 1.37 3.31 2.17	0.39 0.30 0.34 0.13 0.09 0.50 0.69 0.21 0.33 0.20	0.02 0.03  0.04 0.02 0.03 0.02 0.02 0.03 0.01	99.9 100.1 100.0 99.9 100.5 100.1 100.7 101.0 100.3
SC-3-10 SC-20-5 SC-22-10 SC-23-18 SC-26-5 <b>Mean A2</b> <i>lσ</i>	A2 A2 A2 A2 A2	54.1 57.2 52.2 54.3 56.3 <b>54.8</b> 2.0	0.27 0.07 0.15 0.19 0.08 <i>0.15</i> 0.08	9.50 0.92 2.25 4.70 1.31 3.74 3.54	0.55 0.87 1.21 0.79 0.75 <b>0.83</b> 0.24	2.18 3.00 8.80 2.16 3.60 3.95 2.78	0.16 0.67 0.46 0.62 0.46 <i>0.47</i> 0.18	27.1 35.2 31.6 32.6 35.8 32.5 3.5	5.30 0.93 2.00 2.92 0.98 2.43 1.80	0.57 0.14 0.44 0.87 0.19 <b>0.44</b> 0.30	0.05 0.04 0.06 0.06 0.01 <b>0.04</b> 0.02	99.8 99.0 99.2 99.2 99.5 <b>99.</b> 3
SC-3-1 SC-11-2 SC-14-1 SC-29-11 SC-30-5 Mean B1	B1 B1 B1 B1 B1	54.9 41.5 59.4 46.8 45.7 <b>49.7</b> 7.3	0.08 0.02 0.03 0.15 0.05 <b>0.07</b> 0.05	2.76 0.48 0.27 3.10 0.99 1.52 1.32	0.68 0.49 0.49 0.78 0.72 <b>0.63</b> 0.13	18.0 12.6 2.7 13.0 12.4 11.7 5.6	0.83 0.70 0.34 0.64 0.75 <b>0.65</b> 0.19	20.8 43.1 36.3 32.0 37.9 34.0 8.4	1.14 0.87 0.32 2.47 0.76 1.11 0.81	0.36 0.14 0.02 1.49 0.40 <b>0.48</b> 0.58	0.12 0.01  0.17 0.07 <b>0.09</b> 0.07	99.9 99.9 100.0 100.6 99.8 100.0
SC-23-6 SC-22-12	B2 B3	53.5 49.6	0.13 0.09	3.10 2.09	0.69 0.64	5.8 13.7	0.63 0.64	33.1 31.5	1.11 1.34	1.00 1.18	0.13 0.04	99.2 100.8

-- Not detected.

abundant Ni- and Co-poor metal (Fig. 10), and "low" CInormalized abundances of volatile elements (Fig. 9). Group A2 chondrules are similar to A1 chondrules in bulk composition, but have slightly higher FeO and lower CaO in the silicates and, because they contain higher Si than the other classes, are often porphyritic pyroxene or poikilitic pyroxene chondrules. Five of the six group A2 chondrules are porphyritic pyroxene chondrules. Mesostases in both group A1 and A2 chondrules contain high abundance of Al<sub>2</sub>O<sub>3</sub> and CaO. In contrast, group B1 chondrules, containing high-FeO silicates, and mesostases that are enriched in SiO<sub>2</sub>, are listed as having "normal" redox state and volatiles in Table IX. Group A5 similarly have high-FeO silicates and mesostases, noted for significant amounts of normative albite, and are also considered "normal" in these points.

Group B1 chondrules are noted for containing significant amounts of normative quartz. Many authors have noted that the high SiO<sub>2</sub> of the mesostasis and the absence of pyroxene suggest that these chondrules experienced supercooling during their formation (Blander *et al.* 1976, Kimura and Yagi 1980, DeHart *et al.* 1992, Jones 1990, Nagahara *et al.* 1994). In contrast, the A groups have mesostasis compositions (i.e., feldspar normative) approximating the

composition of the melt expected after crystallization, which implies cooling rates slow enough for equilibration.

Chondrule textures, well summarized by the scheme of Gooding and Keil (1981) with minor modification to allow for poikilitic and other textures, depend on whether or not complete melting occurred during chondrule formation, the number of nuclei available for crystallization, and the cooling rates (Tsuchiyama et al. 1980a,b, Lofgren and Russell 1986, Lofgren 1989). The first two factors are related, since complete melting destroys nuclei. There has been much discussion over the relative importance of peak temperatures and compositions (Lofgren and Russell 1986, Tsuchiyama et al. 1980a,b, Connolly and Hewins 1991), but if the chondrules are not closed systems during their formation, then the two will be interrelated and it is not clear which is the dependent variable. Cooling rates seem to generally vary from ~100 K/hr for porphyritic (e.g., Lofgren 1989) to ~1000 K/hr for nonporphyritic chondrules (e.g., Hewins 1988; Lofgren 1989). It has also been argued that some chondrules experienced multi-stage cooling, ~300 K/hr above 1570 K and ~3000 K/hr below 1570 K (Planner and Keil 1982). Whatever the details, the conclusions of all these studies are that the textures seem to require a great variety of chondrule formation conditions

and are not inconsistent with the conclusion that group B chondrules cooled faster than group A chondrules.

Open-System Theories—Experimental and Theoretical Predictions

The facility for volatile-loss from molten chondrule droplets has been demonstrated in many experimental studies (Gooding and Muenow 1977, Tsuchiyama et al. 1981, Radomsky and Hewins 1990, Lewis et al. 1993). Along with volatility, the loss rate depends on the nature of the precursor material and the temperature, pressure, oxygen fugacity, cooling rate, and internal chemical changes that occur in the chondrule during its excursion to high temperatures (e.g., reduction of FeO to Fe increases its volatility). Since major elements also become volatile at high temperatures in a hydrogen-rich atmosphere, for chondrules with similar starting compositions and sizes there should be correlated variations in chemical, isotopic, mineralogical properties, and size if the chondrules suffered major evaporative loss during their formation.

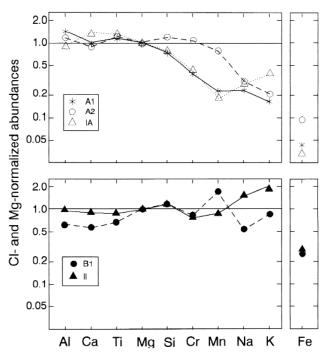


FIG. 7. CI- and Mg-normalized elemental abundances in Semarkona chondrules, as determined by defocused electron microbeam analysis. Data for A1, A2, and B1 chondrules are from the present study, and data for type IA and II chondrules are from Jones and Scott (1989) and Jones (1990). Our data agree fairly well with literature data, i.e., group A and type IA chondrules generally show volatility-controlled elemental patterns, while group B and type II chondrules show flat patterns, although literature data are systematically higher in Na<sub>2</sub>O and K<sub>2</sub>O relative to the present data and literature MnO data.

The results of some of the experimental studies are summarized in Figs. 11 and 12. The trajectories caused by the evaporation of major elements which were determined by Hashimoto et al. (1979), Hashimoto (1983), and King (1983) are shown in Fig. 11. Various starting compositions and various conditions yield similar results; Hashimoto and his colleagues used a mixture of oxides approximating chondritic compositions for their work, while King used U.S. Geological Survey standard rock BCR-1. Nagahara et al. (1989) and Wang et al. (1993) have obtained similar results using pure olivine and Allende powder, respectively. Since Fe is much more volatile than any other elements present in the starting material, the compositions of the residual solids first move toward the MgO-rich corner of the FeO-MgO-(CaO + Al<sub>2</sub>O<sub>3</sub>) ternary (Fig. 11a). SiO<sub>2</sub> is lost more rapidly than MgO, but much less than FeO. After most of the FeO has evaporated and when SiO<sub>2</sub>/MgO reaches 1.7, SiO<sub>2</sub> and MgO evaporate congruently and the residues migrate to the CaO + Al<sub>2</sub>O<sub>3</sub> corner (Fig. 11b). The elemental abundance changes observed to occur during Hashimoto's (1983) experiments are also shown as abundance plots in Fig. 12a. Mg and Si show 20–30% loss in the experiments, while Fe shows more than an order of magnitude loss, depending on temperature and duration of the experiment.

