

## Spinel-bearing, Al-rich chondrules in two chondrite finds from Roosevelt County, New Mexico: Indicators of nebular and parent body processes

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**Abstract**—Two rare, spinel-bearing, Al-rich chondrules have been identified in new chondrite finds from Roosevelt County, New Mexico—RC 071 (L4) and RC 072 (L5). These chondrules have unusual mineralogies, dominated by highly and asymmetrically zoned, Al-Cr-rich spinels. Two alternatives exist to explain the origin of this zoning—fractional crystallization or metamorphism. It appears that fractional crystallization formed the zoning of the trivalent cations (Al,Cr) and caused a localized depletion in chromites around the large Al-Cr-rich spinels. The origin of the zoning of the divalent cations (Fe,Mg,Zn) is less certain. Diffusive exchange and partitioning of Fe and Mg between olivine and spinel during parent body metamorphism can explain the asymmetric zoning of these elements. Unfortunately, appropriate studies of natural and experimental systems to evaluate the formation of zoning of the divalent cations by fractional crystallization have not yet been conducted. The bulk compositions of the chondrules suggest affinities with the Na-Al-Cr-rich chondrules, as would be expected from the abundance of Al-Cr-rich spinels. Melting of rare and unusual precursors produced the compositions of Na-Al-Cr-rich chondrules, possibly including a spinel-rich precursor enriched in Cr<sub>2</sub>O<sub>3</sub> and ZnO. The two chondrules we studied have larger modal abundances of Al-Cr-rich spinels than reported in other Na-Al-Cr-rich chondrules of similar composition, and Al-rich chondrules even more enriched in spinel are reported in the literature. These differences indicate that factors other than bulk composition control the mineralogy of the chondrules. The most important of these factors are the temperature to which the molten chondrule was heated and the cooling rate during crystallization. These two chondrules cooled rapidly from near the liquidus, as indicated by the zoning, occurrence and sizes of spinels, radiating chondrule textures and localized chromite depletions. The range of mineralogies in other Al-rich chondrules of similar composition reflect a range of peak temperatures and cooling rates. We see no reason to believe that this range is fundamentally different from the range of thermal histories experienced by “normal” Fe-Mg-rich chondrules.

### INTRODUCTION

CHONDRITES AND THEIR COMPONENTS CONTAIN a vast amount of information regarding the processes that occurred in the early solar system, and numerous studies have therefore been carried out to unravel their histories. Special attention has been paid in the past 10 years to deciphering the histories of the common Fe-Mg-rich chondrules. For example, studies of the least altered ordinary chondrites (*e.g.*, Gooding *et al.*, 1980; Grossman and Wasson, 1982; Jones and Scott, 1989) have attempted to define the compositions of the solid precursors from which these chondrules formed by melting. Furthermore, dynamic crystallization experiments (*e.g.*, Hewins, 1988; Lofgren, 1989) and study of chondrules in the most primitive chondrites (*e.g.*, Jones and Scott, 1989; Jones, 1990) were carried out to constrain the conditions under which chondrules formed. Finally, measurements of zoning and homogenization of chondrule silicates (*e.g.*, Miyamoto *et al.*, 1986; Scott and Jones, 1990; McCoy *et al.*, 1991) have contributed to understanding the conditions under which chondrites were modified.

Less attention, however, has been paid to a group of rare, yet ubiquitous Al-rich chondrules. Bischoff and Keil (1983, 1984) determined the bulk compositions of Al-rich chondrules, as well as conducted detailed studies of the mineralogy and textures of selected chondrules, in order to infer thermal histories and physical settings of their formation. While these studies focused primarily on the formation of Al-rich chondrules, other authors (Fudali and Noonan, 1975; Wlotzka, 1985, 1987) examined the histories of chondrules during thermal metamorphism. Experiments by Stolper and Paque (1986) on some CAI compositions, which are similar to compositions of Al-rich chondrules, allow

speculations on the thermal histories of Al-rich chondrules during crystallization and observations of resulting textures.

We have identified two spinel-bearing, Al-rich chondrules from two chondrites recently found in Roosevelt County, New Mexico. These chondrites are metamorphosed, and our studies have focused on deciphering the roles of crystallization and subsequent metamorphism in the history of these Al-rich chondrules.

### SAMPLES AND TECHNIQUES

Roosevelt County 071 and 072 were recovered by Ivan E. Wilson from Roosevelt County, New Mexico, USA, in T2S, R33E, Section 33 of Roosevelt County (approximate coordinates 34°05'N, 103°30'W). RC 071 was recovered on 8 July 1989 and RC 072 was found in October of 1989. The original masses were 5.28 grams for RC 071 and 9.79 grams for RC 072. Polished thin section UH-37 and the remaining mass of 4.82 grams of RC 071 and polished thin section UH-1 of RC 072 are in the collection of the Planetary Geoscience Division, University of Hawaii. The remaining mass of RC 072 (9.05 grams) is in the possession of the finder.

Wavelength dispersive analyses of randomly selected olivines and pyroxenes throughout the chondrites, and bulk analyses of Al-rich chondrules were performed on an ARL EMX-SM microprobe operated at an accelerating potential of 15 keV, a beam current of about 20 nA and counting times of 10 seconds. Bulk chondrule compositions were measured using a broad (40 μm) beam, and analyses were corrected using the methods of Lux *et al.* (1980), as modified by Jones and Scott (1989). Wavelength dispersive analyses and scanning electron microscopy of pyroxenes throughout RC 071 and of individual phases in the Al-rich chondrules were performed on a JEOL 733 superprobe operated at 15 keV, 20 nA sample current and counting times up to 40 seconds. Differential matrix effects were corrected using the method of Bence and Albee (1968). Natural and synthetic minerals of well-known compositions were used.

Noble gas concentrations in RC 071 were determined by L. Schultz



FIG. 1. Backscattered electron image of RC 071-A1. Spinel (S) occur in a partial ring offset from the edge of the chondrule. Olivines (O) occur at both the edge and interior of the chondrule. The remainder of the chondrule has a radiating texture defined by two types of feldspathic material and opaque phases. Irregular white veins are hydrated iron oxides caused by terrestrial weathering. The outer edges of the spinels are lighter due to zoning and enrichment in FeO and Cr<sub>2</sub>O<sub>3</sub>. Scale bar = 100  $\mu$ m.

(pers. comm., 1989). The concentrations and isotopic compositions of He, Ne and Ar were measured using standard mass spectrometry techniques.

#### ROOSEVELT COUNTY 071

RC 071 is classified as an L4 ordinary chondrite. The L classification is based on the mean Fa content of olivine (Fa<sub>24.7</sub>,  $\sigma$  = 0.8, N = 20) and mean Fs content of low-Ca pyroxenes (Fs<sub>19.9</sub>,  $\sigma$  = 0.4, N = 20). These values are within the ranges for equilibrated L group chondrites given by Gomes and Keil (1980). Classification as petrologic type 4 (Van Schmus and Wood, 1967) is based on the presence of clearly delineated chondrules and polysynthetically twinned low-Ca clinopyroxene. The Wo content of low-Ca pyroxene is 1.5 mole%, which is slightly above the range of Wo 0.4–1.2 given by Scott *et al.* (1986) for *most* type 3 and 4 chondrites. These authors also reported a few L4 chondrites with Wo up to 1.6 mole%.

