Origin of the high-temperature fraction of C2 chondrites

LAWRENCE GROSSMAN

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, U.S.A.

and

EDWARD OLSEN

Department of Geology, Field Museum of Natural History, Chicago, Illinois 60605, U.S.A.

(Received 7 May 1973; accepted in revised form 8 August 1973)

Abstract—The coarse-grained fraction of C2 chondrites is composed mostly of single crystals and aggregates of crystals of Mg-rich olivine and pyroxene. They do not possess compelling textural evidence of being the solidification products of rapidly-quenched molten droplets. Metal inclusions in the silicates contain 3.82-8.88 mole% Ni, 0.16-0.70 per cent Co, 0.17-1.07 per cent Cr and up to 5.70 per cent P. Thermodynamic calculations show that alloys of these compositions may be condensates from the solar nebula. The implication is that the high-temperature fraction of C2 chondrites consists mostly of high-temperature condensates. Chemical data show that the high-temperature fraction has an Fe/Mg atomic ratio of ≤ 0.31 compared to 1.3 in the matrix, indicating that much of the iron has been lost from the high-temperature fraction and converted to the troilite and oxidized iron of the low-temperature fraction. The presence of low-Ni metal grains in the aggregates and high Ni/Fe and Co/Fe ratios in the matrix of some C2's indicates preferential loss of early Ni–Co-rich metal from the high-temperature fraction during condensation.

Introduction

CARBONACEOUS chondrites comprise the most primitive known meteorite group. It is certain they have never been involved in planetary processes that significantly modified their original states. Although the Cl's are the most primitive in terms of elemental abundances, the C2's and C3's are more varied mineralogically, with potentially greater information content. Anders (1964) and Larimer and Anders (1967) have proposed a two-component model for carbonaceous chondrites in which a high-temperature, volatile-free fraction consisting of chondrules and metal grains coexists with a low-temperature, volatile-rich fraction. Recent studies of the high-temperature fractions of several C2 and C3 meteorites have led to discoveries of materials which have been interpreted as primitive, high-temperature condensates: Ca-Al-silicate glasses in C2 meteorites (Fuchs et al., 1973), Ca-Ti-Al-rich aggregates in C3 meteorites (Fuchs, 1969; Keil et al., 1969; Kurat, 1970; Marvin et al., 1970; Grossman, 1972) and O18-deficient forsterite and enstatite grains (Onuma et al., 1972). In addition, Olsen et al. (1973) reported C2 metal grains with unusual compositions and textural relations suggestive of direct condensation. It is the purpose of this paper to treat quantitatively the condensation of metal in terms of several models, to apply these models to the observed compositions of C2 metal grains and to determine details of the early stages of the condensation of the solar system.

Petrographic and Textural Observations

The most thoroughly studied of the C2 meteorites in Table 1 is Murchison (Fuchs et al., 1973). Metal in eight additional C2's was analyzed and petrographic

Table 1. Compositions of metal grains

			Comp	osition (mole	%)	
Meteorite	\mathbf{Grain}	Fe	Ni	Co	Cr	P
Cold Bokkeveld	1	90-11	8.27	0.53	0.33	0.79
	2	90.57	7.03	0.46	1.07	0.86
	3	91.73	6.37	0.34	0.99	0.56
	4	94.67	4.06	0.29	0.68	0.29
	5	93.67	5.38	0.35	0.62	0.00
Essebi	1	$92 \cdot 31$	6.27	0.40	0.76	0.27
	2	90.60	7.72	$0 \cdot 42$	0.77	0.52
	3	89.49	8.88	0.45	0.30	0.92
	4	$92 \cdot 45$	5.69	0.35	0.72	0.81
Crescent	1	92.68	5.75	0.36	0.72	0.47
	2	93.69	4.40	0.31	0.54	1.05
	3	93.48	4.88	0.16	0.69	0.78
	4	93.38	4.96	0.18	0.61	0.88
	5	93.04	5.02	0.36	0.83	0.76
Al Rais	1	$92 \cdot 85$	5.39	0.36	0.30	1.08
	2	93.68	5.25	0.35	0.47	0.27
	3	93.38	5.40	0.34	0.47	0.43
	4	92.93	5.71	0.30	0.41	0.65
	5	93.76	5.05	0.34	0.42	0.45
	6	91.78	6.46	0.30	0.51	0.92
	7	93.73	$5 \cdot 34$	0.30	0.17	0.47
Nogoya	1	93.64	4.88	0.36	0.65	0.45
Mighei	1	93.47	5.00	0.32	0.63	0.60
	2	94.06	4.06	0.528	1.00	0.60
Murchison	1	$92 \cdot 82$	5.27	0.38	1.02	0.50
	2	94.18	4.08	0.30	0.84	0.57
	3	94.47	3.82	0.30	0.86	0.57
	4	93.46	4.65	0.33	0.91	0.66
	5	91.26	7.08	0.39	0.74	0.52
	6	$92 \cdot 45$	5.34	0.70	0.84	0.66
	7	$92 \cdot 84$	5.27	0.38	0.90	0.63
	8	93.56	4.76	0.33	0.69	0.66
	9	93.72	4.55	0.36	0.78	0.57
	10	93.93	4.58	0.33	0.53	0.65
	11	93.69	4.56	0.30	0.83	0.63
	12	92.83	5.98	0.40	0.22	0.56
	13	$91 \cdot 77$	$6 \cdot 64$	0.41	0.59	0.58
Murray	1	86.97	6.67	0.26	0.40	5.70
	2	89.59	6.19	0.37	0.38	3.45
	3	94.01	4.86	0.35	0.42	0.34
Renazzo	1	$94 \cdot 21$	5.15	0.32	0.24	0.09
	2	$94 \cdot 15$	$5 \cdot 32$	0.32	0.22	0.00
	3	93.94	5.60	0.30	0.17	0.00

