American Mineralogist, Volume 69, pages 880–888, 1984

Manganiferous orthopyroxene and olivine in the Allende meteorite

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Abstract

Numerous orthopyroxene grains averaging (in wt.%) 4.2% MnO, 32.3% MgO and 1.4% FeO and several olivine grains averaging 1.2% MnO, 49.5% MgO and 9.2% FeO occur within a thick relatively coarse-grained rim around an unusually large porphyritic chondrule in the Allende CV3 carbonaceous chondrite. Orthopyroxenes and olivines with such high Mn and low Fe have not previously been reported from meteorites and are rare on Earth, primarily occurring in metamorphosed evaporites and calc-silicate deposits. Relative to opaque matrix, the rim is mildly depleted in refractories, enriched in Cr and Na and greatly enriched in Mn.

The bulk enrichments in Cr, Na and Mn in the rim approximately mirror the depletions of these elements in CV chondrules. It thus is possible that the rim acquired, by condensation, volatilized Cr, Na and Mn which were lost from chondrule precursors during heating. The manganiferous orthopyroxene and olivine grew in the Mn-rich rim at elevated temperatures, probably ≥1000°C. The apparent absence of other grains of MnO-rich pyroxene and olivine within the opaque silicate matrix and other relatively coarse-grained rims in Allende and other CV3 chondrites attests to the unique history of this particular chondrule rim.

Introduction

Most terrestrial manganiferous pyroxenes and olivines occur in iron-rich rocks and are themselves rich in iron (e.g., Dodd, 1963; Davidson and Mathison, 1973; Deer et al., 1966, 1978). Manganiferous pyroxenes with low FeO are quite rare, primarily occurring in metamorphosed evaporite deposits (Brown et al., 1980; Gordon et al, 1981) and Mn-bearing calc-silicate deposits (e.g., Kobayashi, 1977; Peters et al., 1977). I have found grains of low-FeO, manganiferous orthopyroxene and olivine within a relatively coarse-grained rim around a large chondrule in the Allende meteorite. (The rim is coarse-grained relative to opaque matrix.) Meteoritic olivines and pyroxenes with these compositions have not previously been reported. Allende, a CV3 carbonaceous chondrite, has been described in great detail (e.g., Clarke et al., 1970; Simon and Haggerty, 1979, 1980; Bunch and Chang, 1979; Bunch et al., 1980), but attention has focused primarily on its Ca,Al,Ti-rich refractory inclusions (e.g., Allen et al., 1978; Grossman, 1980; Mason and Taylor, 1982; Kornacki and Wood, 1984; and numerous references cited in these papers). The major components of Allende are chondrules, refractory and mafic inclusions and Fe-rich opaque silicate matrix material. The opaque matrix consists primarily of small grains of FeO-rich olivine (Fa_{50}), pentlandite, metallic Fe,Ni, Ca-rich pyroxene, nepheline and sodalite (Clarke et al., 1970; Housley and Cirlin, 1983).

Grossman (1975), Wark and Lovering (1977) and MacPherson et al. (1981) described layered rims on different kinds of refractory inclusions in Allende, but rims around the mafic chondrules have not been described in detail. Chondrules in Allende and other CV3 chondrites have two major types of rims: opaque matrix or relatively coarse-grained material (A. E. Rubin, unpublished data). Some chondrule rims are transitional, however, and many chondrules lack rims altogether. The relatively coarse-grained material generally appears to be opaque matrix material that has been metamorphosed or partly melted (either before or after accreting around the chondrules).

Analytical procedures

The following polished thin sections were examined microscopically, in transmitted and reflected light: Allende, CV3 (USNM 4744-1 and 4744-2, LC 130 and 131); Leoville, CV3 (USNM 3535-3); Vigarano, CV3 (USNM 477-1); Kaba, CV3 (USNM 1052-1); Isna, CO3 (LC 953); Lancé, CO3 (LC 959); Colony, CO3 (USNM 6264-1 and 6264-3); Semarkona, LL3 (USNM 1805-1 and 1805-4); and Bishunpur, LL3 (LC 304 and 305). Sections labelled USNM are from the Smithsonian Institution; those labelled LC are from the Leonard Collection, UCLA. Minerals were analyzed with the automated ARL electron microprobe at UCLA, using crystal spectrometers and following standard correction procedures (Bence and Albee, 1968). Natural and synthetic standards having compositions similar to the unknowns were used. Minor oxides had the following detection limits (in wt.%):

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Fig. 1a. Unusually large compound chondrule (chondrule 1) in Allende. The chondrule is multi-layered, consisting of (from the center outward) a barred olivine chondrule, a porphyritic olivine-pyroxene chondrule, an exceptionally manganiferous relatively coarse-grained rim and a thin rim of opaque silicate matrix. Thin rings of troilite and pentlandite occur immediately outside the barred olivine chondrule, the porphyritic olivine-pyroxene chondrule and the relatively coarse-grained rim. The entire assemblage is about 5 mm in apparent diameter. Transmitted light.