The temperature dependence of the olivine: pyroxene ratios is shown in Fig. 12b. Thus, bulk compositions which are originally olivine-normative first become pyroxenitic (with about 40% of the original mass evaporated at  $\sim 1500^{\circ}\text{C}$ ) due to preferential loss of Fe, then forsteritic ( $T = 1500-2300^{\circ}\text{C}$ , >40 wt% evaporated) due to loss of SiO<sub>2</sub>. Over most reasonable chondrule-forming temperatures the melt is essentially olivine-normative, although the amount of pyroxene can rise to quite high values, with the melt being almost entirely pyroxene-normative at  $1500^{\circ}\text{C}$  after 45% of the material has evaporated. The reaction apparently occurring under these conditions is of the sort

$$\begin{array}{c} 2Fe_{2}SiO_{4(l)} + Mg_{2}SiO_{4(l)} + 5H_{2(g)} \rightarrow \\ 2MgSiO_{3(l)} + 4Fe_{(l)} + SiO_{(g)} + 5H_{2}O_{(g)}. \end{array} \eqno(1)$$

Assuming that p(O) is governed by  $H_2/H_2O$  equilibria, as seems likely in view of the abundance of  $H_2$  in the cosmos, the relationship between olivine composition and temperature, T, is

$$\log \left[ \frac{P(H_2O)}{P(H_2)} \right] = \log[X_{Fa}] - \frac{1837}{T} + 1.64, \tag{2}$$

assuming cosmic abundances as given by Anders and Grevesse (1989), taking thermodynamic data from JANAF tables, and with  $X_{Fa}$  as the molar fraction of fayalite in the

TABLE VIIIA
Bulk Composition of Semarkona Chondrules as Determined by Instrumental Neutron Activation Analysis

Chon.	Mass mg	Dim. mm		Sc <u>μg</u> g	La ng g	Sm ng g	Eu <u>ng</u> g	Yb ng g	Lu ng g			Cr ug g	Mn mg g	Na <u>mg</u> g	K mg g	Ir ng g	Cο <u>μ</u> g g	Ni <u>mg</u> g	Fe mg g	Au ng g	As μg g	Ga <u>µg</u> g	Sb <u>µ</u> g g	Se μg g	Zn <u>µg</u> g
Group A1																									
SC-2-8	0.37	0.88	8.3	12.4	380	126	78	374	58	73	141	2.81	1.11	1.69	0.17	115	147	3.21	44	16	0.85	< 0.1	< 0.3	6.70	80
SC-2-12	0.92	0.93	9.6	10.8	297	159	48	302	29	47	96	2.87	2.00	4.30	0.25	153	326	5.61	199	93	0.32	<3.8	30.06	1.80	15
SC-3-3	0.55	0.65	9.0	9.4	331	147	22	251	30	54	98	1.80	0.85	2.42		529	432	8.89	127	34	1.11	2.33	0.01	6.95	55
SC-22-4	1.25	1.12	11.9	7.8	183	201		204	27	60	114	2.71				277	679	13.0	210	64	1.08	4.22	0.03	6.30	107
SC-23-5	1.08	1.19	10.5	8.1	229	166	25	194	35			1.76					504	10.7	150	39			5 0.05		
SC-28-12	0.25	0.47	30.7		424			298				3.23						5.59					0.01		
SC-30-6	0.30	0.88		13.0				345		-		3.99				-	607	14.8	177	106			0.09		
SC-31-1	0.65			10.9				326				2.31						4.70					0.05		
Mean A1	0100	0.87		10.3				287				2.69						8.31					0.04		
$1\sigma$				1.7		83	57	65	15		33	0.69						4.21		31			0.03		
Group A2																									
SC-2-13	0.15	0.49	10.5	8.5	376	176	47	499	43	54	107	2.69	0.86	2.70		642	748	13.6	175	59	2.06	7.70	0.01	16.4	62
SC-3-10	0.85	0.70	20.0		662	342	49	410	73	91	109	3.71	1.33	3.64		63	85	1.84	38	22	0.45	0.42	0.01	2.50	
SC-20-5	0.10	0.41		7.4		197		198	63			3.21					356	9.02	146	119	1.58				
SC-22-10	0.21	0.59		7.1		182		288				3.16						10.2		148			0.12		
SC-23-18	0.40	0.41	13.4		311	251						3.57					217	4.73	77	51	0.84	1.12		6.33	47
SC-26-5	0.05	0.23	15.5			149		90	23			0.83						1.78		32			0.05	13.1	30
Mean A2	0.00	0.47	13.6			216		295				2.86						6.86					0.05		
$1\sigma$			3.93		186		16	146				1.06						4.83		50			0.05		
Group B1																									
SC-3-1	0.57	0.92	8.2	5.7	247	90	66	227	26	45	87	4.36	5.28	2.52		244	260	8.73	151	143	0.97	4.23	0.16	3.48	28
SC-11-2	0.84	1.30	15.8		269	168		287								1121	567	17.5	158	168	1.20	6.29	< 0.1	6.68	36
SC-14-1	3.53	2.05		6.5	212	235		137				3.44					17		139				0.02		
SC-29-11	4.05	1.29	9.2	11.1		297	28	283				3.34					54	0.83		8			0.01		
SC-30-5		1.06	17.3		226	249		395				3.08					129	2.88		32			0.02		
Mean B1	0.01	1.32	12.6				48	266				3.45						6.72					0.05		
$1\sigma$			3.98		68	80	42	94	12		31	0.53						6.69		74			0.06		
SC-22-12	1.21	0.88	12.1	7.6	203	208	37	265	42	69	121	3.05	2.55	6.25	0.33	29	77	1.43	96	12	0.38	2.31		2.79	30
SC-23-6		1.16	10.0			199		258			92		1.97								2.13			15.1	67

<sup>--</sup> Not detected.

olivine. The results are plotted in Fig. 13. At temperatures around the melting point of most silicates, there will be considerable reduction of FeO. It requires an increase of  $\rm H_2O/H_2$  of  $\rm >10^3$  over cosmic to prevent the reduction of FeO. If the process were taking place in the presence of carbon, the conditions would be even more highly reducing. After most of the Fe and Na have been lost by evaporation, Si loss causes the fraction of olivine in the solids to increase again by a reaction of the sort

$$2MgSiO_{3(1)} + H_{2(g)} \rightarrow Mg_2SiO_{4(1)} + SiO_{(g)} + H_2O_{(g)}$$
. (3)

The Na data of Tsuchiyama et al. (1981) are also shown in Figs. 12 and 13. At most reasonable chondrule melting temperatures considerable reduction and loss of Na<sub>2</sub>O are also to be expected. In a gas of cosmic composition, Na loss and FeO reduction should be very facile, and a considerable increase in oxygen fugacity is also required to retain Na in the chondrules or prevent reduction.

Another important potential process associated with chondrule formation is recondensation of elements once lost by evaporation. Lewis *et al.* (1993) performed experiments in which spherules of chondritic composition were heated in gaseous environments enriched in Na and found that considerable recondensation of Na in the experimental charges occurred during the lifetime of the experiments. To be relevant to chondrule formation, it would be necessary for the volatiles to remain in the vicinity of the cooling chondrule long enough to enable recondensation which would imply a regolith-like environment. High chondrule densities would aid the process, and this is implied by the abundance of compound chondrules (Gooding and Keil 1981, Wasson *et al.* 1993).

Reduction and evaporation during chondrule formation will have a major effect on the isotopic proportions in chondrules, through either mass fractionation and isotopic exchange with surrounding gases or liquids or mixing of materials from different oxygen reservoirs (Clayton et al.

TABLE VIIIB

Bulk Composition of Krymka Chondrules as Determined by Instrumental Neutron Activation Analysis

Chon.	mass mg	Dim mm	. Al <u>mg</u> g	Ca mg g	Sc <u>µg</u> g	Sm ng g	V <u>μg</u> g	$\frac{Mg}{g}$	Cr mg g	Mn mg g	Na mg g	K mg g	Ir ng g	Cο <u>μg</u> g	Ni <u>mg</u> g	Fe mg g	Au ng g	As μg g	Ga <u>µg</u> g	Se µg g
Group A3															,					
KC-7	0.47			17.1		0.20		149				0.29		554	10.7		90	1.28	2.29	
KC-3	2.00	1.08		22.7		0.32		127	2.94	1.3		0.23	253	240	4.1	99	82	0.73	1.52	9.7
KC-10	0.61			20.8		0.28		153	3.56			0.87	225	414	8.3	150	108		3.41	
KC-15	1.02			15.6		0.39		188		0.46	2.42		419	181	7.9	52	47	2.79		
KC-18	0.97			14.9		0.32		148	3.33	2.03	3.62		556	434	9.3	140	103	0.65		
KC-20	1.01	0.60		13.1	8.9	0.34	86	155		2.03			452	456	11.3	183	50	1.07		
KC-23	0.65	1.07	13.1		11.3		106	159		1.43			528	413	14.8	173	83	1.57		
Mean		0.85		17.3		0.31		154				0.41		385	9.5	135	80		2.45	
$1\sigma$			5.1	3.4	1.2	0.06	15	18	0.59	0.58	1.11	0.23	156	129	3.3	45	24	0.78	1.43	6.3
Group B2																				
KC-1	3.76	1.49	11.8	10.2	7.7	0.22	80	125	3.29	2.96	7.28	0.84	127	196	3.5	127	58	0.34	1.62	5.8
KC-4	6.65	1.40	11.7	13.8	8.1	0.22		113	3.39		6.43		269	339	7.0	175	120		3.26	
KC-6	0.54	0.58	14.8	14.1	9.2	0.42	100	151	4.56		3.72		465	439	11.6	132	81		7.7	12.
KC-5	8.30	0.87	13.7	14.0	9.3	0.22	93	132	2.43		5.91		343	105	1.8	134	72	1.06		10.4
KC-11	3.35	0.98	13.7	13.2	8.8	0.24	86	137	3.89	3.39	7.24	1.16	50	117	1.6	127	25	0.46	1.7	2.6
KC-13	0.96	0.97	12.3	12.9	7.4	0.19	79	133	3.17	2.85	7.19	0.92	188	200	3.3	102	64	1.23	7.1	11.
KC-22	2.15	0.91	14.7	15.1	9.2	0.31	94	128	4.02	2.75	5.98	0.84	398	467	9.5	206	128		2.59	
KC-17	0.56	0.85	15.9	11.7	9.8		91	137	3.94	2.46	8.36	0.66	159	211	6.3	109	102		1.53	
Mean		1.01	13.6	13.1	8.7	0.26	87	132	3.59	2.69	6.51	0.94	250	259	5.6	139	81	0.86	3.71	9.3
$1\sigma$			1.5	1.6	0.8	0.08	9	11	0.65	0.45	1.39	0.24	144	139	3.7	35	34	0.34	2.46	4.9

<sup>--</sup> Not detected.