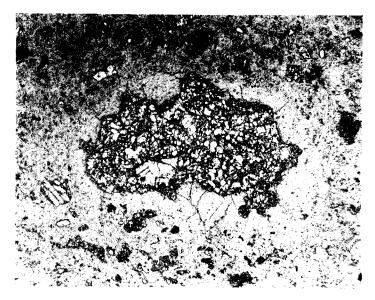


Fig. 1. Mighei. Typical white inclusion (longest dimension 1.7 mm; incident light) consisting primarily of low-iron forsterite and enstatite grains loosely packed together. Matrix is black layer-lattice silicate (medium gray). Note the subhedral shapes of some of the grains as well as the angular, fragmental shapes of the majority of them. Metal (white) occurs as rounded, ovoid grains between silicates and as very small round beads inside some of them. Angular fragments of forsterite and enstatite are also seen in the surrounding matrix, some containing spherical beads of metal. Note that the white inclusion is surrounded by a rim of layer-lattice silicates which is relatively free of small fragmental grains. This feature characterizes all white inclusions in C2 meteorites.



Fig. 2. Murchison. Single grain of euhedral forsterite (241 μm in longest dimension; incident light) removed from white inclusion and set in epoxy resin. Elliptical darker gray area inside forsterite is Ca–Al-silicate glass which, in turn. contains a submicron spherical bead of metal at one end and a larger gas bubble at the other end.

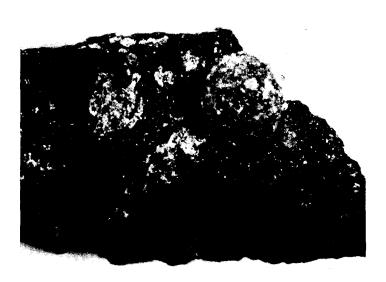


Fig. 3. Murchison. Hand specimen showing numerous typical, irregularly-shaped white inclusions in black layer-lattice silicate matrix and a rare true chondrule (0.9 mm). Note how the meteorite breaks through the friable aggregates but around the tough chondrule.

examination indicated great similarities between them all, except for Renazzo. Although the total carbon and water contents of Renazzo place it in the C2 group, it is exceedingly metal-rich in contrast to the very low metal contents seen in other C2's. In addition, the metal has the lowest Cr and P contents measured in C2 metal. As discussed later, this makes Renazzo anomalous in terms of any condensation model examined in this study.

In this paper, true chondrules are defined as objects containing the following unambiguous evidence of being the solidification products of rapidly-quenched molten droplets; interstitial glass and/or barred and/or radial crystalline textures. These are appropriate criteria since C2's are unequilibrated meteorites. Fuchs et al. (1973) make a distinction between true chondrules and white inclusions. The latter consist of fragile powdery clusters of loosely-packed grains that are easily dislodged and raked out with a needle; whole inclusions are too fragile to remove from the surrounding layer-lattice silicate matrix—they always break with the matrix. They may be rounded or ellipsoidal, but are most generally irregular in shape. Figure 1 shows a polished section of a typical white inclusion made up of forsterite and enstatite grains with some metal blebs. Figure 2 shows a section of a single euhedral forsterite grain removed from such an inclusion. A very small percentage of these white inclusions are composed of Ca-Al-rich phase assemblages, hibonite, diopside, spinel, etc., but the ones of interest in this paper are olivine-pyroxene aggregates.

The friability of these aggregates is due to the absence of interstitial binding material. At least three types of layer-lattice silicates are commonly found coating the aggregates (Fig. 1) or corroding olivine and pyroxene crystals in their interiors. Although many aggregates contain interstitial layer-lattice fibers, still others are relatively fresh and unaltered, with void spaces between the euhedral olivines and pyroxenes. The true chondrules, on the other hand, are quite rare, comprising less than 5 per cent of the total inclusions in the matrix. The matrix breaks around true chondrules leaving them as free-standing beads on broken surfaces, just as in unequilibrated ordinary chondrites. These chondrules are tough, resistant to scratching and crushing and can be removed whole from the matrix. Figure 3 illustrates this difference, with a dozen or more irregular white inclusions of various sizes visible in the matrix and a single true chondrule standing free of the matrix. The grains comprising the chondrules are tightly cemented together by glass and occasionally by a green layer-lattice silicate that appears to replace partially some of the glass.

In addition to the fragile, white, irregular inclusions, single fragments of olivine (and rarely pyroxene) grains are abundant in the matrix. Although most of these grains are fragmental and range from micron to millimeter size, some show one or two crystal faces and a few are euhedral, fully terminated orthorhombic prisms of olivine. The crystal faces of these are highly patterned, giving them a frosted appearance at low magnification. These surfaces are strongly reminiscent of the surfaces of synthetic mineral boules that are formed by direct vapor condensation.