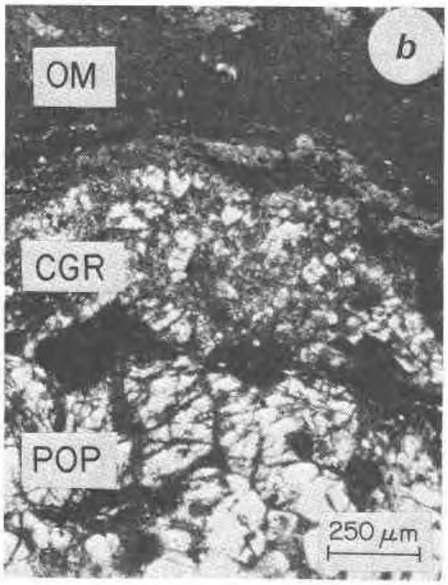

Fig. 1b. Portion of chondrule 1 showing the relatively coarse-grained rim (CGR) with small manganiferous orthopyroxene grains and the porphyritic olivine–pyroxene shell (POP) with larger grains of low-Mn clinoenstatite (near edge of shell) and olivine. The opaque silicate matrix (OM) of Allende surrounds the assemblage. Dark grains are sulfide. Transmitted light.

CaO (0.03), Al_2O_3 and K_2O (0.04), and Cr_2O_3 and MnO (0.07). The bulk compositions of opaque matrix and relatively coarse-grained material were determined with an 80–150 μm diameter electron probe beam. Bence-Albee corrections were applied to all elements except Ni, S and P. Step-scan traverses, using a bar-shaped electron beam (10 × 100 μm in size) and a 10 μm interval, were made across the relatively coarse-grained rim to determine the variation in MnO concentration.

Results

Petrography

Chondrule 1, which is present in the serial Allende thin sections USNM 4744-1 and 4744-2, is an unusually large compound porphyritic chondrule, consisting of an internal barred olivine (BO) chondrule surrounded by a porphyritic olivine–pyroxene (POP) chondrule (Fig. 1). The BO chondrule is ~2400 μm in apparent diameter, including a 200 μm-thick olivine rim. Instead of a glassy mesostasis, the areas between the olivine bars consist of elongated olivine crystallites (20 × 100 μm) and small grains of plagioclase. Thin, partial rings of troilite and pentlandite blebs occur on the inside and outside edges of the olivine rim. The POP chondrule forms a shell ~4400 μm in apparent diameter around the BO chondrule. Olivine phenocrysts within the POP chondrule are adjacent to the internal BO chondrule; grains of polysynthetically twinned clinoenstatite occur near the outer edge of the POP chondrule. Most of these clinoenstatite grains poikilitically enclose small olivine chadacrysts. No glass is apparent in the POP chondrule; instead, elongated olivine crystallites and small grains of plagioclase occur between the phenocrysts, as in the BO chondrule. An elongated grain of sodalite (~20 × 50 μm) also occurs in the POP shell. Immediately surrounding the POP chondrule is a thin ring of troilite and pentlandite. A 170–1000 μm-thick relatively coarse-grained rim surrounds the entire compound chondrule. This rim appears to be holocrystalline, containing olivine and pyroxene grains (3–100 μm) as well as nepheline and sodalite (3–5 μm). A thin partial rim of troilite and pentlandite encloses the relatively coarse-grained rim; this is surrounded by a 50–100 μm-thick rim of the fine-grained, opaque silicate material that constitutes the Allende meteorite matrix.

The manganiferous orthopyroxene and olivine grains occur exclusively within the relatively coarse-grained rim around Allende chondrule 1. Despite a thorough search, such pyroxenes and olivines were not found in Allende's opaque silicate matrix or in ~35 relatively coarse-grained rims around other mafic chondrules in Allende, Leoville, Vigarano, Kaba (all CV3), Isna, Lancé, Colony (all CO3), or Semarkona and Bishunpur (both LL3). The manganiferous pyroxene grains are an abundant constituent of the rim of Allende chondrule 1; they are euhedral to subhedral and range from <5 to 80 μm (typically 60 μm) in diameter. They are colorless and most exhibit parallel (albeit undulose) extinction under crossed nicols, indicat-

Table 1. Representative analyses of Mn-rich orthopryoxene (wt.%) from the relatively coarse-grained rim around Allende chondrule 1