1983, 1985, 1991). While the patterns resulting from mass fractionation are well known and, for oxygen at least, readily quantified (Chiba et al. 1989), predicting the effects of mixing or exchange is impossible without a knowledge of the composition of the components. Laboratory experiments indicate that exchange probably proceeds quickly, with significant changes occurring under laboratory conditions in a matter of a few minutes (Yu et al. 1993).

In summary, the effects to be expected on the basis of laboratory experiments and thermodynamic calculations are:

- (1) Volatility-controlled mass loss, with Mg, Si, Fe, Na, and K being lost in amounts primarily dependent on the volatility of each element.
- (2) A resulting correlation between chondrule size and composition.
- (3) The reduction of FeO to Fe<sup>O</sup>, with the resulting formation of Ni-free metal or a decrease in the total Ni/Fe ratio of any metal present.
- (4) Under suitable conditions, the volatiles lost from chondrules during the highest temperature phases of their formation may recondense on the chondrules as they cooled.
- (5) Inasmuch as the gas present at the time of chondrule formation contains oxygen, interaction with the gas could cause changes to the isotopic composition of the chon-

drules either by exchange (assuming that the gas and chondrules had different oxygen isotope compositions) or by mass fractionation if evaporation occurred.

We will now examine the observational data with a view to determining the extent to which these predictions are fulfilled.

Open-System Theories—Observational Data

Redox state and bulk composition. In Fig. 13 we indicate the oxygen fugacity and temperature required to yield olivine compositions and bulk Na observed for the three primary chondrule groups. Even the highly reduced group A chondrules seem to have melted or partially melted in an environment where p(O) was 2–3 orders of magnitude greater than cosmic. It is interesting to compare the temperature estimates in Fig. 13 with liquidus temperatures calculated from the bulk composition of the chondrules. Following Hewins (1989), we calculated liquidus temperatures using the methods of Herzberg (1979). Calculated liquidus temperatures for group A1, A2, and B1 are ~1710, ~1550 and ~1630°C, respectively. For the A groups, these estimates are in good agreement with the equilibration temperatures calculated from olivine compositions, but for the B group the calculated temperature is overestimated because most of the chondrules were only partially melted.

Although we find that the Na contents of the group A1,

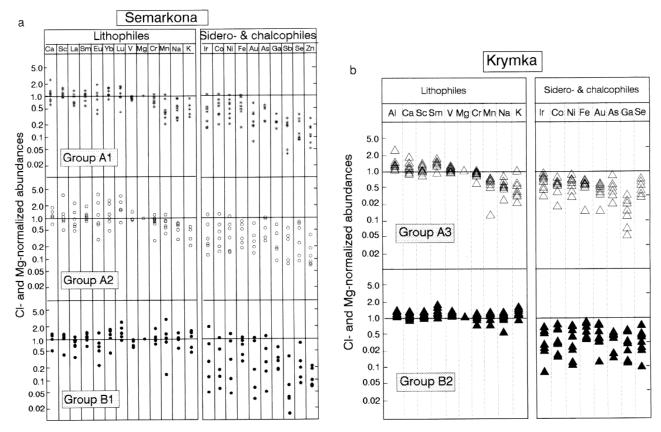
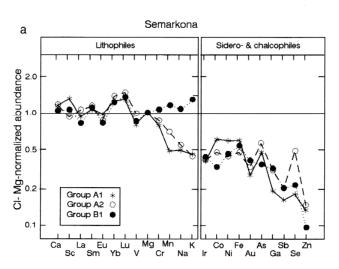


FIG. 8. Compositions of chondrules from (a) Semarkona and (b) Krymka, as determined by instrumental neutron activation analysis during the present study. Abundances are plotted as ratios to CI and Mg in cosmochemical groups, in order of increasing volatility. Group A1–3 chondrules show volatility-controlled elemental abundance patterns for lithophile elements, while group B1,2 chondrules show flat patterns. Siderophile and chalcophile elements are depleted in both group A and B chondrules, with a slight suggestion of a volatility trend.

2 chondrules studied here are depleted typically by factors of about 2, the true extent of the depletion in chondrules at peak temperatures during formation is certainly higher. Not only do some of the INAA chondrules include adhering matrix, but (1) the mesostasis profiles in some group A1 chondrules indicate Na recondensation (DeHart 1989, Matsunami et al. 1993), (2) aqueous alteration may have caused Na to be redistributed from the matrix to the chondrules (Hutchison et al. 1987), and (3) metamorphism may have caused some redistribution of Na, even in the little-metamorphosed Semarkona. Thus, while several group A chondrules sometimes have higher Na concentrations than others, we observe essentially no group B chondrules with lower Na concentrations than normal for group B chondrules.

We tried to further examine our data for evidence of volatile loss by examining element-element plots. Scandium, a typical refractory element, when plotted against Na, should show anti-correlations, but does not. This is because the accuracy of our data, as opposed to its precision, is comparable to the 30-40% difference in Sc produced by mass loss. There is a weak correlation for Sc against Na in Krymka. This might reflect metamorphic redistribution of Na, although the bulk compositional data for the Krymka chondrules suggest that this is not the case. Highly labile elements like Cs, Bi, Tl, Cd, and In show evidence of mobilization in all chondrule groups, with the lithophile element (U, Sr, Rb, and Cs) abundances decreasing with volatility while siderophile (Au, Co, Ag, Ga, Bi, Tl) and, especially, chalcophile (Se, Te, Zn, Cd, In) elements show increases in abundances with volatility (Sears et al. 1995a, Sears and Lipschutz 1994). This was interpreted as evaporative loss of lithophiles, and loss and later recondensation of siderophiles and chalcophiles. Although they are thicker and more common around group A chondrules, metal-sulfide-rich rims are present around group A and B chondrules, indicating that all chondrule groups experienced these processes.



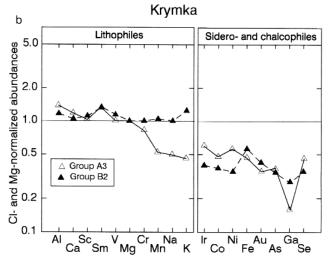


FIG. 9. Chondrule group averages and abundance trends for CI- and Mg-normalized data obtained by INAA from (a) Semarkona and (b) Krymka. In both cases, the abundance patterns for the group B chondrules are flat while those for the A groups show volatility-related depletions. Na, and also K, Mn, and Cr, shows depletions relative to CI proportions. The siderophile and chalcophile elements show volatility-related trends in all chondrule groups.

Anti-correlations have been reported between SiO<sub>2</sub> and refractory oxides (CaO and Al<sub>2</sub>O<sub>3</sub>) in Chainpur (LL3.4) chondrules, and low Si, alkalis, and reduced Fe were reported in chondrules from other ordinary chondrites (Dodd and Walter 1972, Dodd 1974). However, we know that the refractory-rich group A chondrules are smaller than the group B chondrules.

TABLE IX

Qualitative Description of the Formation of the Primary

Chondrule Groups in Terms of the Intensity of the Heating

Event and Subsequent Crystallization

Chon. group	Redox <sup>†</sup>	Volatiles <sup>‡</sup>	Intensity of heating event*	Cooling rate
A1	Low	Low	High, reduction and loss of volatiles during crystallization	Slow, phenocrysts and mesostasis at equilibrium
<b>A</b> 2	Low	Low	High, but slightly less reduction and volatile loss than A1	Same as A1
A5	Normal	Normal	Low, no reduction and mass-loss	Same as A1
B1	Normal	Normal	Low, no reduction and mass-loss	Fast, considerable supercooling

<sup>\* &</sup>quot;Intensity of heating event" refers to the chemical changes caused by the chondrule formation event. The major factor responsible for these was almost certainly temperature, but also time spent at the peak temperature during formation (cooling rate) and the presence or absence of insulating materials (especially oxygen-rich dust).