True chondrules play little part in C2 petrography. They will not be discussed further here, but details of the mineralogy of true chondrules in the Murchison

Meteorite	White inclusions† (vol%)	Single grains and grain fragments (vol%)	Total (col. 1 + 2) (vol %)	Total inclusions (Wt. %)
Al Rais	22	18	40	46
Crescent	21	29	50	56
Essebi	19	14	33	39
Mighei	14	27	41	47
Murchison	23	21	44	50
Average	20	$\boldsymbol{22}$	$\boldsymbol{42}$	48

Table 2. Point counts of inclusions in five C2 meteorites*

meteorite are given in Fuchs et al. (1973). Table 2 shows the results of point-counting sections of 5 of these meteorites. It is evident that the white inclusions and the grain fragments have approximately equal abundance. Together, they are 6–10 times more abundant than true chondrules. Less than 1 per cent of the white inclusions are Ca–Al-rich.

Metal in C2 meteorites is scarce except in Renazzo, as discussed earlier. Most metal grains do not exceed a few tenths of a micron, though some can be found in the 5–10 µm range or rarely, larger. Metal typically occurs as spherical to ovate blebs, poikilitic within the olivine and pyroxene, but with some grains of metal between olivine grains or embaying their surfaces. Although many of these metal blebs are irregular, they always exhibit rounded and curved edges, some being highly spherical and a few being dumb-bell-shaped in three dimensions. This contrasts with the angular metal so typical of ordinary chondrites. Woop (1967) made these same observations, and suggested the C2 metal blebs might have formed as liquid droplets. Some of the grains may indeed have been melted before incorporation into the olivine crystals. On the other hand, metal grains condensed from a vapor commonly lack crystal faces and are nearly spheroidal in shape, as reported by McKay et al. (1972) in lunar breccias.

Although most inclusions typically contain no metal at all or only a sparse few grains (Fig. 1), rare, metal-rich inclusions can be found. Occasionally, grains of metal are found completely isolated in the black matrix, or with olivine inside a true chondrule, but such cases are rare. The dominant poikilitic texture shows that metal formed first, followed by forsterite. The euhedral form of the forsterite shows that the grains crystallized without contacting competing crystals which would have impinged on one another causing the typical hypidiomorphic or protoclastic textures of peridotites and dunites.

Finally, most forsterite grains were observed to have minute ellipsoidal inclusions of glass. One such inclusion can be seen as the darker gray elliptical area in the euhedral forsterite crystal in Fig. 2. The glass compositions have been investigated in some detail by Fuchs et al. (1973) for Murchison. They are Ca-Alsilicate glasses with from 2-9 per cent MgO, very similar in composition to Ca-rich inclusions in Allende. Such glasses may be the quench products of high-temperature condensates (Fuchs et al., 1973; Grossman and Clark, 1973). Aggregates

^{* 200} to 300 points counted for each meteorite section.

[†] Includes all chondrules, but they represent only a small fraction of the total in column 1.

can be found in which nearly every olivine crystal contains at least one such glass inclusion deep in its interior. If the white aggregates are interpreted as oncemolten droplets (chondrules), then the glass inclusions trapped in the interiors of the olivine grains must be close to the initial composition of the liquid from which the olivine crystallized. This leads to the absurd conclusion that the bulk composition of these forsterite-enstatite aggregates is \sim 20 per cent CaO, \sim 20 per cent Al₂O₃, \sim 5 per cent MgO and \sim 50 per cent SiO₂, equal to that of the trapped parent liquid. In addition, in the equilibrium system CaO-MgO-Al₂O₃-SiO₂ (OSBORN et al., 1954), forsterite is not a primary phase for this composition.

The textural relations described in this section may be subject to several interpretations. The possibility that these features, taken together, may be indicative of direct condensation leads us to investigate the compositions of the metal grains in this context.

Analytical Data

OLSEN et al. (1973) initially reported the unusually high Cr and P contents of metal from nine C2 meteorites. For brevity they listed only fifteen representative analyses. Table 1 here lists the full data in mole%. The maximum errors are 1 per cent (relative) for Fe, 5 per cent for Ni and Cr and 10 per cent for Co and P.

In addition to these elements, Al, Si, S, Ti, V, Mn, Cu, Zn, W and Pt were sought but not detected. Detection limits are approximately 200 ppm for Al, Si and S, and approximately 100 ppm for the remainder. Special attention was given to Mn. Of the five elements from atomic number 24 to 28, only Mn was not detected. Its average abundance in meteoritic matter is a factor of 0.7 that of Cr (Cameron, 1968), and were it present in proportion it would be readily detectable by microprobe.

Most of the grains analyzed were too small to permit electron beam traverses to test for homogeneity. Every grain that was large enough was scanned. Ni and Co showed only slight variations in larger grains, with no particular pattern, and within analytical error. Phosphorus, on the other hand, showed highly erratic patterns of sharp peaks and troughs well beyond analytical error. Although no schreibersite could be discerned optically during this study it appears likely that some of the phosphorus enrichment in C2 metal grains is due to submicron inclusions of it. Fuchs et al. (1973) actually noted visible schreibersite in some grains of metal in Murchison. In general, the twelve grains in Table 1 with P above 0.4 per cent must represent metastable solutions, or submicroscopic schreibersite must be present (Goldstein and Doan, 1972).