	1	2	3	4	5	6	7	8	9	10	11	Avg.	Std. Dev.
SiO_2	56.6	57.6	57.5	57.4	57.9	57.5	57.5	57.4	57.6	57.0	57.0	57.4	0.36
Al_2O_3	0.54	0.46	0.35	0.60	0.33	0.54	0.56	0.51	0.37	0.60	0.51	0.49	0.10
Cr_2O_3	1.5	1.7	1.6	1.6	1.6	1.7	1.6	1.6	1.7	1.8	1.6	1.6	0.08
FeO	1.3	1.2	1.3	1.3	1.3	1.4	1.5	1.4	1.5	1.4	1.5	1.4	0.10
MnO	4.5	4.4	4.3	4.5	4.3	4.0	4.2	4.1	4.0	4.3	4.0	4.2	0.19
MgO	32.0	30.8	32.5	32.0	32.8	32.4	32.2	33.1	32.6	32.5	32.2	32.3	0.59
CaO	2.8	2.9	3.1	3.5	3.1	2.8	3.3	2.7	2.9	3.2	3.1	3.0	0.24
Total	99.24	99.06	100.65	100.90	101.33	100.34	100.86	100.81	100.67	100.80	99.91	100.39	
	Structural Formulae Based on 6 Oxygens												
Si	1.986	2.000	1.989	1.984	1.988	1.994	1.987	1.977	1.991	1.969	1.986	1.986	0.008
Al^{IV}	0.014		0.011	0.016	0.012	0.006	0.013		0.009	0.031	0.014	0.011	0.008
Al^{VI}	0.008	0.019	0.003	0.009	0.002	0.016	0.010	0.023	0.006		0.007	0.009	0.007
Cr	0.042	0.048	0.044	0.044	0.043	0.047	0.044	0.044	0.046	0.049	0.044	0.045	0.002
Fe	0.074	0.104	0.073	0.074	0.071	0.098	0.084	0.059	0.087	0.052	0.080	0.078	0.015
Mn	0.134	0.134	0.126	0.132	0.125	0.118	0.123	0.120	0.117	0.126	0.118	0.125	0.006
Mg	1.673	1.650	1.675	1.649	1.679	1.675	1.658	1.699	1.679	1.673	1.672	1.671	0.014
Ca	0.105	0.112	0.115	0.130	0.114	0.104	0.122	0.100	0.107	0.118	0.116	0.113	0.009
Total	4.036	4.067	4.036	4.038	4.034	4.058	4.041	4.022	4.042	4.018	4.037	4.038	

ing that they are orthorhombic. However, a few may be monoclinic. There is no optical evidence of zoning. The grains are too small for the determination of 2*V* or optic sign. Associated with the orthopyroxene grains in the rim are several grains of manganiferous olivine (up to 100 μm). Tiny grains of nepheline and sodalite occur between the orthopyroxene and olivine grains in the rim. Nepheline appears more abundant than sodalite and the abundance of both appears to be greatest in the inner part of the rim, close to the chondrule. Blebs of troilite and pentlandite and (to a far lesser extent) metallic Fe,Ni (awaruite and taenite) also occur in the rim. A few rare grains of low-Mn clinoenstatite with polysynthetic twinning are also present.

Mineralogy

The manganiferous orthopyroxene grains are relatively homogenous in composition (Table 1); individual grains show no appreciable compositional zoning. The orthopyroxene grains average (in wt.%): 4.2% MnO, 32.3% MgO and 1.4% FeO. The calculated structural formulae, based on 6 oxygens, indicate pyroxene stoichiometry. Figure 2 shows that FeO and MnO have an inverse linear correlation ($r = -0.773$, $n = 11$), significant beyond the 99% level. On the other hand, Cr_2O_3 and MnO in the same samples are not correlated ($r = -0.374$).

The olivine grains associated with the manganiferous orthopyroxene grains are themselves relatively rich in MnO, averaging 1.2 wt.% (Table 2); they also contain an average of 9.2 wt.% FeO and 49.5 wt.% MgO. Most terrestrial olivines with >1.0 wt.% MnO are very rich in iron (e.g., 1.01 wt.% MnO and 65.02 wt.% FeO in a fayalite from a ferrogabbro from the Skaergaard Intru-

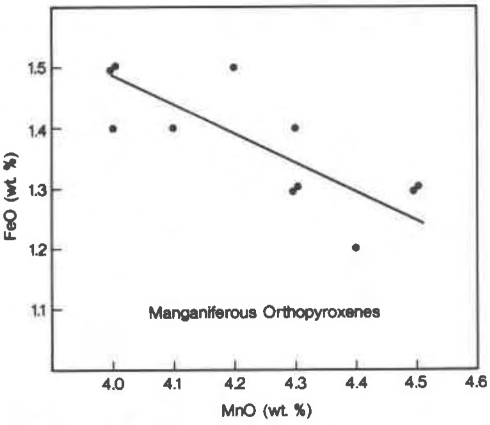

Fig. 2. Plot of FeO vs. MnO in eleven manganiferous orthopyroxene grains in the relatively coarse-grained rim of chondrule 1. The pairs of adjacent points have the same compositions. For these grains, r = −0.773, significant beyond the 99% level.