Other authors have observed anti-correlations between refractories and volatiles (such as Na, K, and Mn) in chondrules (Kurat *et al.* 1983, Jones and Scott 1989, Jones 1990). Kurat *et al.* (1983) attributed this to evaporative loss during chondrule formation, while Jones and Scott (1989) were unable to choose between low volatile concentrations in precursor materials or volatile loss during chondrule formation as the explanation for the volatile depletion in type IA chondrules. However, Scott (1994) has recently taken a different position, favoring an important role of opensystem behavior.

Our data for Semarkona and Krymka chondrules, as well as data for a number of primitive chondritic materials, are plotted alongside the laboratory evaporation data (Fig. 11) in Fig. 14. It is seen that the data follow the evaporation trajectories fairly closely, with matrix and group B1 chondrules being at the beginning of the evaporation paths, group A1 and A2 chondrules lying at intermediate locations on the path, and Ca-, Al-rich POIs and CAIs lying near the end of the trajectory. The distributions along the evaporation trajectories displayed by these primitive components suggest that it is possible they may have originated from the same or similar precursor materials and have undergone different stages of evaporation. They are also consistent with group A1 and A2 chondrules being formed from group B1 chondrules by reduction and evaporation of Fe and Si.

The POIs plot above the trajectory. Silicon-rich materials may have been added to the POI, perhaps in the form of Si-rich recondensates produced from volatiles lost from the chondrules while at peak temperatures, or in the form

<sup>†</sup> Refers to the reduction/oxidation state as determined by the FeO content of the olivine, or the amount and composition of coexisting metal.

<sup>‡</sup> Refers to the abundance of volatile elements.

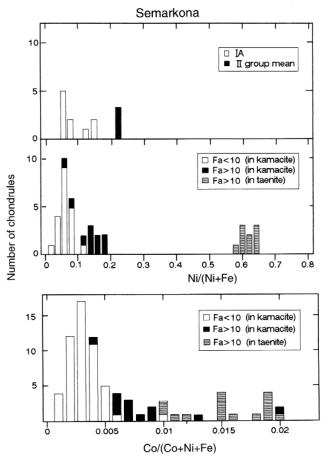


FIG. 10. Ni and Co atomic abundances in chondrule metal of various classes in Semarkona. Metal in type IA (Jones and Scott 1989) and low-Fa (Snellenburg 1978) chondrules mainly occurs as kamacite and is generally poorer in Ni and/or Co than metal in type II (Jones 1990) and high-Fa chondrules (Snellenburg 1978). The tendency for metal in chondrules with low-Fe olivine to be Ni- and Co-poor implies formation by *in situ* reduction, probably during chondrule formation.

of material resembling matrix or group B chondrules. Sheng *et al.* (1991) have discussed evidence for such processes.

Chondrule size distribution. Chondrule size is the primary physical parameter acquired during chondrule formation, although subsequent size sorting may later alter the distribution within a specific class. Group A1–3 chondrules are generally smaller and contain higher abundances of refractory elements and lower abundances of volatile elements than group B1 and B2 chondrules (Fig. 15). The *t* test shows that the size difference between group A and B chondrules is significant at the 99.9% confidence level. Group A chondrules are typically 20–23% (in diameter) smaller than group B chondrules in Semarkona and

Krymka, which corresponds to a difference in mass of about 49-54%.

Gooding (1979) found a weak inverse correlation between Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>O and size in porphyritic chondrules, but he found a positive correlation for nonporphyritic chondrules. He suggested that vapor fractionation had occurred during porphyritic chondrule formation, and these objects remained molten longer than nonporphyritic chondrules.

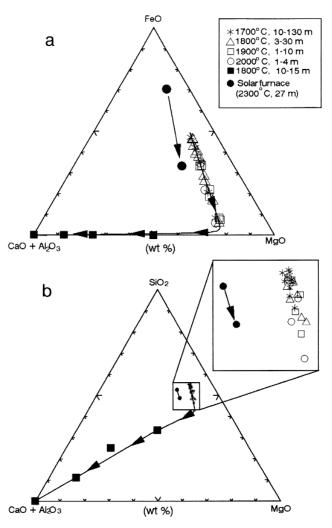


FIG. 11. Trajectories on (a) FeO-MgO-(CaO + Al<sub>2</sub>O<sub>3</sub>) and (b) SiO<sub>2</sub>-MgO-(CaO + Al<sub>2</sub>O<sub>3</sub>) plots for samples heated at the times and temperatures indicated, according to the data of Hashimoto *et al.* (1979; 1800°C, 10-15 min), Hashimoto (1983; 1700-2000°C, 1-130 min), and King (1983; solar furnace). The starting material in Hashimoto's experiments was a mixture of oxides in chondritic proportions, while King used U.S. Geological Survey standard rock BCR-1. The evaporation trajectories reflect increasing volatility along the trend FeO-SiO<sub>2</sub>-MgO-(CaO + Al<sub>2</sub>O<sub>3</sub>). Nagahara *et al.* (1989) reported measurements for olivine, and Wang *et al.* (1993) reported high-temperature measurements for Allende, which yield similar results.

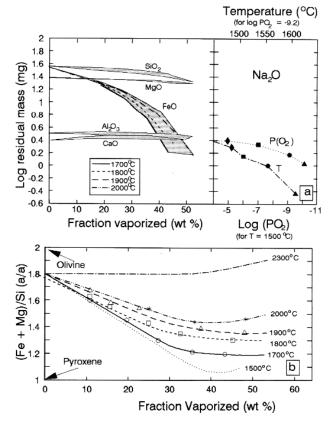


FIG. 12. The results of heat treatments on the composition of silicates of initially chondritic composition plotted so as to show (a) compositions as a function of temperature, fraction vaporized and, in the case of Na, oxygen fugacity, and (b) the olivine/pyroxene ratio. FeO loss is temperature-dependent and approaches 90% in the experiments, while SiO<sub>2</sub> and MgO show 40 and 10% losses, respectively, and CaO and Al<sub>2</sub>O<sub>3</sub> show the expected increase due to mass balance. Na also shows many orders of magnitude loss, depending on temperature and oxygen fugacity. The (Fe + Mg)/Si ratio decreases from an initial value of 1.8 to almost 1.0–1.4 (depending on temperature, excluding the 2300°C curve) corresponding to a major decrease in the olivine/pyroxene ratio as Fe is lost, and then an increase as Si loss becomes important. Lines for 1500 and 2300°C are predicted values. Data from Hashimoto (1983) and Tsuchiyama *et al.* (1981).

However, Gooding did not report any reduction of FeO or major volatile loss (of elements such as Si) during chondrule formation and Grossman and Wasson (1983b) found no correlation between chondrule size and Na content, presumably because their data base contained few group A chondrules.

Since the size difference between group A1, 2, and B1 chondrules indicates that group A1 chondrules typically have ~50% of the mass of group B1 chondrules, mass-balance claculations can be used to test whether evaporation of the appropriate volatiles from compositions of

group B chondrules can result in group A compositions (Table X). In order to explain these differences, a twostep process can be postulated. For group A1 chondrules, in step 1,95% of the FeO is reduced and 95% of the reduced Fe is evaporated, while in step 2, 40% of the SiO<sub>2</sub>, and 15% of the MgO, is lost by evaporation. For the group A2 chondrules, 80% of the FeO is reduced, of which 95% is evaporated, while 30% of the SiO2 and 10% of the MgO are evaporated. These reduction and evaporation processes are reasonably in agreement with experimental data, considering the compositional differences between group B1 chondrules and the starting material used in the heating experiment (e.g., 12% FeO, 50% SiO<sub>2</sub> vs 35% FeO, 35% SiO<sub>2</sub>; Hashimoto 1983). The calculated mass difference resulting from these processes is about 27-36%, while it is 45–54% calculated from the size difference. More SiO<sub>2</sub> may have been lost from group B1 chondrules. The "Calc." columns in Table X are the calculated normalized bulk compositions, which are roughly compatible with the mea-

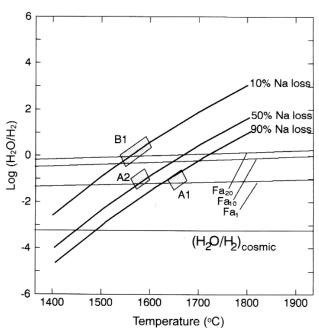


FIG. 13. Evaporation temperatures of Na-bearing phases as a function of oxygen fugacity (expressed as H<sub>2</sub>O/H<sub>2</sub> ratio). Fe reduction/oxidation lines for olivine (for fayalite values of 1, 10, and 20 mol%) and the cosmic H<sub>2</sub>O/H<sub>2</sub> ratio are also indicated. The data show that under cosmic conditions there would be considerable loss of Na and reduction of FeO. 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). The regions in which the fayalite content of the olivine and the bulk Na of the chondrules equal those of the major chondrule groups in Semarkona are indicated. Chondrules of all groups were exposed to oxygen fugacities much higher than expected for a gas of cosmic composition.