THEORY

GROSSMAN (1972) calculated that monatomic Fe, Ni, Co, Cr and Mn were the only significant gaseous species of those elements in the solar nebula in the temperature range $2000-1100^{\circ}\mathrm{K}$ at 10^{-3} atm total pressure. In that study, Fe and Ni were assumed to condense as an alloy, Co as the pure metal, Cr as $\mathrm{Cr_2O_3}$ and Mn as MnS. In this paper, we investigate the compositions of condensate alloys containing all these elements and thus re-examine the condensation temperatures of Co, Cr and Mn.

Assuming the ideal gas law and ideal solid solution behavior, two equations for each element of the forms,

$$P_i/RT + X_iA = N_i^{\text{tot}} \tag{1}$$

$$P_i = K_i X_i \tag{2}$$

are sufficient to derive the condensation curves with the added condition that

$$X_{\rm Fe} + X_{\rm Ni} + X_{\rm Co} + X_{\rm Co} + X_{\rm Mn} = 1. {3}$$

In these equations, P_i , X_i , $N_i^{\rm tot}$ and K_i are the partial pressure, mole fraction, total number of moles per liter and equilibrium constant for the vaporization reaction, respectively, of element i. A is the number of moles of alloy per liter. The $N_i^{\rm tot}$ are calculated as in Grossman (1972) from the assumed total pressure of 10^{-3} atm, the temperature and the solar system abundance data of Cameron (1968). Thermodynamic data were taken from Hultgren et~al. (1964). These 11 equations in 11 unknowns were solved by an iterative procedure on an IBM 360/65 computer at each temperature of interest.

In addition, a separate computation was performed to estimate the condensation temperature of P, an element heretofore overlooked in solar nebula condensation calculations. The temperature variation of the free energy for the reaction

$$3\text{Fe}(c) + \frac{1}{2}P_{0}(g) \rightarrow \text{Fe}_{2}P(c)$$

was taken from Richardson and Jeffes (1948) and the $P_{\rm P_2}$ was taken from the computer calculations upon which the condensation sequence of Grossman (1972) is based. $P_{\rm P_2}$ is on the order of 10^{-11} atm over the entire temperature range considered here.

RESULTS

Equilibrium model. Figure 4 shows the condensation curves derived assuming complete chemical equilibrium between grains and vapor. Fe condenses more gradually than Ni and Co, whose condensation curves are nearly coincident. Co condenses slightly more rapidly than Ni. These three elements condense much more rapidly within the first 50° below the condensation point of the alloy than they do at lower temperatures. Cr, on the other hand, condenses at a relatively slower and more uniform rate over the entire temperature range. Less than 0·1 per cent of the total Mn is condensed as alloy in this temperature range.

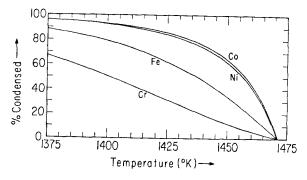


Fig. 4. Condensation curves for Co, Ni, Fe and Cr at 10^{-3} atm total pressure assuming alloy formation, ideal solid solution and complete chemical equilibrium. In contrast to these elements, less than 0.1 per cent of the total Mn is condensed in this temperature range and is not plotted.

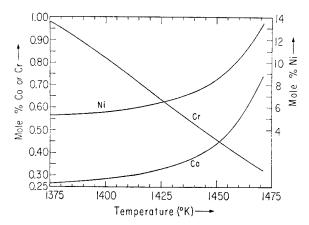


Fig. 5. The temperature dependence of the concentrations of Ni, Co and Cr in a condensate alloy in complete chemical equilibrium with a gas of solar composition at 10^{-3} atm total pressure. The Mn concentration will never exceed 5 ppm in this temperature range and is not plotted. Note the levelling-off of the Ni and Co concentrations at the low-temperature end.

Figure 5 shows the concentrations of Ni, Co and Cr in the alloy as a function of temperature. Note that the Ni and Co concentrations decrease with temperature while Cr increases. To a first approximation, this model predicts concentration ranges for these three elements in the ranges of those observed in Table 1. Particularly gratifying is the match between predicted and observed Cr contents which are an order of magnitude higher than those in iron meteorites and in most chondritic metal. Similarly, the Mn contents are predicted never to exceed several tens of ppm which would be undetectable with the microprobe, as is the case for the metal grains in Table 1.