Table 2. Manganiferous olivine and low-Mn clinopyroxene in the relatively coarse-grained rim and plagioclase and low-Mn olivine and pyroxene in Allende chondrule 1

	1	2	3	4	5
No. of grains	5	2	15	2	5
SiO_2	40.5	59.2	42.4	59.8	48.9
Al_2O_3	<0.04	0.61	<0.04	0.45	30.6
Cr_2O_3	0.08	0.57	0.12	0.54	nd*
FeO	9.2	1.2	4.0	0.94	0.40
MnO	1.2	0.49	0.61	0.28	nd
MgO	49.5	38.2	53.7	37.5	nd
CaO	0.24	0.46	0.17	0.45	15.8
Na_2O	nd	nd	nd	nd	4.1
K_2O	nd	nd	nd	nd	0.17
Total	100.72	100.73	101.00	99.96	99.97

1. Manganiferous olivine in relatively coarse-grained rim.
2. Low-Mn clinoenstatite in relatively coarse-grained rim.
3. Olivine in chondrule 1.
4. Low-Ca pyroxene in chondrule 1.
5. Calcic plagioclase in chondrule 1.

*nd = not determined.

sion; Deer and Wager, 1939). Most tephroites also occur in iron-rich environments (Deer et al., 1966, p. 9). The olivine grains in the relatively coarse-grained rim appear to be slightly zoned; grain edges are 1–2 wt.% richer in FeO than grain interiors. Two polysynthetically twinned clinoenstatite grains averaging 1.2 wt.% FeO and 0.49 wt.% MnO (Table 2) were found toward the outer edge of the rim. The compositions of these two grains are similar to those within the chondrule (Table 2) as well as other chondrules and chondrule fragments throughout Allende (Simon and Haggerty, 1980).

Olivine and clinoenstatite within the chondrule are compositionally homogeneous (Table 2); their compositions are similar to those in chondrules throughout the meteorite except for their somewhat higher MnO content (e.g., Simon and Haggerty, 1980; A. E. Rubin, unpublished data). The higher MnO in these grains may have been acquired by diffusion from the manganiferous grains in the relatively coarse-grained rim. Plagioclase in the chondrule is calcic ($Ab_{32}Or_1$; Table 2) and similar to that in other mafic chondrules in Allende (A. E. Rubin, unpublished data).

Bulk composition

The bulk compositions of the relatively coarse-grained rim around chondrule 1 and average opaque matrix determined by broad-beam electron probe analyses are given in Table 3. Agreement of the opaque matrix analysis with that of McSween and Richardson (1977) and Clarke et al. (1970) is very good. The low totals in the microprobe analyses arise from matrix porosity, plucking during thin section preparation (due to matrix friability), and, to a lesser extent, unanalyzed constituents such as C, Co, Cl and H_2O. However, Clarke et al. (1970) found no H_2O in their wet chemical analysis of opaque matrix.

The relatively coarse-grained rim is extremely rich in MnO (1.5 wt.%) compared to that of opaque matrix (0.2 wt.%) or bulk CI or CV chondrites (Fig. 3). Relative to opaque matrix, the rim is somewhat depleted in refractories, enriched in Cr and Na, greatly enriched in Mn and slightly depleted in K. In addition, the rim is depleted in Fe, Ni, S and P relative to opaque matrix (Fig. 3a).

Allende opaque matrix itself appears rich in Ca relative to bulk CV chondrites (Fig. 3b). The high standard deviation of CaO in the analysis of opaque matrix (Table 3) indicates variable concentrations of Ca. Enrichments in Ca do not correspond in all cases to enrichments in Ti

Table 3. Bulk compositions (wt.%) of the relatively coarse-grained rim compared to Allende opaque matrix determined by broad beam electron probe analysis

	CGR	SD	OM	SD	OM^*	$OM^\dagger$
No. of areas	13		8		≥20	2.9g
SiO_2	36	3	30	1	28.0	33.11
TiO_2	0.1	0.02	0.1	0.02	0.09	0.13
Al_2O_3	3	0.8	3	0.9	2.30	3.07
Cr_2O_3	0.9	0.1	0.4	0.04	0.38	0.55
$FeO^{\S}$	19	4	33	3	31.9	34.68
MnO	1.5	0.4	0.2	0.04	0.21	0.22
$NiO^{\S}$	0.2	0.1	2	0.4	1.83	1.95
MgO	21	3	18	0.9	20.2	21.42
CaO	1.5	0.5	3	2	2.37	2.67
Na_2O	0.8	0.3	0.3	0.3	0.22	0.44
K_2O	0.05	0.04	0.05	0.02	0.01	0.03
$SO_3{}^{\S}$	3	2	4	0.8	2.82	5.99
$P_2O_5{}^{\S}$	0.1	0.03	0.3	0.1	nd¶	0.25
Total	87.15		94.35		90.33	104.98

CGR = relatively coarse-grained rim around chondrule 1.