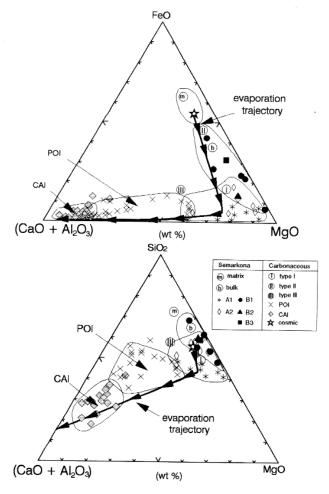


FIG. 14. Ternary plots of FeO,  $SiO_2$ , MgO, and  $CaO + Al_2O_3$  showing the trajectories taken during the laboratory evaporation experiments in Fig. 11, with chondrule and refractory inclusion compositions are indicated. This shows a general similarity between the data presented and the laboratory experiments, although there are some deviations. Matrix data are from Huss  $et\,al.$  (1981), bulk Semarkona data are from Jarosewich (1990), carbonaceous chondrite chondrule data are from McSween (1977a,b,c). POI data are from Sheng  $et\,al.$  (1991), CAI data are from Mason and Taylor (1982), and cosmic data are from Anders and Grevesse (1989).

sured bulk composition of group A1, 2 chondrules. Certainly, many trace elements more volatile than Fe must also have been lost, but their low absolute abundances means that they are not as important in the mass-balance calculations. It is worthwhile to note that this is apparently an oversimplified approach to this subject. The mass-balance calculations can be complicated by many factors involved during or after chondrule formation, such as recondensation of volatiles, as we will mention below. Thus, group A and B chondrules may have formed from similar

precursor materials, by similar processes acting with different intensities, rather than from grossly different precursors.

Metal composition and metal and sulfide distribution. The Ni/Fe or Co/Fe ratios in group A metal are similar to those of cosmic values, although there is a considerable spread, but significantly lower than those of group B metal. The metal is in much higher abundance in group A chondrules. This is most readily explained by the reduction of Fe in group A chondrules or the oxidation of Fe in group B chondrules, rather than due to differences in the composition of the precursor metal. In fact, the higher than cosmic Fe/Ni and Fe/Co ratios in group B metal are to be expected, because most of the Fe is in the silicates. The similarity of the Ni/Fe and Co/Fe ratios in group A metal to cosmic would therefore appear to be without significance.

Olivine/pyroxene abundances. As expected from Eq.

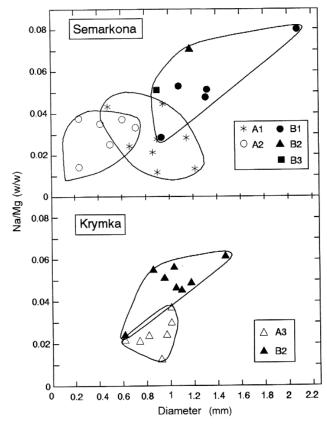


FIG. 15. Mg-normalized Na concentrations against diameter for Semarkona and Krymka chondrules in this study. Group A chondrules, depleted in Na, are generally smaller than group B chondrules. A general correlation between composition and size is strong evidence that the low Na of group A chondrules was likely the result of evaporative loss of Na (along with major moderately volatile elements like Si) during chondrule formation.

TABLE X
Reduction and Evaporation of Major Elements (wt%) to
Give the Observed Size Difference between Group A
and B Chondrules\*

	B1 <sup>¶</sup> Obs.	Step 1 <sup>†</sup> Calc.	Step 2 <sup>†</sup> Calc.	A1 <sup>§</sup> Calc.	A1 <sup>¶</sup> Obs.	Step 1 <sup>‡</sup> Calc.	Step 2 <sup>‡</sup> Calc.	A2§ Calc.	A2 <sup>¶</sup> Obs.
SiO <sub>2</sub>	50	50	30	48	44	50	35	50	54
MgŐ	34	34	29	46	42	34	31	43	33
FeO	12	0.6	0.6	1.0	2.1	2.4	2.4	3.4	4.0
$Al_2O_3$	1.5	1.5	1.5	2.4	5.1	1.5	1.5	2.1	3.7
CaO	1.1	1.1	1.1	1.8	3.2	1.1	1.1	1.5	2.4
Fe (metal)**	0.0	0.57	0.57	0.9	3.4	0.48	0.48	0.7	1.0
Diameter (mm) 0.84				0.72	0.65			0.76	0.67
Mass loss (wt%)		11	25	36		9	18	27	

<sup>\*</sup> Relative losses are estimated from the experimental data of Hashimoto (1983), assuming 1700°C heating and 45–54% total mass loss, which corresponds to the mass differences between group A and B chondrules.

(1), and as discussed above in connection with chondrule classes, chondrules showing reduction and volatile loss should also have lower olivine/pyroxene ratios than others (Fig. 16). Laboratory experiments reproduce the B1–A2–A1 trend rather well (Fig. 12b), indicating that (Fe + Mg)/Si decreases from 2 to 1 and then shows a slight increase. Starting with essentially B1 composition, loss of Fe causes the olivine/pyroxene ratio to decrease to A2 levels until with further heating, Si loss increases the olivine/pyroxene ratio to A1 levels (also see Eq. (3)).

Isotopic data. There are few O isotope data for chondrules from primitive ordinary chondrites. Group B1 chondrules plot within the region of ordinary chondrite chondrules in the three oxygen isotope plot (Fig. 17). We expect group A1-3 chondrules to show evidence for greater exchange with ambient gas, but to date there are no published data for these chondrules and it is difficult to predict the effects of this exchange. The inverse correlation between <sup>16</sup>O and size for Dhajala (H 3.8) chondrules suggests that the surrounding gas was <sup>16</sup>O-rich relative to the ordinary chondrite solids (Clayton et al. 1991), while an <sup>16</sup>O-depleted Mezö Madaras (L3 breccia) glass fragment suggests that it was <sup>16</sup>O-poor (Mayeda et al. 1989). We suspect that the Dhajala chondrule data are more pertinent to the discussion; since Mezö Madaras is a breccia, the glass fragment may be the result of brecciation in a different setting to that of chondrule formation.

Allende-barred olivine chondrules contain heavier oxy-

gen than porphyritic chondrules (Clayton *et al.* 1983, McSween 1985). The difference in the amount of isotopic exchange for barred and prophyritic chondrules presumably resulted from varying degrees of melting. This implies that the ambient gas was <sup>16</sup>O-poor since the barred chondrules were fully molten, suggesting that FeO-rich olivines in the rims of Allende chondrules have heavier oxygen

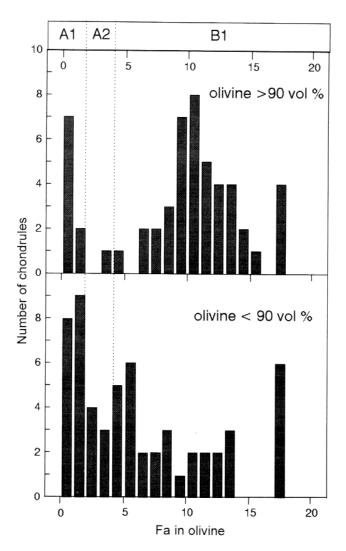


FIG. 16. Histograms of Fa contents of olivines in Semarkona chondrules, with >90 vol% olivine and with <90 vol% olivine. Data are from the present study and Snellenburg (1978). Chondrules with >90% olivine show a bimodal distribution of Fa, with B1 chondrules forming a broad peak at around Fa<sub>10</sub>, and A1 chondrules forming a much narrower peak at Fa <2. Chondrules with <90% olivine have a very different pattern, with a gap between Fa<sub>2</sub> and Fa<sub>4</sub>, occupied by A2 chondrules and the Fa<sub>10</sub> peak missing. These are the trends expected if reduction of FeO in 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).

<sup>†</sup> Step 1, 95% of FeO is reduced, and then 95% of the reduced Fe is evaporated; step 2, 40% of SiO<sub>2</sub>, and 15% of MgO, is evaporated.

 $<sup>\</sup>ddagger$  Step 1, 80% of FeO is reduced, and then 95% of the reduced Fe is evaporated; step 2, 30% of SiO<sub>2</sub>, and 10% of MgO, is evaporated.

<sup>§</sup> Previous column recalculated to 100%.

 $<sup>\</sup>P$  Observed average composition from Table VII, with lithophiles in A1  $\times$ 0.966 for group A1 and  $\times$ 0.990 for group A2 to allow for the addition of metal.

<sup>\*\*</sup> Metal abundances determined from point counting.