Temperature concordance. When condensation temperatures of an individual metal grain in Table 1 are inferred from the curves in Fig. 5, however, the Ni, Co and Cr concentrations each yield temperatures which are often disparate (see Table 3). Of 43 grains, only 12 have Ni equilibration temperatures within analytical error of their respective Co temperatures. Ten grains exhibit temperature concordance for the pair Co-Cr and there are only 6 Ni-Cr concordances. A further serious shortcoming of the model is its complete inability to predict Ni or Co contents below about 4.80 mole % and 0.24 mole %, respectively. This occurs because the Ni and Co curves flatten in the temperature range near total condensation of Fe. Ni, Co and Cr, approaching cosmic concentration ratios in the limit. Eight grains in Table 1 have concentrations below these limits, resulting in 'undefined' condensation temperatures. In addition, the four italicized Ni condensation temperatures in Table 3 are maxima derived from the analytical error bars for grains whose condensation temperatures are otherwise undefined. Another consequence of the flattening of the curves is that the analytical errors for grains with Ni contents on the order of 5 per cent lead to much greater temperature uncertainties

 $\begin{pmatrix} +20^{\circ} \\ -90^{\circ} \end{pmatrix}$ than grains containing 8 per cent Ni (±4°).

Table 3. Condensation temperatures of metal grains

	<u>.</u>	Condensation temperature (${}^{\circ}K$)		
Meteorite	Grain	Ni	Co	\mathbf{Cr}
Cold Bokkeveld	1	1448	1459	1470
	2	1435	1452	1360
	3	1424	1430	1373
	4	$\mathbf{u}^{f *}$	1405	1418
	5	1385	1433	1426
Essebi	1	1422	1444	1408
	2	1444	1447	1406
	3	1453	1451	\mathbf{u}
	4	1403	1433	1413
Crescent	1	1405	1435	1413
	2	u	1418	1437
	3	1325	\mathbf{u}	1417
	4	1347	u	1428
	5	1357	1435	1398
Al Rais	1	1392	1435	u
	2	1375	1433	1447
	3	1390	1430	1448
	4	1404	1411	1457
	5	1359	1430	1455
	6	1425	1412	1442
	7	1382	1412	u
Nogoya	1	1320	1435	1423
Mighei	1	1352	1422	1425
	2	u	1395	1372
Murchison	1	1379	1440	1369
	2	u	1412	1397
	3	\mathbf{u}	1412	1394
	4	1325	1427	1387
	5	1436	1442	1411
	6	1382	1469	1397
	7	1379	1440	1388
	8	1352	1426	1417
	9	u	1435	1405
	10	1281	1426	1439
	11	1255	1412	1398
	12	1414	1444	\mathbf{u}
	13	1429	1446	1430
Murray	1	1436	1393	1454
	2	1425	1440	1460
	3	1309	1433	1455
Renazzo	1	1368	1422	\mathbf{u}
	2	1380	1422	\mathbf{u}
	3	1399	1412	\mathbf{u}

^{*} u = undefined condensation temperature. The concentration of this element does not plot on the condensate composition curve.

Italicized condensation temperatures are derived from concentrations at the extremes of analytical error bars. These grains would otherwise have undefined condensation temperatures.

Seven grains have undefined Cr condensation temperatures because their Cr concentrations lie below the initial Cr content of a condensate alloy at 10^{-3} atm. Two of these would be defined at 10^{-4} atm as the initial concentration of Cr drops to 0.27 mole% at this pressure. Three of the remainder represent all those measured in Renazzo, which is anomalous relative to other C2's in terms of its texture and exceedingly high abundance of metal. We shall therefore exclude Renazzo metal from consideration in this context.

Thermodynamic data. The free energies of the gaseous metals considered here are known to $\pm 2 \,\text{kcal/mole}$ in this temperature range (Hultgren et al., 1964). In order to investigate the effects of errors of this magnitude, we increased the free energy of Cr(g) by 2 kcal/mole and solved the identical system of equations whose results were discussed above. The result was to slide the entire Cr composition curve upward in temperature by 45° relative to the other elements, i.e. each Cr content then appeared 45° above the temperature at which it became stable in the original computation, with only very minor changes in the Ni and Co curves. Because both the Ni and Cr temperatures are systematically lower than the Co temperatures, relatively minor changes in free energy data for selected elements in certain directions would lead to markedly improved concordance. Within the margins of error in the thermodynamic data for the gaseous metals, it appears that a single set of free energy data exists which will lead to internally concordant condensation temperatures for the majority of the grains in Table 3. Remaining discordance could be caused by analytical error, non-ideal solution effects, errors in abundance data and pressure variations.

Undefined Ni and Co temperatures. Errors in thermodynamic data, however, cannot fully account for the small number of grains with Ni and Co contents significantly below the cosmic limits. Even in the extreme and unlikely case that the thermal data are in error by so much that the Ni and Co contents actually begin low and rise to cosmic levels with falling temperature, then all the grains with greater-than-cosmic Ni and Co concentrations would be inexplicable.

One explanation could be that the relative abundances of these elements in CAMERON (1968) are so in error as to yield limiting Ni and Co concentrations in the condensation model which are too high. In this regard, it is interesting to note that the new abundances of CAMERON (1973) produce higher limiting Ni and Co concentrations, resulting in a greater number of grains with undefined condensation temperatures.

Disequilibrium models. Because the early, high-temperature metal is enriched in Ni and Co relative to the bulk composition of the system, a model involving removal of early metal grains from further equilibration must result in achieving ultimate Ni and Co concentrations below the limiting values in the equilibrium model. Consequently, we have investigated in detail the following disequilibrium models, among others:

- (i) Equilibration of metal down to 1445°K, removal of this metal, followed by successive 5° stages of equilibration and removal.
- (ii) Stepwise 5° stages of equilibration and removal from initial condensation downward.