OM = opaque matrix. SD = standard deviation of mean.

*(McSween and Richardson, 1977).

§All Fe, Ni, S and P are expressed as oxides.

†(After Clarke et al., 1970). Analysis also includes 0.11 wt.% CoO and 0.36 wt.% C. This analysis was done by wet chemical methods.

¶nd = not determined.

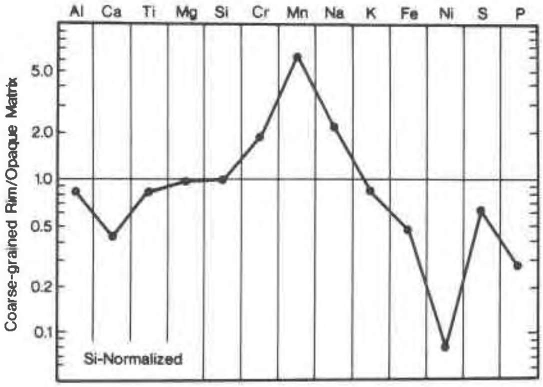

Fig. 3a. The mean composition of the relatively coarse-grained rim around chondrule 1 in Allende normalized to that of the opaque silicate matrix and to Si. The rim is depleted in refractories, enriched in Cr and Na, greatly enriched in Mn and depleted in Fe, Ni, S and P. Lithophiles are plotted from left to right in order of increasing volatility.

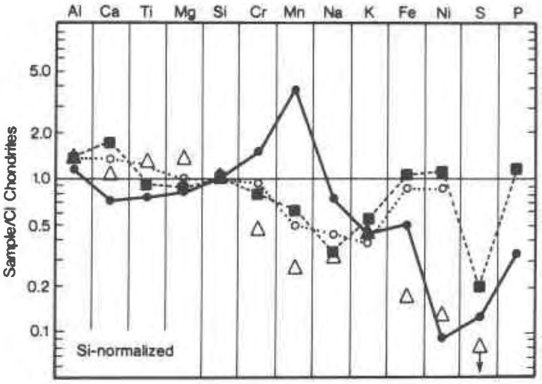

Fig. 3b. The mean compositions of the relatively coarse-grained rim (solid line with closed circles), opaque silicate matrix (dashed line with squares), bulk CV chondrites (dotted line with open circles) and CV chondrules (triangles) normalized to CI chondrites and to Si. CV chondrule data are from Simon and Haggerty (1980) and McSween (1977), as compiled by Grossman and Wasson (1983). Lithophiles are plotted from left to right in order of increasing volatility.

and/or Al. This is probably due to small grains of diopside and hedenbergite which occur randomly throughout the Allende opaque matrix (e.g., J. N. Grossman and A. E. Rubin, unpublished data). Thus, the depletion of Ca in the relatively coarse-grained rim relative to inclusion-free opaque matrix is not as great as it appears in Figure 3a.

Step-scan traverses across the rim show a decrease in MnO with increasing distance from the chondrule (Fig. 4). The outer edge of the rim contains ~0.9 wt.% MnO, whereas the portion of the rim adjacent to the chondrule contains >2.5 wt.%. The peaks in Figure 4 are due to large grains of manganiferous orthopyroxene.

Discussion

Formation of compound chondrule

The round outlines and igneous textures of chondrules indicate that they were once freely-floating droplets of silicate melt. Most workers believe that chondrules formed by melting pre-existing solids (e.g., Dodd, 1978; Gooding, 1979; Grossman et al., 1979; Gooding et al., 1980; Gooding and Keil, 1981; Grossman and Wasson, 1983). Compound chondrules probably formed by low-velocity collisions in which at least one chondrule was liquid or plastic (i.e., a partially solidified crystal-liquid mush) at the time of encounter (Van Schmus, 1969; Gooding and Keil, 1981).