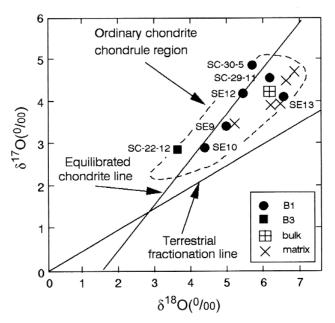


FIG. 17. Three-isotope plot for Semarkona chondrules, matrix and bulk samples. Group B chondrules and matrix and bulk chondrite are all plotted in the region defined by ordinary chondrite chondrules (dashed balloon). To date, there are no data for chondrules known to be members of group A. (Data from Lu 1992, Clayton et al. 1991, Grossman et al. 1987.)

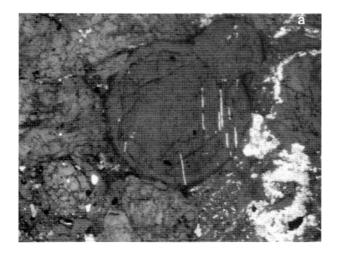
than the FeO-poor olivines inside the chondrule (Rubin et al. 1990). Similarly, higher FeO is associated with heavier oxygen in zoned olivines in Allende chondrules (Weinbruch et al. 1989). This suggests that Allende chondrule rims were exposed to an environment containing relatively heavier oxygen during their formation than that which was present at the time of chondrule core formation. Weisberg et al. (1992) have observed a similar effect in the rims of chondrules in the Renazzo chondrite. Clayton et al. (1983) suggested that the ambient gas for both ordinary and carbonaceous chondrites probably had an oxygen isotope composition near the terrestrial fractionation line and we therefore suggest that group A chondrules in ordinary chondrites may have a lighter oxygen composition than that of the group B ordinary chondrite chondrules; however, this warrants further investigation.

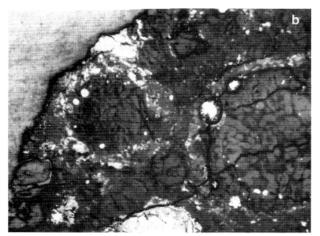
In contrast to oxygen isotopes, Si isotopes in ordinary chondrites define a slope 1/2 mass-dependent fractionation line, with small chondrules having heavier Si isotopes than large ones (Clayton *et al.* 1985). The same authors have interpreted this as a reflection of greater evaporative loss of lighter Si isotopes in the smaller chondrules.

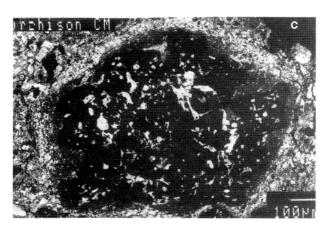
Recondensation. Cathodoluminescence studies reveal that some chondrules in Semarkona contain compositionally zoned mesostases, in which the central mesostasis regions are nonluminescent while the outer regions luminesce blue. Electron microprobe analyses indicate that the luminescent regions contain much higher Na<sub>2</sub>O (DeHart 1989). This was also observed by thermoluminescence imagery (Matsunami et al. 1993) and these authors argued that the zoning was caused by recondensation of volatiles lost during chondrule formation, analogous to Lewis et al.'s results (1993) for laboratory heating of silicate beads in a Na-rich environment. Thus, we suspect that at least some chondrules are high in Na and other volatile elements as a result of recondensation, with considerable facility, onto the cooling chondrule rather than volatile loss having not occurred. Ikeda and Kimura (1985) described petrographic evidence for Na recondensation in chondrules in a CO chondrite. Sears and Lipschutz (1994) recently explained some unusual abundance patterns for highly mobile siderophile and chalcophile elements in terms of recondensation of elements onto rims, almost certainly lost during chondrule formation. Figure 18a shows a group B chondrule in which sulfide clearly entered the structure following crystallization.

Group A chondrules in primitive ordinary chondrites are much more likely to have thick, metal-sulfide-rich rims than group B chondrules (Table VI; Huang et al. 1993), and there are many similarities in the chondrules of ordinary and carbonaceous chondrites (Scott and Taylor 1983). Group A chondrules in the Murchison CM chondrite contain thick fine-grained rims, often with complex Fe/Mg zoning, while group B chondrules contain only very thin rims (Sears et al. 1993). There is a striking similarity between the metal and sulfide distribution around Semarkona group A chondrules and the complex zoning often observed around Murchison group A chondrules, and it seems possible that the Murchison group A chondrule rims are the aqueously altered versions of the metal-sulfiderich rims on Semarkona group A chondrules (Figs. 18b and 18c). They display similar plots of rim thickness to chondrule diameter, although Murchison chondrules tend to be smaller (Fig. 6). Many chondrule rims are enriched in the alkali elements which are depleted in the chondrules (Alexander 1994). The depletion of Na in many chondrules and the Na/Al ratio of the bulk meteorites implies that the chondrule and the rim/matrix are complementary, although no obvious correlations exist between Na enrichment in rims and its depletion in the host chondrule. However, as discussed by Alexander (1994) the lack of obvious correlation is not conclusive evidence against volatile loss from chondrules. Instead, it may be due to (1) volatiles may have recondensed on much more material than is present in the rim and (2) alkali metal abundances in rims may have been altered by secondary processes. Zanda et al. (1995) have shown evidence for recondensation of sulfides, lost from chondrules, on rims. King and King (1981) argued that the textures of the rims are consistent with vapor deposition, and Allen et al. (1980) suggested that the lack of

charged-particle tracks in the chondrule surfaces indicates that the chondrules have not existed in free space for any significant length of time. Hewins (1989) also discussed the idea that chondrule rims were produced by recondensation and suggested that the Fa-rich zones on individual olivine







grains reflect reaction with ambient gases, as did several other authors (Peck and Wood 1987, Weinbruch *et al.* 1989, Hua *et al.* 1988). Since rims are preferentially associated with group A chondrules it seems likely that they resulted from the redeposition of volatiles lost from the chondrules during their high-temperature phases, onto the surfaces of the chondrules. Group A chondrules have thicker rims than group B chondrules. The main cause, we suspect, is very likely that they evaporated and recondensed a larger mass of material.

While group A chondrules are expected (and are observed) to be depleted in sulfides, there is no evidence in the bulk Se and Zn for such a trend in the present data (Fig. 19). This is almost certainly because the present group A chondrules contained appreciable amounts of sulfide-and metal-rich rim material. We might conclude from Fig. 19 that since group A and B chondrules contain similar amounts of Se and Zn, the redistribution of sulfides from the interior to the rims of group A chondrules may have occurred and it has not resulted in the net loss of these elements relative to group B values. We note however, that both group A and group B chondrules have Se and Zn concentrations well below CI values.

#### Condensation Theories

By "condensation theories" we mean those in which chondrules are thought to have formed directly by the crystallization of droplets from cooling nebular gases. Such theories successfully account for some important properties displayed by chondrites of all classes and some of the refractory inclusions abundant in carbonaceous chondrites (McSween 1977b). It is fairly difficult to distinguish between the products of condensation and the residues of evaporation because the thermodynamically predicted trajectories are the same, except for the discontinuities caused by the appearance of discrete phases present in the conden-

FIG. 18. (a) Reflected light microphotograph of a group B1 chondrule (without fine-grained rim) in Semarkona showing thin blades of sulfide which may have migrated along the grain boundaries between pyroxene crystals after the formation of the chondrule. The presence of sulfides inside this chondrule cannot be attributed to their presence oin the chondrule precursors. Reflected light microphotographs of (b) metalsulfide-rich rims around group A chondrules in Semarkona and (c) a complex multilayered fine-grained rim around a group A chondrule in the murchison CM2 chondrite (Metzler et al. 1992). There is a striking similarity between the metal-sulfide distribution around group A chondrules in Semarkona and Murchison, except that Murchison chondrule rims have been aqueously altered. Apparently, rim formation on group A chondrules is common to both ordinary and carbonaceous chondrite formation environments and, in both cases, rim thickness may be determined by the host chondrule groups, as expected if the rim is produced by the recondensation of volatiles lost from the host chondrule during its formation.

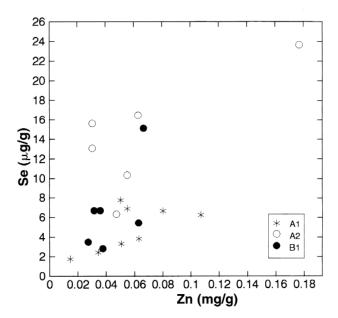


FIG. 19. Se vs Zn in Semarkona chondrules. Although grop A chondrules are depleted in volatile lithophiles with respect to group B chondrules, the two groups have similar concentrations of these two volatile chalcophile elements. Either group B chondrules also lost volatile chalcophiles (as discussed by Sears and Lipschuz 1994 and Sears et al. 1995a), or the present group A chondrule samples were analyzed with considerable amount of rim material. We suspect that both explanations are partially true.

sation calculations which are absent from the evaporation trajectories (Hashimoto 1983). However, the introduction of alkalis and other volatile components (such as FeS) into the solidified chondrules at lower temperatures is required by the condensation theories (Grossman 1988). This is certainly feasible, since very small degrees of metamorphism, or introduction of volatiles during aqueous alteration, cannot be ruled out entirely and they appear to have been important processes in the histories of certain CAIs. The major problem with the condensation origin of chondrules concerns the difficulty of making liquid condensates in an astrophysical setting, particularly given the modern ideas of solar nebular conditions (see review by Wood and Morfill 1988). In addition, the presence of relict grains in some chondrules argues against condensation theories, since they would have evaporated in a high-nebular temperature.