These models produce very similar results. The Ni and Co contents of condensate alloys now fall to 1·29 per cent and 0·05 per cent, respectively, by 1400°K. All grains have defined Ni and Co temperatures. According to these models, the majority of the grains have condensation temperatures between 1425°K and 1440°K. A marked improvement in temperature concordance takes place, but this is largely due to the greater rate of change of composition with temperature in these models relative to the equilibrium case. If our interpretation is correct, and these grains are condensate alloys, fractionation of metal during condensation may have been an important event in their genesis.

Phosphorus. Phosphorus was found to condense as schreibersite at 1416° K, according to the equilibrium model at 10^{-3} atm. Higher activities of iron in this temperature range result from the disequilibrium models and the schreibersite condensation temperature is 1422° K, according to model (i). Uncertainty in the schreibersite free energy data leads to an error estimate of $\pm 20^{\circ}$ in the phosphorus condensation temperature. At these temperatures, schreibersite would have begun to form on the exposed surfaces of condensed metal grains. We are unable to predict the concentration in any particular grain; however, the upper limit to the mean concentration should be in the range of 1-3 mole %, according to the equilibrium model and assuming total condensation of phosphorus.

DISCUSSION

Comparison with previous data. The equilibrium model computed here yields a slightly lower condensation point (1471°K) and a slightly higher initial Ni content (13·4 mole%) for the alloy than previously calculated by Grossman (1972) due to our use of newer thermodynamic data and to our consideration of the alloying effects of Co and Cr. The pressure dependence of the initial Ni content was found to remain the same. The condensation sequence of Grossman (1972) must be altered further, as follows. At 10⁻³ atm, Co does not condense as the pure metal at 1274°K but begins to condense in solid solution in nickel-iron at 1471°K and is nearly totally condensed at 1350°K. Similarly, Cr also begins to condense in the alloy at 1471°K, rather than as Cr₂O₃ at 1294°K. Cr, however, is only about 80 per cent condensed at 1350° and the remaining Cr may form FeCr₂O₄ or MgCr₂O₄ in this temperature range. High quality thermodynamic data are lacking for these phases, but it is possible that they may go into solid solution in previously condensed spinel. The MnS condensation temperature is unchanged since practically no Mn enters the metal phase.

Iron meteorites. The data presented here indicate that a primitive nickel–iron condensate should contain 0.32 mole% Cr at its condensation point at 10^{-3} atm and even higher concentrations at lower temperatures. This minimum Cr content drops only to 0.27 mole% at 10^{-5} atm.

ARRHENIUS and Alfvén (1971) have recently suggested the possibility that the iron meteorites grew directly from a vapor phase. Scott (1972) has proposed that the iron meteorites of group IVb are high-temperature condensates, based on the fact that the abundances of many refractory elements relative to Ni are near their cosmic values. This is not necessarily a valid criterion. Inspection of the non-coincident condensation curves in Fig. 4 reveals that high-temperature condensates

need not have cosmic siderophile-element/Ni ratios. Furthermore, if the most refractory siderophiles were fractionated with the refractory lithophile elements before iron condensed (Grossman, 1973; Wänke et al., 1973), an even poorer approach to cosmic ratios would have resulted. The Cr concentration in group IVb is only about 200 ppm at the most, a factor of 15 lower than the minimum Cr content attainable by a primitive condensate alloy. In fact, the data reviewed by Scott (1972) suggest, on the basis of Cr and Ni contents, that no group of iron meteorites is a primitive condensate. This conclusion is unaltered by the fractionation effects considered above and is in direct opposition to the suggestion of Arrhenius and Alfvén (1971). Condensate alloys containing 200 ppm Cr would only be predicted if Cr(g) were 8 kcal/mole more stable than indicated by the data used here. The maximum error, however, in the free energy of Cr(g) is only 2 kcal/mole.

If no iron meteorite is a primitive condensate, then what process is responsible for the refractory element contents of group IVb irons? This metal may have equilibrated after condensation with silicate materials containing the high-temperature condensate, Ca-Al-rich component, unlike the pallasites which are depleted in Ir relative to Pt (Turekian et al., 1973).

Pressures and temperatures of condensation. The fact that some of the metal is enclosed by forsterite crystals implies that iron crystallized before forsterite. From the condensation sequence of Grossman (1972), this implies pressures in excess of 7×10^{-5} atm. Attributing generous errors of $\pm 10^{\circ}$ to the condensation points of metal and forsterite leads to an uncertainty of about two orders of magnitude (from 3×10^{-6} to 5×10^{-4} atm) in the total pressure at which the condensation curves intersect. The equilibrium model at 10⁻³ atm pressure predicts grain-gas equilibration temperatures for metal grains of these compositions between 1350 and 1450°K. The disequilibrium models suggest temperatures on the order of 1425-1440°K. The models also predict these grains to be phosphorus-bearing, since schreibersite condenses in the same range. The indicated temperature range for most of the grains is below the condensation point of forsterite, 1444°K, at this pressure. Thus, using 10^{-3} atm, the observed textures and compositions can be interpreted as indicative of condensation of Ni-Co-rich metal at 1471°K, followed by condensation of forsterite crystals at 1444°K and lower, trapping inside them metal grains having compositions in equilibrium with the vapor at their temperature of entrapment. The disequilibrium models require removal of early Ni-Co-rich metal before the condensation of forsterite. In either case, a time lag between condensation of the first metal and crystallization of silicates is implied. Such a time lag is only possible at pressures greater than that of the intersection point of the metal and forsterite condensation curves. In addition, if condensation occurred at or below this pressure, one might expect to find numerous instances of forsterite enclosed by metal. Metal was never observed to enclose silicates.