TABLE 1. Noble gas data for Roosevelt County 071.

Isotope	Concentration
<sup>3</sup> He	7.75
<sup>4</sup> He	488
<sup>20</sup> Ne	2.07
<sup>21</sup> Ne	2.28
<sup>22</sup> Ne	2.44
<sup>36</sup> Ar	1.37
<sup>38</sup> Ar	0.38
<sup>40</sup> Ar	1477

Values are  $\times 10^{-8}$  cm<sup>3</sup>g<sup>-1</sup>, measured at standard temperature and pressure.

Source: L. Schultz, pers. comm., 1989.

RC 071 is pervasively weathered, with hydrated iron oxides occurring as veins, patches and pigments throughout. Large (~80  $\mu$ m) grains of Fe,Ni metal (both kamacite and taenite) and troilite are present, but have been altered significantly at their edges.

RC 071 has a patchy appearance in both thin section and hand sample, apparently resulting from heterogeneous shock effects. Some areas of the meteorite are only lightly shocked, with olivines showing undulatory extinction. Other areas are heavily shocked, with olivines exhibiting mosaicism and show shock darkening with shock-induced veins consisting of metallic Fe,Ni and troilite, and shock induced intergrowths of Fe,Ni metal and troilite. These features correspond to shock stage 4 of Stöffler *et al.* (1991). RC 071 is not brecciated, since individual mineral grains cross borders between regions exhibiting different shock effects and vaguely resembling clasts. Solar-wind implanted gases were not found (Table 1) and, thus, the meteorite is not a regolith breccia. RC 071 is a heterogeneously shocked meteorite cross-cut by shock veins.

#### ROOSEVELT COUNTY 072

RC 072 is classified as an L5 chondrite. The L classification is based on the mean Fa content of olivine (Fa<sub>24.4</sub>,  $\sigma$  = 0.8, N = 15) and Fs content of low-Ca pyroxene (Fs<sub>21.2</sub>,  $\sigma$  = 0.9, N = 15), both of which are within the ranges for equilibrated L chondrites given by Gomes and Keil (1980). Classification as petrologic type 5 (Van Schmus and Wood, 1967) is based on poorly delineated chondrule boundaries, the occurrence of only rare polysynthetically twinned low-Ca clinopyroxene, and the

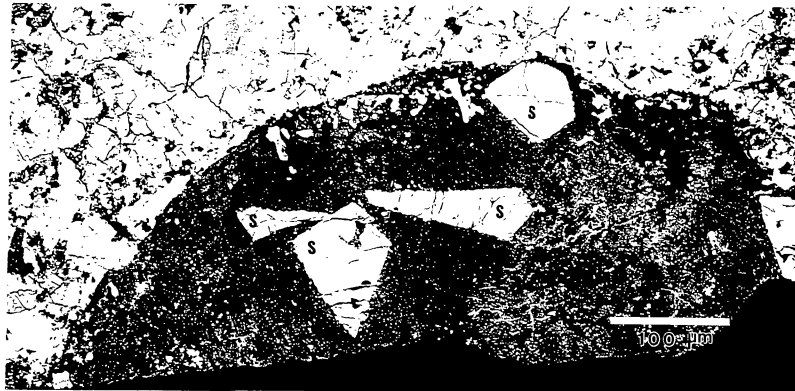


FIG. 2. Backscattered electron image of RC 072-A1. The chondrule is a semi-circular fragment. The location of the chondrule on the outer edge of the meteorite not covered by fusion crust suggests that part of the chondrule was lost during terrestrial weathering, not by fragmentation on the parent body or during atmospheric entry. Large picotitic spinels (S) dominate the chondrule. The areas adjacent to the picotitic spinels are darker due to a lack of chromite. Scale bar = 100  $\mu$ m.

TABLE 2. Mean compositions of phases, range of spinel compositions and bulk chondrule composition (in wt.%) for Al-rich chondrule in Roosevelt County 071.

	(1)	(2)	(3)	(4)	(5)	(6)
SiO <sub>2</sub>	—	—	37.8 <i>0.44</i>	46.3 <i>0.98</i>	65.4 <i>4.0</i>	37.8
Al <sub>2</sub> O <sub>3</sub>	48.6 <i>5.4</i>	39.7–55.3	0.08 <i>0.09</i>	33.8 <i>1.0</i>	22.9 <i>2.3</i>	20.5
Cr <sub>2</sub> O <sub>3</sub>	15.5 <i>5.5</i>	8.4–24.7	0.11 <i>0.07</i>	0.10 <i>0.16</i>	0.02 <i>0.02</i>	3.2
TiO <sub>2</sub>	—	—	0.28 <i>0.51</i>	0.06 <i>0.02</i>	0.03 <i>0.02</i>	0.85
MgO	13.0 <i>1.7</i>	9.9–15.0	38.3 <i>0.72</i>	0.32 <i>0.60</i>	0.19 <i>0.32</i>	14.1
MnO	—	—	0.42 <i>0.12</i>	0.01 <i>0.01</i>	—	0.23
FeO	22.3 <i>2.3</i>	19.3–26.3	23.1 <i>0.83</i>	0.77 <i>0.36</i>	0.83 <i>0.24</i>	10.6
CaO	—	—	0.03 <i>0.02</i>	17.2 <i>0.86</i>	3.9 <i>2.6</i>	3.2
Na <sub>2</sub> O	—	—	—	1.5 <i>0.18</i>	5.7 <i>0.38</i>	2.8
K <sub>2</sub> O	—	—	—	0.04 <i>0.01</i>	0.30 <i>0.13</i>	0.08
ZnO	0.74 <i>0.27</i>	0.35–1.1	—	—	—	0.19
FeS	—	—	—	—	—	0.33
Fe,Ni	—	—	—	—	—	6.7
Total	100.14	—	100.12	100.10	99.27	100.58
N	10	—	14	6	4	—

(1) Spinel, (2) Range of compositions in spinels, (3) Olivines, (4) Crystalline Feldspar, (5) Glassy Feldspathic Mesostasis, (6) Bulk Composition.

Italicized figures represent 1 $\sigma$  for N analyses.

— indicates elements which were not analyzed.

Wo content of low-Ca pyroxene of 1.5 mole%, which is within the range for type 5 chondrites given by Scott *et al.* (1986).

The meteorite is weathered. Silicates are stained a uniform brown, and hydrated iron oxides occur as veins throughout the rock. Metallic Fe,Ni and troilite show weathered grain boundaries, but moderately-sized, unweathered grains (up to 45  $\mu$ m) exist. Olivine throughout the thin section shows undulatory extinction, corresponding to shock stage 2 of Stöfler *et al.* (1991). RC 071 and 072 are not paired with each other, based on differences in petrologic type and shock features, and are not paired with previously described chondrites from Roosevelt County.