In order to incorporate the volatile components in chondrules it is necessary to greatly perturb the chondrule-forming process by involving shock-induced transient high-nebular pressures (Wood 1962), hydrogen-depleted nebular compositions (Herndon and Suess 1977), or non-equilibrium condensation processes (Blander and Katz 1967, Blander 1983). However, even these variants fail to explain

the high cooling rates of chondrules (Miyamato et al. 1986, Hewins 1988, Lofgren 1989), the presence of relic grains in some chondrules (Nagahara 1981, Rambaldi and Wasson 1982), and, most importantly, the chemical and isotopic diversities shown by the chondrules (Clayton et al. 1983, Gooding et al. 1983, Sears et al. 1992), since condensation processes should produce chemically and isotopically uniform chondrules. The relatively Ni-poor metal compositions in type 3 ordinary chondrites have also been used to argue against nebular condensation theories (Gooding 1979), which apparently predict the metal-rich chondrules should contain a higher abundance of Ni in their metal than metal-poor chondrules. This is not observed (Gooding 1979, Huang et al. 1993).

## Closed-System Theories

The fundamental tenet of the precursor theories is that either the heating was too brief or the peak temperatures involved were too low to cause the reduction and evaporative loss of volatiles during chondrule formation, and that all the compositional variations displayed by chondrules reflect heterogeneity in the precursors (Grossman and Wasson 1982, 1983b, Grossman 1988, Hewins 1991, Connolly *et al.* 1993, Eisenhour and Buseck 1993). This is an idea which is difficult to test experimentally because we know little or nothing about chondrule precursors.

It is worth stressing that this theory requires that the precursors are themselves the product of volatility-related processes, since the data lie close to the fractionation lines in Fig. 14. The chondrule precursors would also have to be produced by a process coupling reduction or oxidation and depletion in volatiles. Thus, the precursors must have been fractionated condensates. It seems unlikely to us that such condensates could have avoided being remixed, perhaps in most cases, in the environment of the early solar system. However, there must be exceptions to this generalization. One example is the CAIs, whose overabundance in CV chondrites causes this class to have high refractory element abundances. Another is the Bencubbin/Weatherford chondritic breccias, consisting solely of BO-textured chondrules (Weisberg et al. 1990).

It is possible to use factor analysis to describe the compositions of Semarkona chondrules in terms of specific "components," as suggested by Grossman and Wasson (1982). Using factor analysis, Grossman and Wasson (1982) identified five components: (1) chondritic metal and sulfide; (2) refractory metal; (3) coarse-grained, refractory, FeO-poor, olivine-rich silicates; (4) fine-grained, low-temperature, pyroxene-rich silicates; and (5) a volatile lithophile-rich component. Similarly, Hewins (1991) proposed two types of precursor components in group A chondrules (forsterite + Na-free refractory component, and forsterite + Pyroxene + albite). These authors suggest that chondrules sam-

pled various mixtures of these solid components, and that the mixtures melted or incompletely melted during chondrule formation to give rise to the mineralogical and chemical variations found in chondrules. These mass-balance calculations are a useful means of describing chondrule compositions, but without further evidence they do not prove or disprove the existence of these precursor components. It is a mathematical formulation to sort out and quantify components in an assemblage, and is thus a description. Since chondrules are constrained to be mixtures of discrete thermodynamically stable minerals, this methodology sorts out these phases. Many processes may produce fractionations, mostly based on elemental volatilities, generally all-or-nothing processes. These components could equally well have been produced by chondrule-forming processes involving only one fairly similar type of precursor component, the chondritic component (cosmic abundances).

The presence of sulfides within the least altered chondrules have suggested, to some authors, that volatile loss during chondrule formation was insignificant (Grossman and Wasson 1982, 1983b, Grossman 1988). However, most group A1 chondrules, and to a lesser extent group A3 chondrules, are essentially sulfide-free, while containing significant metal (3-4 wt%). In contrast, group B1 and B2 chondrules, which contain relatively little metal (<0.5 wt%), normally contain abundant sulfides in the chondrule interior. Thus, the observation that chondrules contain sulfides is an oversimplification, and the present data indicate that the chondrules which may have suffered the greatest compositional changes during formation (group A) contain little or no sulfides. The Semarkona B1 chondrule shown in Fig. 18a contains sulfides in the interstices between thin blades of pyroxene, showing that in this case the sulfide entered the chondrule after solidification. It is also possible that the presence of sulfides indicates very brief heating for group B chondrules (Zanda et al. 1995).

Another argument against the need for multiple chondrule precursors in most cases is the low Ni content of the metal in group A chondrules. If equilibrium thermodynamics and cosmic abundances are used as a guide, it is reasonable to expect that metallic precursors would be enriched in Ni (Sears 1980). Other than the formation of metal by the reduction of FeO, it is difficult to envisage a process whereby metal may be Ni-poor. We also suggest that the volatile siderophile and chalcophile abundance patterns in chondrules, as reported by Sears and Lipschutz (1994), cannot easily be explained by precursor mixing. Volatilitydriven redistribution of these elements during chondrule formation is a more reasonable process. Another problem with the precursor mixing theory is the difference in size between group A and group B chondrules and the complex trends in olivine and pyroxene abundances as a function of FeO content in the olivine. If group A chondrules formed from smaller precursor dust balls, (1) why should they be more reduced and volatile-poor, and (2) why should those with 2–4 wt% FeO be pyroxene-rich?

It seems to us that the coincidences required to explain all of the properties of group A chondrules by precursor mixing in a closed system as the major process make it difficult to accept. It seems reasonable that volatile-poor refractory material might exist in the precursor mixtures, but not why (1) elemental and isotopic compositions and olivine/pyroxene proportions should vary with size as they do, (2) compositional zoning in the mesostasis of group A chondrules should be present, or (3) thick rims should be preferentially associated with group A chondrules. Most of the arguments in favor of the closed-system theory are arguments by default, based on null hypotheses. We argue that the most reasonable approach is to more thoroughly explore the processes expected to be associated with chondrule formation rather than attribute the properties of chondrules to variable proportions of precursors.

The major uncertainty in our understanding of chondrule history is the cause of the pulse heating which was obviously a very important process in early solar system history. What the present studies have contributed to our understanding of the event, whatever it was, shows a considerable range in its intensity and the subsequent history of the chondrules.

Variation in the Intensity and Nature of the Heating Event

While the volatile-poor and highly reduced group A1 chondrules experienced higher temperatures during formation than the volatile-rich, more oxidized group B1 chondrules, the events which characterize the primary chondrule groups reflect not only the intensity of the primary heating event but also the cooling rates and crystallization histories following peak temperatures.

The crystallization histories of chondrules have been discussed by many authors (e.g., Sorby 1877, Fujii and Miyamoto 1983, Kimura and Yagi 1980, Blander et al. 1976, Planner and Keil 1982, Snellenburg 1978, Jones and Scott 1989, Jones 1990), usually with reference to the Fe-Mg-Si and Si-Mg-Al phase diagrams of Muan and Osborn (1956). The equilibrium crystallization sequence in which olivine crystallizes first to produce a residual SiO2-rich glass, which then reacts to produce pyroxene, seems to have been followed by group A1, A2, and A5 chondrules. However, the largest chondrule class in primitive ordinary chondrites, group B1, crystallized with considerable departure from equilibrium so that very little pyroxene was formed and the mesostasis contains a considerable excess of SiO<sub>2</sub>. Sorby (1877) was the first to suggest that most chondrules were supercooled droplets and the conclusion has often been repeated, with increasingly sophisticated data and arguments (Blander et al. 1976, Kimura and Yagi 1980, DeHart 1989, Snellenburg 1978, Jones 1990). The diversity of primary chondrules thus reflects the crystallization histories as well as the bulk chondrule compositional properties, as determined by the intensity of the chondrule-forming event (i.e., mainly temperature and time). It is possible to draw a qualitative grid of the varied histories of chondrules (Table IX). Some chondrules have suffered considerable mass loss, and may have experienced recondensation of some or most of those volatiles (Lewis *et al.* 1993, Ikeda and Kimura 1985, Matsunami *et al.* 1993, Huang *et al.* 1993).