In Allende chondrule 1 (Fig. 1), the internal BO chondrule must have formed first. When its precursor was melted, immiscible sulfide-rich liquid separated from the silicate liquid, forming the ring of troilite and pentlandite blebs on the inside edge of the BO chondrule's thick olivine rim as a result of centrifugal force. The solidified BO chondrule then collided (at low relative velocities) with a larger liquid droplet, which later became the outer POP chondrule upon crystallizing. Olivine in the liquid droplet nucleated first—in contact with the rim of the BO chondrule. With progressive crystallization, the SiO_2 content of the remaining liquid increased sufficiently to cause clinoenstatite to crystallize near the outer edge. Immiscible sulfide- and metal-rich liquids were trapped inside the POP chondrule and crystallized as blebs of troilite and pentlandite, and to a lesser extent, awaruite and taenite. Elongated olivine crystallites and small grains of calcic plagioclase grew in the glass throughout the compound chondrule, either during slow cooling or a subsequent episode of reheating. The thin ring of troilite and pentlandite between the chondrule and the relatively coarse-grained rim may have formed in one of a number of different ways: (1) condensation of sulfide on the chondrule surface, (2) accretion, or (3) expulsion from the chondrule and entrapment by accretion of the relatively coarse-grained rim. The outermost rim of opaque matrix material must have been acquired by the chondrule after the chondrule had already cooled. The assemblage experienced no episodes of significant heating thereafter. Alternatively, it is possible that the already-solidified BO chondrite accreted a rim of material that was subsequently melted to produce the outer POP shell.

Formation of relatively coarse-grained rim

Huss et al. (1981) found that recrystallized matrix material in type 3 ordinary chondrites is coarser-grained and depleted in bulk FeO/(FeO+MgO), Ni and S relative to opaque matrix. From these considerations as well as the lesser friability and porosity of recrystallized matrix, its closer approach to whole rock bulk composition, and its increasing predominance over opaque matrix in more metamorphosed type 3 chondrites, Huss et al. inferred that recrystallized matrix material formed from opaque matrix by thermal metamorphism. Most relatively coarse-grained rims around mafic chondrules in Allende are depleted in bulk FeO/(FeO+MgO), Ni and S relative to Allende opaque matrix (A. E. Rubin, unpublished data), suggesting that the relatively coarse-grained chondrule rims in CV3 chondrites also formed from opaque matrix material by thermal metamorphism.

However, it is impossible to account for the enrichment in moderately volatile elements in the rim of chondrule 1 by metamorphism of normal opaque matrix material. I suggest that this rim acquired its high concentrations of these elements in the solar nebula, as detailed below. The data of McSween (1977) and Simon and Haggerty (1980), compiled by Grossman and Wasson (1983), indicate that CV chondrules are depleted in Cr and Na and greatly depleted in Mn relative to bulk CV and CI chondrites. Potassium in CV chondrules is depleted relative to CI chondrites, but not relative to bulk CV chondrites. Relative to opaque matrix (thought by Scott et al. (1982) to be chondrule precursor material), CV chondrules are depleted in Cr, Mn and K, but not Na. If the wet chemical data for opaque matrix (Clarke et al., 1970) are used, CV chondrules appear slightly depleted in Na relative to opaque matrix. These depletions of CV chondrules in the moderate volatiles may have been caused by volatilization of chondrule precursor materials during chondrule formation. However, Na is more volatile than Mn and it is difficult to explain the larger depletion of Mn relative to Na in CV chondrules by volatilization. It is nevertheless possible that volatilized Na condensed back onto the CV chondrules. This is supported by the moderate enrichment of Na relative to Cr on the surfaces of separated chondrules from the Chainpur LL3 ordinary chondrite (Grossman and Wasson, 1982). This does not explain why Mn did not also condense onto the chondrules, unless we assume that much of the Mn had already condensed onto the precursors of materials akin to the rim of chondrule 1 (see below).

Alternatively, Cr and Mn in CV chondrules may have been partially reduced (Grossman and Wasson, 1983) and lost from chondrules as part of a dense, immiscible metal-sulfide liquid. The only evidence supporting this possibility is the occurrence of minor amounts of Cr in kamacite (<0.2 wt.%) and Fe sulfide (<0.8 wt.%) in some type 3 ordinary chondrites (e.g., Rambaldi and Wasson, 1981). It is also possible that the chondrule precursors themselves were depleted in these elements due to previous solid–solid and solid–gas fractionations in the solar nebula.

The moderate enrichments in Cr and Na and great enrichment in Mn in the rim of chondrule 1 relative to bulk CV chondrites (Fig. 3b) approximately mirror the depletions of these elements observed in the CV chondrules. (Potassium in the rim is enriched relative to CV chondrules and bulk CV chondrites.) It is thus possible that the rim acquired these volatile elements by condensation after they were lost from chondrule precursors during a heating event. This would require the rim to have been very close to the precursors that were volatilized. The rim itself may either have been a clump of opaque matrix or have already accreted around the chondrule when it acquired these volatile elements. The depletions in Fe, Ni and S in the rim relative to opaque matrix may possibly have been caused by outward migration of these elements as a dense immiscible liquid during a subsequent heating episode. (Some Mn, Na and K may have been lost as well.) The ring of troilite and pentlandite surrounding the rim may contain some of this Fe, Ni and S; this ring was not included in the broad-beam probe analysis of the rim.