#### AL-RICH CHONDRULES

We found one spinel-bearing Al-rich chondrule in each polished thin section of RC 071 and RC 072 (Figs. 1, 2). Al-rich chondrules are arbitrarily defined as containing >10 wt.% bulk Al<sub>2</sub>O<sub>3</sub> (Bischoff and Keil, 1984), and both chondrules, here referred to as RC 071-Al and RC 072-Al, satisfy this criterion (Tables 2, 3).

#### Descriptions

##### RC 071-Al

RC 071-Al is circular in thin section (Fig. 1). It is dominated by large spinel phenocrysts and has a radiating texture defined by two types of feldspathic materials, olivines and opaque phases. Mean compositions of individual phases, as well as the bulk composition, are shown in Table 2.

The most striking feature of RC 071-Al is the high abundance of optically transparent, pink spinels. The spinels are picotitic

TABLE 3. Mean compositions of phases, range of spinel compositions and bulk chondrule composition (in wt.%) for Al-rich chondrule in Roosevelt County 072.

	(1)	(2)	(3)	(4)	(5)
SiO <sub>2</sub>	—	—	38.2 <i>0.41</i>	62.1 <i>0.71</i>	47.6
Al <sub>2</sub> O <sub>3</sub>	48.3 <i>5.7</i>	39.1–54.2	0.17 <i>0.17</i>	24.8 <i>0.44</i>	24.0
Cr <sub>2</sub> O <sub>3</sub>	16.7 <i>5.7</i>	10.5–25.4	0.14 <i>0.04</i>	0.06 <i>0.05</i>	2.9
TiO <sub>2</sub>	0.15 <i>0.09</i>	0.05–0.27	0.16 <i>0.02</i>	0.95 <i>0.40</i>	1.3
MgO	12.8 <i>1.7</i>	10.2–14.6	38.8 <i>1.0</i>	0.09 <i>0.02</i>	4.4
MnO	0.26 <i>0.08</i>	0.16–0.37	0.52 <i>0.02</i>	—	0.11
FeO	20.0 <i>1.6</i>	18.2–22.4	22.7 <i>0.16</i>	0.84 <i>0.52</i>	5.8
CaO	—	—	0.08 <i>0.03</i>	5.1 <i>0.45</i>	4.2
Na <sub>2</sub> O	—	—	—	5.6 <i>0.26</i>	5.9
K <sub>2</sub> O	—	—	—	0.24 <i>0.03</i>	0.16
ZnO	0.83 <i>0.07</i>	0.69–0.90	—	—	0.11
FeS	—	—	—	—	0.05
Fe,Ni	—	—	—	—	0.32
Total	99.04	—	100.77	99.78	96.85
N	10	—	3	4	—

(1) Spinel, (2) Range of compositions in spinels, (3) Olivines, (4) Crystalline Feldspar, (5) Bulk Composition.

Italicized figures represent 1 $\sigma$  for N analyses.

— indicates elements not analyzed.

(appreciable Cr, Al > Cr, 1 < Fe/Mg < 3) and comprise 21.1 vol.% of the chondrule, based on modal analysis of 1065 points. These spinels form a ring offset from, but close to, the edge of the chondrule (Fig. 1). They are euhedral to subhedral, with connected spinels having rounded faces towards the chondrule rim, range from 30–100  $\mu$ m in diameter, and are highly zoned towards the rim of the chondrule. Zoning profiles for the major elements Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, FeO and MgO are illustrated in Fig. 3a, while the zoning profile for ZnO is shown in Fig. 3b. The zoning profiles in these spinels are *extremely* asymmetric. Cr<sub>2</sub>O<sub>3</sub> and FeO are highest at the grain edge nearest the chondrule rim and decrease towards the chondrule interior, while Al<sub>2</sub>O<sub>3</sub> and MgO are lowest at the grain edge closest to the chondrule exterior and increase towards the chondrule center. Zoning profiles for MnO and TiO<sub>2</sub> mimic the behavior of FeO and Cr<sub>2</sub>O<sub>3</sub>. The compositional range in this single spinel is similar to the entire range of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, FeO and MgO in all picotitic spinels in RC 071-Al as determined by point analyses (Table 2). Thus, most of the compositional variability of these spinels is a result of zoning, rather than grain-to-grain heterogeneities. Concentrations of ZnO in these spinels is high, up to 1.1 wt.%.

Olivines up to 50  $\mu$ m in diameter occur both near the edge and in the interior of the chondrule. They are equilibrated (Fa<sub>25.0</sub>,  $\sigma$  = 1.0, N = 14) and essentially identical to olivines throughout RC 071 (Fa<sub>24.7</sub>). They are surprisingly high in some minor elements when compared to olivines in other equilibrated chondrites (McCoy *et al.*, 1991). The apparent high amounts of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> may be the result of beam overlap during microprobe analysis with minute ilmenite and chromite grains, which were



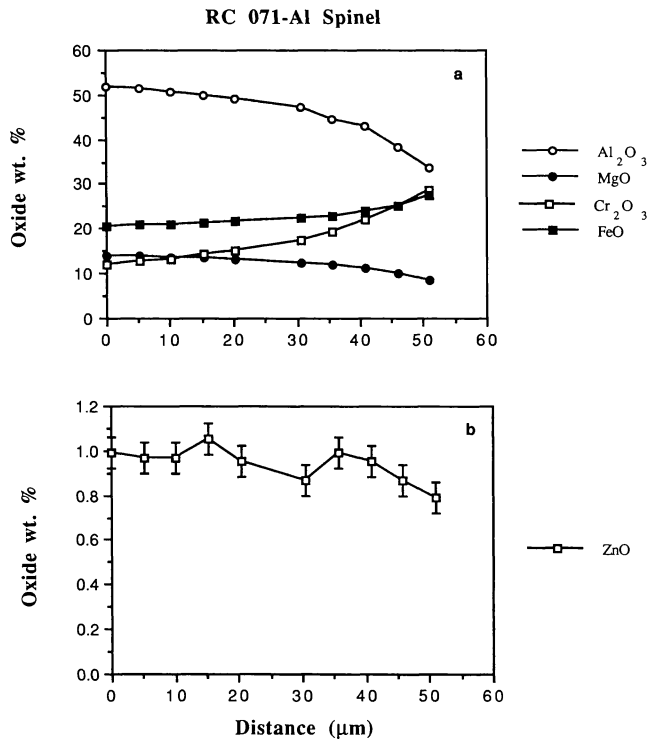


FIG. 3. Rim to rim zoning profiles across one of the most-highly zoned spinels in RC 071-Al. Extreme asymmetry exists in the zoning within the spinel grains. (a) Zoning profiles for Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO and MgO. FeO and Cr<sub>2</sub>O<sub>3</sub> are enriched at the grain edge towards the chondrule exterior, while Al<sub>2</sub>O<sub>3</sub> and MgO are depleted. (b) Zoning profile for ZnO mimics the trends of MgO and Al<sub>2</sub>O<sub>3</sub>. Error bars on ZnO data points illustrate analytical uncertainty.

observed as inclusions in back-scattered electron images. Other minor elements are probably elevated because of the crystallization of these olivines from a melt significantly enriched in these elements.