The trapped glass inclusions (Fig. 2) suggest that condensation, melting and quenching of Ca–Al-rich phases also took place before forsterite condensation. This series of events is consistent with the condensation sequence at pressures of 10^{-3} – 10^{-5} atm.

Fe and Mg in C2 chondrites. In order to account for volatile element depletion

patterns, Anders (1964, 1968, 1971) and Larimer and Anders (1967) have proposed that the C2's are composed of 55 per cent by weight fine-grained, volatile-rich, low-temperature matrix material and 45 per cent coarse-grained, volatile-free, high-temperature fraction. They identified this fraction as chondrules plus metal. We observe that true chondrules comprise less than 5 per cent by volume of the C2's, but that the total coarse-grained fraction indeed constitutes 48 per cent by weight (see Table 2). This value is in excellent agreement with the content of high-temperature fraction in C2's as inferred from the latest trace element data, 0.492 ± 0.038 (Krähenbühl et al., 1973). We interpret the bulk of the coarse-grained fraction as primitive, high-temperature condensates and, as such, it should be volatile-free.

For Murchison, we calculate from the point-counts and the analyzed Fe° content (Jarosewich, 1971) that the mean Fe/Mg atomic ratio of the aggregates is 0·13, assuming that all the metal is in the coarse-grained fraction. This figure includes the oxidized iron in solution in the silicates in addition to that present as alloy (Fuchs et al., 1973). The calculated ratio is a factor of 6·5 lower than the cosmic ratio, implying loss of Fe relative to Mg. One section of Murchison was anomalously rich in metal in contrast to all other sections of Murchison and the other C2's studied. In this section, a point-count was made of metal and silicate in only the most metal-rich inclusions in order to determine the maximum Fe/Mg ratio observed. The highest value was 23 per cent by volume. When oxidized iron is also considered, this value corresponds to an Fe/Mg atomic ratio of 1·27, a factor of ten higher than the above estimate.

In view of the wide range of observed Fe/Mg ratios in individual aggregates, a better estimate of the mean can probably be made in the following way. The average of 40 spot analyses of the Murchison matrix gives an Fe/Mg atomic ratio of 1·27 (Fuchs et al., 1973) compared to the ratio for the bulk meteorite, 0·79. Table 2 shows that Murchison contains 50 per cent by weight matrix material. From these data, we calculate that the high-temperature fraction has an Fe/Mg ratio of 0·31. This ratio is a factor of 2·4 higher than our earlier estimate for the average aggregate, but still well below the ratio for the bulk meteorite. This ratio may still represent only an upper limit because of the occurrence of patches of an unidentified Fe-S-O phase (Fuchs et al., 1973) in the matrix. The spot analyses avoided such areas.

The origin of the high-temperature fraction. Any theory of the origin of the high-temperature fraction of C2 chondrites must account for the difference in Fe/Mg ratio between it and the matrix.

In those models which postulate that the high-temperature fraction is composed of chondrules formed by the melting and devolatilization of fine-grained, low-temperature condensates during local events in the nebula (LARIMER and ANDERS, 1967; ANDERS, 1968, 1971), oxidized iron is presumably reduced to liquid metal which separates partially from the molten silicates due to liquid immiscibility. Before incorporation into the meteorite parent bodies, these metal droplets freeze, become oxidized or converted to troilite and are no longer recognizable as high-temperature constituents. As mentioned previously, however, the textural features

of these aggregates are inconsistent with their having crystallized from rapidly-quenched molten droplets. It could be postulated that they were once true chondrules which have undergone extensive reaction in which interstitial glass was massively converted to layer-lattice silicates. In addition to the fact that layer-lattice-free aggregates contain no interstitial glass, another problem with such a model would be the large-scale chemical exchange necessary: in order to account for the Ca-Al-rich glass inclusions by a chondrule model, the hypothetical interstitial glass would have to have had a composition very similar to them. In addition, Onuma et al. (1972) have shown that the oxygen isotopic compositions of low-iron olivines and pyroxenes in C2 chondrites are inconsistent with their derivation by melting of the matrix.

The textures and metal grain compositions in the bulk of the high-temperature fraction can be satisfied by a model involving re-heating of the matrix only if the matrix is vaporized and re-condensed directly to the crystalline state.

If the high-temperature fraction is composed mostly of primitive, high-temperature condensates, the textures and most of the metal compositions can be explained by the equilibrium model. The forsterite-enstatite-metal aggregates may be high-temperature condensates which escaped alteration to magnetite, troilite and hydrated silicates during the low-temperature stage of the nebula. Being relatively coarse-grained, the aggregates failed to accrete the volatile elements. They may be derived from a hotter part of the nebula than the matrix. Condensate metal which was not trapped inside condensing forsterite was exposed to the low-temperature nebular gas and was able to react with it to form troilite and oxidized iron, thus becoming part of the low-temperature fraction.