Of course, it is possible that the Cr, Na and Mn enrichments in the rim have nothing to do with the depletions of these elements in CV chondrules. If this is the case, the unusual bulk composition of the rim remains unexplained.

The step-scan traverses across the rim (Fig. 4) show that Mn is progressively depleted toward the outer edge of the rim. This may indicate that the rim was already around the chondrule when the rim was heated; Mn may then have been lost to space from the rim's outer boundary. This is supported by the apparent decrease in abundance of nepheline and sodalite toward the rim's outer boundary, perhaps reflecting a corresponding loss of Na. A second alternative is that Mn may have diffused down a chemical potential gradient toward a Mn sink outside the rim. Such a sink could consist of pyroxene grains with low MnO residing in the matrix. A third alternative is that the chondrule may have accreted a succession of decreas-

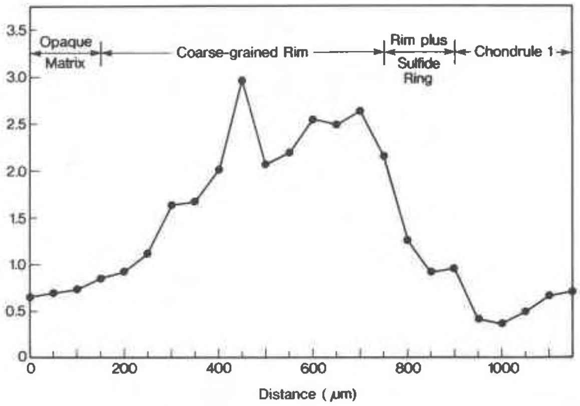

Fig. 4. Step-scan traverse across the relatively coarse-grained rim using a 100 × 10 μm broad electron beam. Each plotted point is the average of five data points collected at 10 μm intervals. The MnO content of the rim decreases away from the chondrule. Peaks are due to coarse manganiferous pyroxene grains within the rim. Traverses across the rim on other sides of the chondrule (not shown) document similar trends of MnO decrease away from the chondrule.

ingly manganiferous rims. This seems unlikely in view of the absence of textural evidence for discrete layering within the rim.

In any case, the extraordinary bulk composition of this rim and the apparent absence of other such manganiferous rims attest to an unusual and possibly unique history.

Crystallization of manganiferous grains

It is difficult to establish the exact temperature to which the relatively coarse-grained rim was raised during the heating event. The olivine–orthopyroxene geothermometer (Sack, 1980) is calibrated only for Fe–Mg exchange and does not account for significant amounts of Ca and Mn. From an extrapolation of the low-pressure enstatite–diopside solvus (Nehru, 1976), the average Ca and Mg content of the manganiferous orthopyroxene grains (Table 1) suggests equilibrium at a temperature of ~1145°C. The apparent lack of excess diopside makes this temperature a minimum. However, it is possible that the abundant Mn in the enstatite significantly affects Ca solubility, thus rendering this temperature inaccurate. The presence of a few round blebs of troilite, pentlandite, awaruite and taenite in the rim suggests that the Fe–Ni–S eutectic temperature of 950–1000°C was reached. I conclude that the temperature was probably $\geq$1000°C. The manganiferous orthopyroxene and olivine grains in the rim grew at this temperature. The two grains of low-Mn clinoenstatite near the outside edge of the rim are not in equilibrium with the manganiferous orthopyroxene and olivine grains and may be exotic grains that were captured as projectiles in the nebula. These clinoenstatite grains are very similar in composition to the pyroxenes in many of Allende's mafic chondrules and may have been derived from such chondrules.

In orthopyroxenes, both Mn and Fe^{2+} preferentially enter the M2 site, although the preference of Mn for M2 is greater than that of Fe^{2+} (e.g., Cameron and Papike, 1981). The preference of Fe^{2+} for M2 increases with orthopyroxene Ca content and decreases with temperature (e.g., Virgo and Hafner, 1969; Smyth, 1973; Saxena et al., 1974). The high Ca concentration in the manganiferous orthopyroxene grains thus increased the preference of Fe^{2+} for M2. The replacement of Fe^{2+} by Mn in M2 accounts for the significant inverse correlation between FeO and MnO in the manganiferous orthopyroxene grains (Fig. 2). However, this is not a simple 1-to-1 replacement; Mn and Fe^{2+} are partitioned to different extents into olivine and orthopyroxene and between M1 and M2 in the orthopyroxene. Thus, some of the scatter in Figure 2 may be due to these partitioning differences.