Two distinct types of feldspathic materials are present in this chondrule (Fig. 1). These are a crystalline feldspar (An<sub>86</sub>) and a glassy material of An<sub>27</sub> (Table 2, Fig. 4a). This glassy material is optically isotropic and back-scattered electron images show no distinct phases. These two types of material were probably formed by fractional crystallization, producing a Ca-rich crystalline feldspar and a Na-rich melt. The preservation of this glass in a petrologic type 4 chondrite is unusual. The glass, however, is relatively low in CaO, and McCoy *et al.* (1991) found that low-CaO glasses apparently resist devitrification, even in type 5 chondrites.

Opaque phases are too small for reliable quantitative analysis. Abundant Fe,Ni metal (up to 5 μm in diameter) was observed, and this is reflected in the bulk composition of 6.7 wt.% metallic Fe,Ni (Table 2). Minor amounts of troilite (0.33 wt.%) and ilmenite were identified. A second type of spinel was found and EDS analysis shows almost exclusively Fe and Cr, thus it appears to be a chromite, quite distinct in composition from the large picotitic spinels. The chromites are found throughout the chondrule, except in a zone extending out 30 μm for the picotitic spinels (Figs. 4a,b).

Bischoff and Keil (1984) arbitrarily subdivided Al-rich chondrules into four subtypes: Ca-Al-rich chondrules (Na<sub>2</sub>O ≤ 5.0 wt.%), (Ca,Na)-Al-rich chondrules (Na<sub>2</sub>O > 5.0 wt.%), Na-Al-rich chondrules (CaO ≤ 2.6 wt.%, Na<sub>2</sub>O > 4.1 wt.%) and Na-Al-Cr-rich chondrules (CaO < 4.8 wt.%, Cr<sub>2</sub>O<sub>3</sub> ≥ 2.4 wt.%, Na<sub>2</sub>O > 4.7 wt.%). The relatively high bulk Cr<sub>2</sub>O<sub>3</sub> concentration of RC 071-Al (3.2 wt.%) suggests grouping with the Na-Al-Cr-rich chondrules. In Figs. 5a-c, Cr<sub>2</sub>O<sub>3</sub> is plotted against Na<sub>2</sub>O, CaO, and SiO<sub>2</sub>, respectively. Bulk compositions of three groups of chondrules (data from Bischoff and Keil, 1984) are plotted with RC 071-Al. In plots of Cr<sub>2</sub>O<sub>3</sub> vs. CaO (Fig. 5b) and Cr<sub>2</sub>O<sub>3</sub> vs. SiO<sub>2</sub> (Fig. 5c), RC 071-Al plots in the field of Na-Al-Cr-rich chondrules. In a plot of Na<sub>2</sub>O vs. Cr<sub>2</sub>O<sub>3</sub> (Fig. 5a), RC 071-Al plots below other Na-Al-Cr-rich chondrules. RC 071-Al contains 2.8 wt.% Na<sub>2</sub>O (Table 2), well below the arbitrary lower

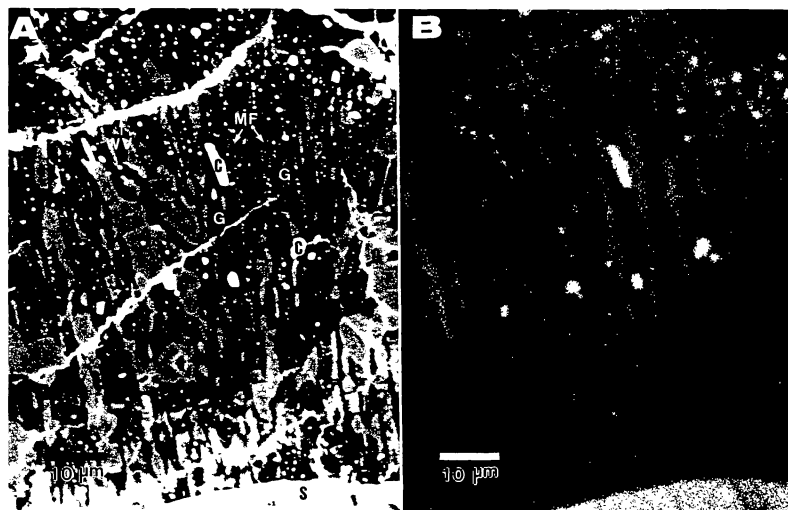


FIG. 4. The same area in RC 071-Al illustrated in both backscattered electrons (A) and Cr K $\alpha$  X-rays (B). In (A), picotitic spinels (S), olivines (O), microcrystalline feldspar (MF), glass (G), chromites (C) and weathering veins (WV) are present. Cr K $\alpha$  X-rays (B) show locations of picotitic spinels (bottom) and chromites. However, chromite is absent within 30 μm of the outer edge of the picotitic spinel. Scale bars = 10 μm.