It is helpful to briefly consider chondrule textures in light of the variety of chondrule histories depicted in Table IX. Several authors have pointed out that the degree of supercooling affects chondrule textures (Lofgren 1974, Kimura and Yagi 1980, Kurat 1967), and therefore textural differences between group A and group B chondrules are to be expected. This is observed in that most group A chondrules are granular, whereas most B chondrules are fairly coarse-grained and porphyritic. Similarly, several authors have pointed out that the presence of nucleation centers is a major constraint on the textures of chondrules. Chondrules which experienced temperatures above the liquidus are expected to contain fewer nucleation centers than those which were heated up to, or just below, the liquidus. On this basis, one would expect finer-grained textures for group A chondrules than for group B chondrules, and this is observed in most cases. Given the variety of chondrule histories and bulk compositions, the range of textures is not surprising, even without considering potential stochastic factors such as unusual precursor compositions or external influences on the chondrule at its molten stage (such as impact with dust or other chondrules; Hewins 1989, Wasson et al. 1993). Nor is it especially surprising that the correlations between textures and compositions appeared to be so poor (Grossman and Wasson 1983b), although there is now more evidence of such correlations.

The group A5 chondrules in Semarkona have received little discussion in the literature, presumably because they constitute only about 5% of the chondrules in the primitive ordinary chondrites (Huang et al. 1994). Nevertheless, they demonstrate that a primary chondrule type has properties that resemble those of chondrules in equilibrated chondrites. This is not to imply that these chondrules experienced metamorphism prior to emplacement in the meteorite, an idea discussed by Dodd (1978) and Scott (1984), or that their presence reflects brecciation. The group A5 chondrules in Semarkona are just as heterogeneous as the other chondrule groups, and their olivines are lower in FeO and higher in CaO than the A5 chondrule olivines in equilibrated chondrites. Rather, their presence in Semarkona indicates that the chondrule-forming process was capable of producing chondrules with phase compositions reasonably similar to those of chondrules in equilibrated chondrites, as well as the better known A1, A2, and B1 groups.

Tables IX begs the major question of why some chondrules suffered greater compositional changes during their formation than others, and why some underwent supercooling and some did not. This is a topic which has been of considerable concern, but which, of necessity, remains speculative. Given that reduction and volatile loss are to be expected during chondrule formation, the real challenge is to explain the lack of such effects among the group B chondrules. Their textures indicate that they reached temperatures sufficiently high to lose Na and reduce Fe. Yu and Hewins (1994) have recently shown experimentally that even the briefest flash-heating event will cause the loss of volatiles during chondrule formation. Thus, several authors have argued that group B chondrules formed through ablation processes, and not elevated temperatures (Dodd 1974, Podolak et al. 1993, Liffman 1992), Such processes might also produce rims on chondrules, although it seems doubtful that they would explain the volatile-rich nature of group B chondrules or the volatile-rich outer zones of group A chondrule mesostases, which seem to require recondensation. Convinced that even group B chondrules have been close to the liquidus, Wood (1985) proposed that increasing the oxygen to cation ratio, by increasing the dust/gas ratio by factors of 1000, would make the environment sufficiently oxidizing by vaporizing the dust, so that Na would be refractory and Fe not be reduced, an idea which had been pursued by Wood and Hashimoto (1993), Hewins (1989), and Boss and Graham (1993). Most group B chondrules have clearly not experienced the complete or near-complete melting of group A chondrules because they often contain relict grains (Nagahara 1981, Rambaldi 1981). Dodd (1978) was convinced that the coarse textures of group B chondrules were inconsistent with complete melting, and therefore suggested that these chondrules were the reworked pieces of previously existing igneous rocks. However, recent laboratory crystallization experiments can reproduce the coarse-grained textures, if nucleation centers are present and supercooling occurs (Lofgren 1989, Hewins 1988, Kimura and Yagi 1980). The lack of spread in the oxygen isotope ratios of group B chondrules from type 3 ordinary chondrites may suggest multiple stages of reworking, consistent with the presence of relict grains absent in group A chondrules (Clayton et al. 1991).

The point we wish to stress is the diversity of chondrule bulk compositions and phase compositions and we suspect that this places important constraints on the environment and mechanism for chondrule formation. We think that dust in some form, either dispersed in space or on the regolith of an accreting asteroid-sized object, was subject to frequent pulses of heating which varied considerably in their intensity and frequency. Where events were few, but

very intense, vaporization and reduction occurred and the ambient gas became enriched in the volatiles which could then recondense on the chondrules or form rims. Where the events were more frequent, but less intense, and oxygen fugacity had been elevated by vaporizing dust, evaporation was thus restricted. Some cross-contamination occurred, so that fragments of group A chondrules found their way into the group B chondrules as relict grains. These processes probably represent different but nearby locations, in the same general region of the early solar system.

Since chondrules are nearly always a major fraction of all chondrite groups, it seems obvious that chondrule properties are critical in understanding the overall properties of these groups and their origin. It seems to us that variations in the intensity and frequency of the chondrule-forming processes may explain, in part, the chondrite groups: carbonaceous chondrites contain predominantly A1-like chondrules (FeO-poor olivine and similar CL properties as A1), enstatite chondrites contain predominantly A2like chondrules (predominantly FeO-poor pyroxene and a small amount of FeO-poor olivine), and ordinary chondrites contain A1, A2, A5, and predominantly group B1 chondrules. Not only the chondrule properties but also the sizes of the chondrules are reflected in this chondrule group distribution (Grossman 1988). However, this is only part of the story since variations in the nature and abundance of the other components, such as the carbonaceous and matrix material, the metal and sulfide, and the refractory inclusions, also play an important part. However, it would mean that one of the major differences between the enstatite, ordinary, and carbonaceous chondrites formation environments was the intensity and frequency of the heat sources and the associated volatile loss, reduction, and recondensation processes during chondrule formation.

## SUMMARY AND CONCLUSIONS

Chondrules in Semarkona and Krymka show great diversity in their properties, with a large fraction (35% by number) being groups A1, A3, and A2 (approximately equivalent to "type IA" and type IB" chondrules of previous workers), which have volatile element depletions (with abundances decreasing with volatility from Mg to K), contain highly reduced silicates (Fa < 4 mol%) and abundant Ni-poor metal (mean Ni <  $\sim$ 7%), often have metalsulfide-rich rims, and occasionally have compositionally zoned mesostases (Na and other volatiles being higher in the outer regions). Group A1 and A3 chondrules have grains which are predominantly olivine, with lesser amounts of pyroxene, while group A2 chondrules are frequently pyroxene-rich. The largest chondrule groups (~60% by number) are termed B1 and B2 (broadly equivalent to "type II," "clastic" or "lithic" chondrules of previous workers); they contain CI proportions of lithophile

elements, oxidized silicates, little metal, thinner, less frequent metal–sulfide-rich rims, and common relict grains, and no compositional zoning of the mesostasis has been observed. Group A chondrules are typically  $\sim 20-23\%$  (in diameter) smaller than group B chondrules, which consist almost entirely of olivine except some RP chondrules. Group A chondrules appear to have followed the equilibrium crystallization sequence, and have feldspar-normative mesostases, whereas group B1 chondrules underwent considerable supercooling and contain mesostases with appreciable SiO<sub>2</sub> in their norms. An additional fairly rare group (about 5% by number), not previously recognized as an important primary group, has the bulk properties of group B1 and B2 chondrules, but followed equilibrium crystallization processes and have Na-feldspar-normative mesostases.

It is argued that thermodynamic and laboratory data on the chemical and physical changes expected to occur during chondrule formation (heating, melting, evaporation, recondensation) can produce the trends observed in the properties of chondrules, and can, acting with varying intensities and degrees of completeness, explain the diversity of chondrule types observed, including size differences. Oxygen isotope data for all chondrule types are incomplete, but they also suggest open-system behavior for chondrules during their formation. Since smaller chondrules sometimes contain lighter oxygen, the ambient gas may have had compositions close to the terrestrial fractionation line. Silicon isotope data suggest that some chondrules may have experienced evaporative loss of Si during formation. We suggest that the diversity of chondrules need not necessarily be attributed to variations in the properties and abundances of precursors alone, although this can sometimes be an important factor, and that chondrule types can be derived from a fairly similar precursor of solar composition. Multiple precursor models are poorly constrained and difficult to test, and they appear to fail to explain most of the properties of chondrules. They often require unusual coincidences, which are more simply explained in a straightforward fashion by open-system processes accompanying chondrule formation.

Since chondrules are a major component of the chondrites, any insights into their formation holds promise of improving our understanding of the formation of the chondrite classes. The chondrule formation scenario proposed here suggests that the chondrite classes reflect the heat flashes of the chondrule-forming process. These heat flashes, lightning or any of the other many processes that might have occurred in the nebula or perhaps intense impacts on non-nebular small planetesimal surfaces, can be responsible for the group A1 chondrules that are common in the carbonaceous chondrites, while slightly less intense heat flashes are responsible for the common group A2 chondrules in the enstatite chondrites. The ordinary chon-

drite chondrules experienced both of the former types of heat flashes, but most of them experienced a much larger number of the less intense heat flash, so that there are more group B than group A chondrules.

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