The lack of significant inverse correlation between Cr_2O_3 and MnO in the manganiferous othropyroxene grains suggests that Cr must have preferentially entered the M1 site, whereas Mn entered M2. Thus, Cr occurs as Cr^{3+}, which is smaller than Cr^{2+} and more easily accommodated in M1.

Because Mn,Fe-rich pyroxenes are much more common in terrestrial rocks than Mn,Mg-rich pyroxenes, one possible mechanism for the formation of the Mn,Mg-rich pyroxene grains in the relatively coarse-grained rim is by reduction of FeO in pre-existing Mn,Fe-rich pyroxene grains. However, the inferred +3 oxidation state of Cr in the pyroxene and the absence of significant amounts of metallic Fe associated with the pyroxene suggest that little reduction occurred.

Another possible mechanism for the formation of the manganiferous orthopyroxene grains is by condensation of Mn onto pre-existing enstatite grains in the solar nebula. In equilibrium condensation of a cooling gas of solar composition at pressures greater than 7.1×10^{-5} atm, metallic Fe condenses before forsterite (Grossman and Larimer, 1974). At 10^{-3} atm, forsterite begins to react with the gas to form enstatite at 1349 K (Grossman and Larimer, 1974). Significant amounts of FeO do not occur in the olivine or pyroxene until temperatures of 700 K are reached during cooling (Grossman, 1972). Thus, if Mn condenses as an oxide at temperatures considerably above 700 K (Wai and Wasson, 1977), then Mn,Mg-rich pyroxenes could have formed in the nebula by Mn condensation onto pre-existing grains of enstatite. The observation that Mn,Mg-rich pyroxenes are very rare or absent in the opaque matrix or in other relatively coarse-grained rims around chondrules in Allende and other CV3 chondrites indicates that condensation of MnO onto pyroxene was highly localized. It is possible that some very fine-grained orthopyroxenes (consequently having very high surface/volume ratios) were able to preferentially adsorb MnO as it condensed. These pyroxenes must then have remained together and been eventually incorporated into the relatively coarse-grained rim around chondrule 1. The manganiferous olivines either acquired their Mn by condensation or by equilibration with the Mn-rich pyroxenes. This model does not seem very plausible in view of the ad hoc processes required, but it cannot be entirely discounted.

Terrestrial Mg,Mn-rich orthopyroxenes primarily form in metamorphosed evaporites or calc-silicate deposits. The bulk compositions of these rocks are low in Fe, rich in Mn and have high Mg/Fe ratios. As low-Ca pyroxenes grew in these rocks during metamorphism, Mg and Mn preferentially entered the M1 and M2 sites, respectively. Most of the available Fe^{2+} also entered M2, but the low bulk Fe in the rocks left many M2 sites vacant and thus available for other cations. These were filled primarily by Mg and, to a lesser extent, by Ca. In many of these rocks, much of the Ca was partitioned into a coexisting Mn-rich clinopyroxene (e.g., Brown et al., 1980).

Compared to Allende opaque matrix, the relatively coarse-grained rim around chondrule 1 also has a bulk composition with low Fe, high Mn and a high Mg/Fe ratio. Nevertheless, the rim is still considerably richer in Fe than the terrestrial metamorphosed evaporites and calc-silicates. It seems most probable that the manganiferous orthopyroxene and olivine grains grew in the rim during metamorphism, having acquired their unusual compositions from the high bulk Mn and Cr in the rim. (The rim probably became enriched in these elements by condensation, after they were lost from CV chondrules during chondrule formation.) When the rim was heated enough to permit grain growth, most Mn was partitioned into the M2 site of the orthopyroxene and most Fe^{2+} was partitioned into the coexisting olivine. However, Mn was not sufficiently abundant to fill all of the orthopyroxene M2 sites; these were filled by Ca and whatever Mg was left over from entering M1 (as well as olivine). Thus, Mg,Mn-rich orthopyroxene grains averaging 3.0 wt.% CaO were formed. Although this CaO concentration is relatively high, a few terrestrial orthopyroxenes have even higher CaO (e.g., Deer et al., 1978, p. 61).

Acknowledgments

I thank R. Jones, J. N. Grossman and P. Rosener for technical assistance, J. T. Wasson, J. N. Grossman, S. S. Sorensen, P. Warren, R. T. Dodd and D. Peacor for helpful discussions, D. J. Rubin for her help in typing the manuscript, and an anonymous reviewer for useful comments. This work was supported by National Aeronautics and Space Administration grant NAG 9-40.

Note added in proof:

After this paper went to press, A. S. Kornacki informed me that he also found an occurrence of MnO-rich pyroxene grains within a relatively coarse-grained chondrule rim in Allende. Thus, the processes that formed these grains happened more than once in the solar nebula.

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Manuscript received, November 8, 1983;
accepted for publication, May 1, 1984.