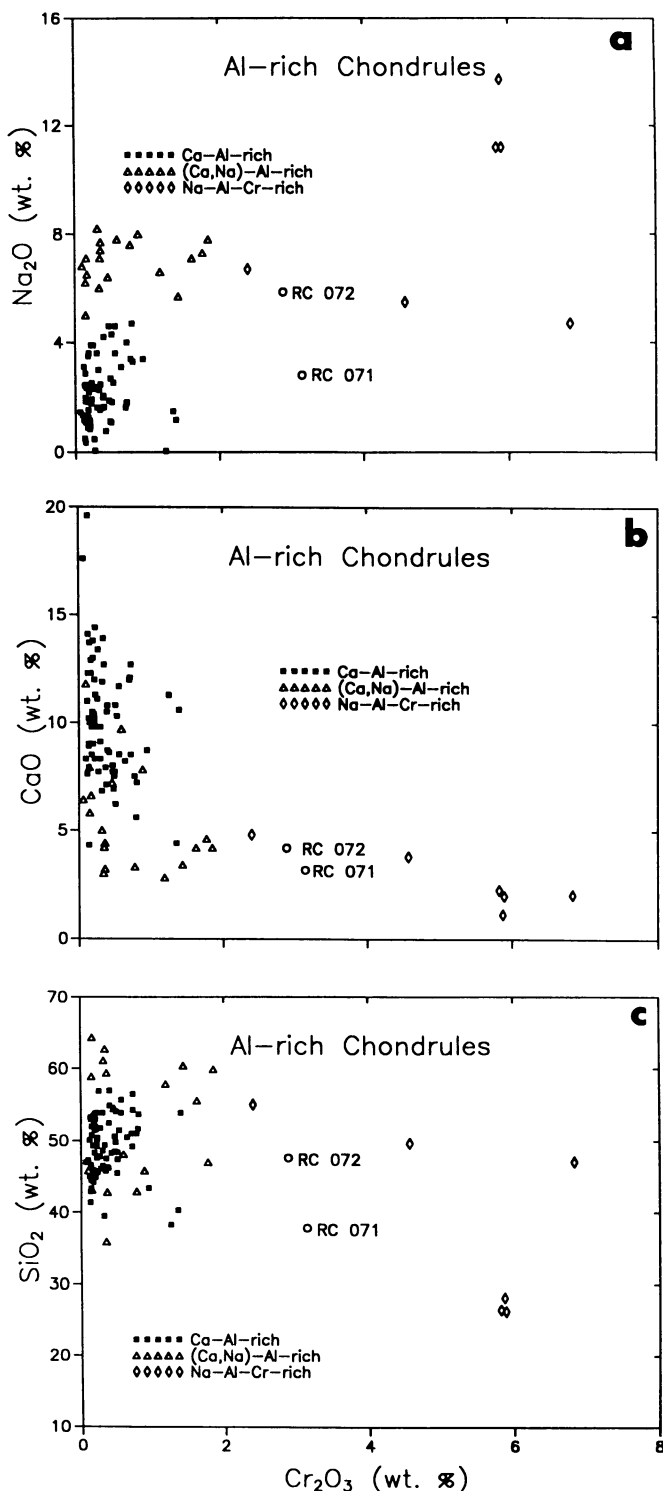


FIG. 5. Comparison of the bulk compositions of chondrules RC 071-Al and RC 072-Al with bulk compositions of Al-rich chondrules from other ordinary chondrites (Bischoff and Keil, 1983).

limit of 4.7 wt.%  $\text{Na}_2\text{O}$  for Na-Al-Cr-rich chondrules defined by Bischoff and Keil (1984). Bischoff (1984) reports other chondrules which are Cr-rich but Na-poor.

### RC 072-Al

RC 072-Al (Fig. 2) is a semi-circular fragment. The chondrule fragment is located on the outer surface of the meteorite and the broken edge of the chondrule is not covered by fusion crust. It is likely that the chondrule was fragmented and lost during terrestrial weathering, rather than on the meteorite parent body or during atmospheric entry. This chondrule is also dominated by picotitic spinels, which comprise 14.2 vol.%, based on modal analysis of 2053 points. The remainder of the chondrule has a microcrystalline texture and consists of feldspar, olivines and opaque phases. Mean compositions of individual phases are shown in Table 3.

The picotitic spinels range from 50–100  $\mu\text{m}$  in diameter and occur as euhedral crystals both on the edge of the chondrule, as well as in a cluster in the middle of the chondrule. The range in compositions of spinels in RC 072-Al and RC 071-Al are similar. As in RC 072-Al, picotitic spinels in RC 072-Al are zoned.  $\text{Cr}_2\text{O}_3$  zoning in one spinel of RC 072-Al ranges from 25.4 wt.% at the crystal edge closest to the chondrule rim, to 18.5 wt.% in the core of the crystal, and 10.5 wt.% at the crystal edge closest to the chondrule center.

Olivines ( $\text{Fa}_{24.7}$ ,  $\sigma = 0.6$ ,  $N = 3$ ) are commonly nucleated at the chondrule edge and are homogeneous and identical in composition to olivines throughout the chondrite ( $\text{Fa}_{24.4}$ ). As in RC 071-Al, minor element concentrations are elevated in the olivines of RC 072-Al and apparent  $\text{Al}_2\text{O}_3$  concentrations may be due to beam overlap with micron-sized chromites enclosed in the olivines.

A single type of feldspar is present in RC 072-Al. It is microcrystalline and has a composition of  $\text{An}_{33}$  (Table 3). No Fe,Ni metal was observed. Small crystals of troilite and ilmenite were observed and chromites are also present, but again are depleted in zones around the large picotitic spinels (Fig. 2).

The bulk composition of RC 072-Al plots in the compositional fields of Na-Al-Cr-rich chondrules defined by Bischoff and Keil (1984) (Figs. 5a–c).

### Discussion

The conventional view of chondrite genesis involves the production of chondrules by melting of pre-existing dust in the solar nebula by transient heating phenomena to form molten droplets, which solidified rapidly. The chondrules then aggregated with matrix and other components into parent bodies, where they were metamorphosed to form the various petrologic types. Chondritic meteorites contain information on all of these stages, and Al-rich chondrules expand our understanding of these processes and materials in the early history of the solar system.

### Spinel Crystallization and Chondrite Metamorphism

Before inferences can be made about the origin and crystallization of these Al-rich chondrules, we must unravel those properties attributable to metamorphism. The equilibration of chondrule olivines is certainly a metamorphic effect. Additionally, the similarity in olivine compositions within the chondrule and throughout the chondrite argue that the chondrules were not added to the chondrites in a later brecciation event. The lack of identifiable clasts also argues against these chondrites being breccias.

The zoning in the picotitic spinels of RC 071-Al and RC 072-Al is dramatic and its origin and preservation may have important implications for the metamorphic history of these chondrites. Bischoff and Keil (1984) observed similar zoning in a spinel from a Ca-Al-rich chondrule. These authors attributed the zoning to  $\text{Cr}_2\text{O}_3$ -depletion of the melt during crystallization and growth of the spinel from a  $\text{Cr}_2\text{O}_3$ -rich nucleus at the chondrule rim. The existence of similar zoning in RC 071-Al and RC 072-Al, which have experienced metamorphism, also raises the possibility that the zoning was formed or modified by diffusion during equilibration.

At least some of the features observed in these chondrules are readily explained by fractional crystallization and are inconsistent with an origin by metamorphic equilibration. Experiments with CAI compositions (Stolper and Paque, 1986) similar to those of Al-rich chondrules, demonstrated that spinels preferentially nucleate on the surface of the charge and grow into the interior of the chondrule. This type of growth, coupled with the depletion of  $\text{Cr}_2\text{O}_3$  from the melt (Bischoff and Keil, 1984), readily explains the asymmetric zoning of the spinels. Although the spinels in RC 071-Al are offset from the edge of the chondrule in the plane of the thin section, it is possible that they are attached in a third dimension. The depletion of the small chromites around the large, picotitic spinels also favors an origin by crystallization: the rapid crystallization of picotitic spinels depletes the surrounding melt in  $\text{Cr}_2\text{O}_3$ , so that chromites cannot crystallize, except in more distant portion of the melt which were not depleted in  $\text{Cr}_2\text{O}_3$ . We can envision no metamorphic process which would leave the area around the large spinels devoid of the smaller chromites.

The formation of the zoning within and, therefore, the composition of the picotitic spinels is less clear. It is important to remember that the spinel structure incorporates the trivalent cations (Al,Cr) in the B site, while the divalent cations (Fe,Mg,Zn) are incorporated in the A site. Fudali and Noonan (1975) made the following observations about diffusion in spinels: (1) Fe-Mg exchange in the A site of the spinel structure is slower in Mg-rich spinels than it is in the Mg-poor chromites and (2) for a single spinel grain, Fe-Mg exchange in the A site is faster than Al-Cr exchange in the B site, and the two exchanges are largely independent of one another. The assertion of independence of diffusion is only partially true. While the diffusion of Al-Cr is independent of Fe-Mg, the inverse is not entirely true. We know that the partitioning of Fe and Mg between olivine and spinel is dependent on temperature and Cr/Al ratio in the spinel (Irvine, 1965), and this is the basis of the olivine-spinel geothermometer. Subsequent investigators calibrated this thermometer (Jackson, 1969; Fabries, 1979; Engi, 1983) and it has been applied to meteoritic systems by Wlotzka (1985, 1987) and Johnson and Prinz (1991). Although considerable uncertainty exists in the calibration of this thermometer, it can be used to deduce relative temperatures. The result of this two site structure is that the zoning of different elements can result from different processes (*i.e.*, crystallization, equilibration).

The trivalent cations Al and Cr are highly and asymmetrically zoned in the picotitic spinels. A possible interpretation is that  $\text{Cr}_2\text{O}_3$  increases towards the edge of the chondrule as a result of diffusive exchange with the matrix material, leading to the highly asymmetric zoning. However, this interpretation is inconsistent with what we know about diffusion and observe in chondritic

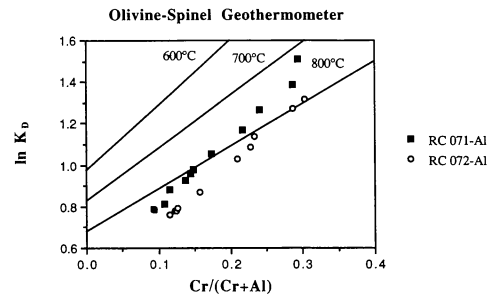


FIG. 6. Olivine spinel thermometry diagram using the empirical calibration curves of Fabries (1979).  $K_D$  equals the Fe/Mg ratio in spinel divided by the same ratio in olivine. Data for spinels in RC 071-Al and RC 072-Al plot at around 800 °C. Additionally, RC 072 (L5) spinels plot at slightly higher temperatures than RC 071 (L4) spinels, consistent with the petrologic type assignments.

systems modified by diffusion. At temperatures appropriate to chondritic metamorphism, grain boundary diffusion is significantly faster than volume diffusion. The result of these relative rates is that diffusional modification does not occur just at the edge of the grain closest to the chondrule exterior, but at all edges of the grain. In RC 071-Al, olivines both outside and inside the partial ring of spinels are equilibrated, demonstrating that the spinels did not act as a barrier to diffusion. Symmetric zoning is observed in chondritic minerals which have been altered by diffusional modification. Taenite grains in metamorphosed chondrites exhibit symmetric Ni zoning (Wood, 1967) and olivines and pyroxenes in type 3.1–4 chondrites show symmetric zoning for a host of elements (Miyamoto *et al.*, 1986; Scott and Jones, 1990; McCoy *et al.*, 1991). These considerations argue that  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  zoning was not established by exchange of these elements between the spinels and the matrix during metamorphism, but rather by fractional crystallization.

The origin of the zoning of the divalent cations (Fe,Mg,Zn) is more difficult to interpret. It is possible that metamorphism has modified the zoning and concentrations of these elements. According to the theoretical basis of the olivine-spinel geothermometer, spinels with increasing Cr/Al ratios should have higher Fe/Mg (and presumably Fe/Zn) ratios. This is exactly the behavior observed. In fact, application of this thermometer to olivine-spinel pairs in RC 071-Al and RC 072-Al yields temperatures of about 800 °C (Fig. 6), approximately those expected for type 4 and 5 chondrites. Additionally, temperatures obtained for RC 072-Al (L5) are slightly higher than for RC 071-Al (L4), as would be expected. It is well known that ZnO is often enriched in spinels of higher petrologic type, and numerous authors have argued that ZnO is redistributed during metamorphism (Grossman and Wasson, 1985; Johnson and Prinz, 1991). The lack of equilibration in the spinel, as shown by zoning in  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ , places doubts on whether these calculations yield meaningful temperature estimates. Johnson and Prinz (1991) expressed similar doubts about temperature estimates for unequilibrated type 3.0 to 4 chondrites.

The alternative mechanism for the formation of the zoning of the divalent cations, fractional crystallization, appears impossible to assess. The spinels studied here are composed primarily of four end members—spinel *sensu stricto* ( $\text{MgAl}_2\text{O}_4$ ), hercynite ( $\text{FeAl}_2\text{O}_4$ ), magnesiochromite ( $\text{MgCr}_2\text{O}_4$ ) and chromite ( $\text{FeCr}_2\text{O}_4$ ). Unfortunately, much of the literature data on



spinel zoning in experimental and natural systems is inappropriate to evaluate the zoning in these chondrule spinels. Experimental work aimed at understanding terrestrial systems involves trivalent iron in the end member magnetite ( $\text{Fe}_3\text{O}_4$ ). Unfortunately, most well-documented lunar spinels often incorporate significant amounts of titanium as an ulvospinel ( $\text{Fe}_2\text{TiO}_4$ ) component. Fe is enriched as Ti is enriched, because of the coupled charge substitution of ( $\text{Fe}^{2+}, \text{Ti}^{4+}$ ) for ( $\text{Al}^{3+}, \text{Cr}^{3+}$ ). This trend is observed even in the very low-Ti basalts (Vaniman and Papike, 1977). Spinels of appropriate composition occur in lunar highland rocks but are homogeneous, due to the slow cooling they experienced during crystallization (Papike *et al.*, 1991). The experiments of Stolper and Paque (1986) on CAI compositions, although useful for textural information, shed no light on the chemical zoning of spinels, since they produced nearly pure  $\text{MgAl}_2\text{O}_4$ .

In summary, it appears that the zoning of the trivalent cations (Al, Cr) was established during crystallization of the spinels and has not been modified significantly during subsequent metamorphism. The zoning of the divalent cations (Fe, Mg, Zn) may well have been altered by metamorphic equilibration. The zoning observed is generally consistent with metamorphic equilibration, but both the exact temperatures given by the olivine-spinel geothermometer and the use of this thermometer on spinels that retain zoning of the trivalent cations formed by crystallization remains in doubt. We are unable to evaluate origin of the zoning of the divalent cations in the context of fractional crystallization. This conclusion implies remarkably slow diffusion rates for the trivalent cations relative to the divalent cations. This is qualitatively consistent with our knowledge of diffusion in spinels (*e.g.*, Fudali and Noonan, 1975). Quantitative assessment of these diffusion rates has not been conducted to the best of our knowledge.

#### Chondrule Formation

The formation of chondrules by melting of solid precursor materials has been favored for both Fe-Mg chondrules (Gooding *et al.*, 1980; Taylor *et al.*, 1983; Grossman, 1988) and Al-rich chondrules (Bischoff and Keil, 1984). Bischoff and Keil (1984) proposed a MgO-FeO-SiO<sub>2</sub>-rich component, a highly-refractory component rich in CaO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and MgO, and a volatile-rich component high in Na<sub>2</sub>O, K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> as the precursor components. The source of Cr<sub>2</sub>O<sub>3</sub>, a major component in some Al-rich chondrules, was not considered in the compositions of these precursors. Plots of Na<sub>2</sub>O versus Cr<sub>2</sub>O<sub>3</sub> (Fig. 5a) and SiO<sub>2</sub> versus Cr<sub>2</sub>O<sub>3</sub> (Fig. 5c) show no strong correlations, suggesting that neither the volatile component or the MgO-FeO-SiO<sub>2</sub>-component appear to have contained the Cr<sub>2</sub>O<sub>3</sub>. CaO (refractory component) versus Cr<sub>2</sub>O<sub>3</sub> show an inverse correlation (Fig. 5b), suggesting that Cr<sub>2</sub>O<sub>3</sub> was likewise not contained in the refractory component. One possibility is a spinel-rich precursor. This would explain the abundance of spinels in these Al-rich chondrules. Likewise, if the Zn is inherited from the precursor and not a result of metamorphic redistribution, the spinel-rich precursor may be the source of ZnO.

Alternative models exist to explain the formation of Al-rich chondrules. Bischoff *et al.* (1989) measured rare-earth elements in Al-rich chondrules. Based on similarities between bulk rare earth elements in Al-rich chondrules and REE's in mesostases from Fe-Mg-rich chondrules, these authors concluded that dur-

ing chondrule collisions, "common" Fe-Mg-rich chondrules lost their mesostasis by ejection. This lost mesostasis then crystallized to form Al-rich chondrules. The large sizes of RC 071-Al and RC 072-Al would require almost complete loss of mesostasis from a very large Fe-Mg-rich chondrule. Such a model fails to explain several features. First, Jones (1990) show that type II chondrules, which are one of the most abundant types of large Fe-Mg-rich chondrules, formed by closed system fractional crystallization and have not lost mesostasis. Secondly, the bulk compositions of these chondrules are quite different from compositions of Fe-Mg-rich chondrule mesostasis, most notably containing much larger abundances of Cr<sub>2</sub>O<sub>3</sub>. Finally, the mineralogy reported in these Al-rich chondrules (*i.e.*, large picotitic spinels) are not generally observed in Fe-Mg-rich chondrule mesostasis.

#### Crystallization Thermal History

The shapes and textures of the chondrules provide important constraints on the physical setting and thermal histories during chondrule formation and crystallization. Taylor *et al.* (1983) summarized the evidence for formation of chondrules in the solar nebula. The spherical shapes of RC 071-Al and RC 072-Al indicate formation as freely floating, independent objects. Two lines of evidence suggest that these molten droplets crystallized from at or above the liquidus. Experiments with Fe-Mg chondrule compositions produce radiating textures when cooling from at or above the liquidus (Hewins, 1988). This type of radiating texture is present in RC 071-Al. Experiments by Stolper and Paque (1986) showed that spinels preferentially nucleate on the surface of the charge when cooled from above the liquidus. Spinels are found at or near the edge of the chondrule in both RC 071-Al and RC 072-Al. In RC 072-Al, equant spinels are found in the chondrule interior. Cooling from above the liquidus produced ragged spinels in the chondrule interior, while cooling from slightly below the liquidus produced equant spinels in the chondrule interior. Thus, RC 072-Al may have cooled from slightly below the liquidus, or the spinels may have detached from the edge of the chondrule. Further, cooling from above the liquidus should yield euhedral spinels (Stolper and Paque, 1986), as is the case with the chondrules studied here. The liquidus temperature of Stolper and Paque's (1986) experiments is 1550 °C, in the range of liquidus temperatures reported by Hewins (1983) (1440–1580 °C) for Fe-Mg-rich chondrules. Thus, peak temperatures for Al-rich chondrules were similar to those for Fe-Mg-rich chondrules.

Rapid cooling rates for these chondrules can be inferred from a variety of properties. The first of these is the marked zoning shown by Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> in the picotitic spinels. As argued above, these zoning profiles were not significantly modified by metamorphism. Formation during crystallization argues for rapid cooling rates of these chondrules. Coarse spinels were produced by Stolper and Paque (1986), ranging from ~10–100 μm in size at a cooling rate of 1000 °C/hr, to as large as 2 mm at 2 °C/hr. Since the spinels observed in the Al-rich chondrules are in the 100 μm range, cooling rates of at least 1000 °C/hr or more are indicated. Finally, the lack of chromites in zones around the picotitic spinels indicates rapid cooling rates and severe disequilibrium within the chondrule melt. The crystallizing picotitic spinels may have incorporated all the Cr<sub>2</sub>O<sub>3</sub> within 30 μm,

but rapid cooling rates prevented the incorporation of all Cr<sub>2</sub>O<sub>3</sub> from throughout the chondrule melt.

### Chondrule Classification

The Al-rich chondrules studied here have compositional affinities to the Na-Al-Cr-rich chondrules, whose compositional limits were arbitrarily chosen by Bischoff and Keil (1984), based on only six individual chondrules. RC 071-Al and RC 072-Al expand this group beyond the boundaries given by these authors. Chondrules rich in Al and Cr are not necessarily rich in Na, and it may be appropriate to rename the group "Al-Cr-rich" chondrules. Despite this small difference, the chondrules we have studied do not have compositions drastically different from other Al-Cr-rich chondrules. The high volume percent of spinels observed in RC 071-Al and RC 072-Al, however, were not reported for any of the six Al-Cr-rich chondrules studied by Bischoff and Keil (1983, 1984). To be sure, other authors have reported chondrules which were almost entirely composed of spinels (Tieschitz—Wlotzka, 1983; Burdett—Bischoff and Keil, 1984), but the bulk compositions of these chondrules were not reported. In short, crystallization of chondrules with nearly identical bulk compositions result in vastly different modal mineralogies, particularly the abundance of spinel. Thus, the modal mineralogy is dependent not only on the bulk composition of the chondrules, but on other factors, such as peak temperature and, to a lesser extent, cooling rate, all of which affect the crystallization of spinel. Therefore, a range of peak temperatures and cooling rates must be responsible for the formation of the Al-Cr-rich chondrules, and we see no reason to believe that this range is significantly different from that experienced by the "common" Fe-Mg-rich chondrules.

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### REFERENCES

- BENCE A. E. AND ALBEE A. L. (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.* **76**, 382–403.
- BISCHOFF A. (1984) Refraktäre und intermediäre Chondren und Einschlüsse in Chondriten. Ph.D. dissertation, Universität Münster. 147 pp.
- BISCHOFF A. AND KEIL K. (1983) Catalog of Al-rich chondrules, inclusions and fragments in ordinary chondrites. *Special Publication Number 22*, UNM Institute of Meteoritics, 33 pp.
- BISCHOFF A. AND KEIL K. (1984) Al-rich objects in ordinary chondrites: Related origin of carbonaceous and ordinary chondrites and their constituents. *Geochim. Cosmochim. Acta* **48**, 693–709.
- BISCHOFF A., PALME H. AND SPETTEL B. (1989) Al-rich chondrules from the Ybbsitz H4-chondrite: Evidence for formation by collision and splashing. *Earth Planet. Sci. Lett.* **93**, 170–180.
- ENGI M. (1983) Equilibria involving Al-Cr spinel: Mg-Fe exchange with olivine. Experiments, thermodynamic analysis, and consequences for geothermometry. *Amer. J. Sci.* **283-A**, 29–71.
- FABRIES J. (1979) Spinel-olivine geothermometry in peridotites from ultramafic complexes. *Contrib. Mineral. Petrol.* **68**, 325.
- FUDALI R. F. AND NOONAN A. F. (1975) Gobabeb, a new chondrite: The coexistence of equilibrated silicates and unequilibrated spinels. *Meteoritics* **10**, 31–40.
- GOMES C. B. AND KEIL K. (1980) *Brazilian Stone Meteorites*. Univ. of New Mexico Press. 161 pp.
- GOODING J. L., KEIL K., FUKUOKA T. AND SCHMITT R. A. (1980) Elemental abundances in chondrules from unequilibrated chondrites: Evidence for chondrule origin by melting of pre-existing materials. *Earth Planet. Sci. Lett.* **50**, 171–180.
- GROSSMAN J. N. (1988) Formation of chondrules. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 680–696. Univ. of Arizona Press.
- GROSSMAN J. N. AND WASSON J. T. (1982) Evidence for primitive nebular components in chondrules from the Chainpur chondrite. *Geochim. Cosmochim. Acta* **46**, 1081–1099.
- GROSSMAN J. N. AND WASSON J. T. (1985) The origin and history of the metal and sulfide components of chondrites. *Geochim. Cosmochim. Acta* **49**, 925–939.
- HEWINS R. H. (1983) Dynamic crystallization experiments as constraints on chondrule genesis. In *Chondrules and Their Origins* (ed. E. A. King), pp. 122–133. Lunar and Planetary Institute.
- HEWINS R. H. (1988) Experimental studies of chondrules. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 660–679. Univ. of Arizona Press.
- IRVINE T. N. (1965) Chromian spinel as a petrogenetic indicator, part 1. Theory. *Canadian J. Earth Sci.* **2**, 648–672.
- JACKSON E. D. (1969) Chemical variation in coexisting chromite and olivine in chromite zones of the Stillwater Complex. *Econ. Geol.* **4**, 41–71.
- JOHNSON C. A. AND PRINZ M. (1991) Chromite and olivine in type II chondrules in carbonaceous and ordinary chondrites: Implications for thermal histories and group differences. *Geochim. Cosmochim. Acta* **55**, 893–904.
- JONES R. H. (1990) Petrology and mineralogy of type II, FeO-rich chondrules in Semarkona (LL3.0): Origin by closed-system fractional crystallization, with evidence for supercooling. *Geochim. Cosmochim. Acta* **54**, 1785–1802.
- JONES R. H. AND SCOTT E. R. D. (1989) Petrology and thermal history of type IA chondrules in the Semarkona (LL3.0) chondrite. *Proc. Lunar Planet. Sci. Conf.* **19th**, 523–536.
- LOFGREN G. E. (1989) Dynamic crystallization of chondrule melts of porphyritic olivine compositions: Textures experimental and natural. *Geochim. Cosmochim. Acta* **53**, 461–470.
- LUX G., KEIL K. AND TAYLOR G. J. (1980) Metamorphism of the H-group chondrites: Implications from compositional and textural trends in chondrules. *Geochim. Cosmochim. Acta* **44**, 841–855.
- MCCOY T. J., SCOTT E. R. D., JONES R. H., KEIL K. AND TAYLOR G. J. (1991) Composition of chondrule silicates in LL3-5 chondrites and implications for their nebular history and parent body metamorphism. *Geochim. Cosmochim. Acta* **55**, 601–620.
- MIYAMOTO M., MCKAY D. S., MCKAY G. A. AND DUKE M. B. (1986) Chemical zoning and homogenization of olivines in ordinary chondrites and implications for thermal histories of chondrites. *J. Geophys. Res.* **91**, 12804–12816.
- PAPIKE J., TAYLOR L. AND SIMON S. (1991) Lunar minerals. In *Lunar Sourcebook* (eds. G. H. Heiken, D. T. Vaniman and B. M. French), pp. 121–181. Cambridge Univ. Press.
- SCOTT E. R. D. AND JONES R. H. (1990) Disentangling nebular and asteroidal features of CO3 carbonaceous chondrite meteorites. *Geochim. Cosmochim. Acta* **54**, 2485–2502.
- SCOTT E. R. D., TAYLOR G. J. AND KEIL K. (1986) Accretion, metamorphism, and brecciation of ordinary chondrites: Evidence from petrologic studies of meteorites from Roosevelt County, New Mexico. *Proc. Lunar Planet. Sci. Conf.* **17th**, E115–E123.
- STÖFFLER D., KEIL K. AND SCOTT E. R. D. (1991) Shock metamorphism of ordinary chondrites. *Geochim. Cosmochim. Acta*, submitted.
- STOLPER E. AND PAQUE J. M. (1986) Crystallization sequences of Ca-Al-rich inclusions from Allende: The effects of cooling rate and maximum temperature. *Geochim. Cosmochim. Acta* **50**, 1785–1806.
- TAYLOR G. J., SCOTT E. R. D. AND KEIL K. (1983) Cosmic setting for



- chondrule formation. In *Chondrules and Their Origins*. (ed. E. A. King), pp. 262–278. Lunar and Planetary Institute.
- VAN SCHMUS W. R. AND WOOD J. A. (1967) A chemical-petrologic classification for the chondritic meteorites. *Geochim. Cosmochim. Acta* **31**, 747–765.
- VANIMAN D. T. AND PAPIKE J. J. (1977) Very low Ti (VLT) basalts: A new mare rock type from the Apollo 17 drill core. *Proc. Lunar Sci. Conf.* **8th**, 1443–1471.
- WLOTZKA F. (1983) Composition of chondrules, fragments and matrix in the unequilibrated ordinary chondrites Tieschitz and Sharps. In *Chondrules and Their Origins* (ed. E. A. King), pp. 296–318. Lunar and Planetary Institute.
- WLOTZKA F. (1985) Olivine-spinel and olivine-ilmenite thermometry in chondrite of different petrologic type (abstract). *Lunar Planet. Sci.* **16**, 918–919.
- WLOTZKA F. (1987) Equilibration temperatures and cooling rates of chondrites: A new approach (abstract). *Meteoritics* **22**, 529–531.
- WOOD J. A. (1967) Chondrites: Their metallic minerals, thermal histories, and parent planets. *Icarus* **6**, 1–49.