Disequilibrium condensation models postulated to account for the low-Ni metal grains require Ni-Co-rich metal to be lost from the high-temperature fraction during condensation. If all the material in the C2's once condensed from a vapor of C1 composition, the amount of iron lost from the high-temperature fraction slightly exceeded the amount added to the low-temperature fraction because the bulk Fe/Mg ratio of the C2's is 0.95 that of C1's (LARIMER and ANDERS, 1970). A similar conclusion was reached by Wood (1967) although he interpreted the olivine aggregates as chondrules which he believed to be liquid condensates. Because C1 and C2 chondrites have nearly the same Fe/Mg ratio, the disequilibrium models requiring removal of metal from its condensation site also require low-temperature alteration of this metal in its new location, followed by transport of magnesium silicate aggregates complementary to this metal from the same condensation site to this location. Here they were incorporated into meteorite parent bodies before they had a chance to alter to hydrous silicates. If valid, this model predicts that the Ni/Fe and Co/Fe ratios in the matrix of the C2's should be greater than in the high-temperature metal grains. This is apparently the case for Ni in Renazzo and Al Rais, as discussed by Wood (1967). He suggested that early-condensing metal was depleted in Ni relative to Fe, leaving the later, fine-grained matrix enriched in Ni. Our condensation data indicate that the early metal should actually be enriched in Ni relative to Fe, making Wood's explanation inadequate. Thus, although the disequilibrium models predict a rather improbable sequence of events, there exists some independent experimental evidence for it.

Conclusions

White olivine-pyroxene-bearing aggregates in C2 meteorites do not satisfy the textural criteria of rapidly-quenched molten droplets. Their chemistry suggests that they cannot be the product of a simple melting of the matrix of the C2's.

Their textures, mineralogy, chemistry and the compositions of their metal grains are consistent with a condensation origin. The Fe/Mg fractionation between matrix and aggregates is a result of the incorporation of only a fraction of the total condensed metal by later forsterite and enstatite crystals. The rest of the metal was converted to troilite and oxidized iron at lower temperatures and incorporated into the matrix. There is some evidence for preferential loss of early Ni–Co-rich metal from the aggregates.

The high-temperature fraction of C2 chondrites is largely composed of primitive condensates. These meteorites may thus contain far more information about the condensation of the solar system than previously believed.

Acknowledgements—We thank STAN JOHNSON of Argonne National Laboratory for his excellent photographic work and Frederic Oldfield for computer calculations. Helpful discussions with O. J. Kleppa and L. H. Fuchs are gratefully acknowledged. Our thanks go to the National Museum of Natural History for providing many of the polished thin sections used in this study. We are indebted to the National Aeronautics and Space Administration for partial support of this work through grants NGR 14-001-249 and NGR 14-052-001. One of the authors (L. G.) was also supported by grants from the Research Corporation and the Louis Block Fund, The University of Chicago.

REFERENCES

Anders E. (1964) Origin, age, and composition of meteorites. Space Sci. Rev. 3, 583-714.

Anders E. (1968) Chemical processes in the early solar system, as inferred from meteorites. *Acc. Chem. Res.* 1, 289–298.

Anders E. (1971) Meteorites and the early solar system. Ann. Rev. Astron. Astrophys. 9, 1-34. Arrhenius G. and Alfvén H. (1971) Fractionation and condensation in space. Earth Planet. Sci. Lett. 10, 253-267.

CAMERON A. G. W. (1968) A new table of abundances of the elements in the solar system. In Origin and Distribution of the Elements (editor L. H. Ahrens), pp. 125-143. Pergamon Press.

CAMERON A. G. W. (1973) Abundances of the elements in the solar system. Space Sci. Rev. in press.

Fuchs L. H. (1969) Occurrence of cordierite and aluminous orthoenstatite in the Allende meteorite. *Amer. Mineral.* **54**, 1645–1653.

Fuchs L. H., Olsen E. and Jensen K. J. (1973) Mineralogy, mineral-chemistry and composition of the Murchison (C2) meteorite. *Smithson. Contrib. Earth Sci.* No. 10, 39 pp.

GOLDSTEIN J. I. and DOAN A. S., Jr. (1972) The effect of phosphorus on the formation of the Widmanstätten pattern in iron meteorites. *Geochim. Cosmochim. Acta* 36, 51-69.

GROSSMAN L. (1972) Condensation in the primitive solar nebula. Geochim. Cosmochim. Acta 36, 597-619.

GROSSMAN L. (1973) Refractory trace elements in Ca-Al-rich inclusions in the Allende meteorite. Geochim. Cosmochim. Acta 37, 1119-1140.

GROSSMAN L. and CLARK S. P., Jr. (1973) High-temperature condensates in chondrites and the environment in which they formed. *Geochim. Cosmochim. Acta* 37, 635-649.

HULTGREN R., ORR R. L. and KELLEY K. K. (1964 and later) Loose-leaf supplements to Selected Values of Thermodynamic Properties of Metals and Alloys. University of California, Berkeley. JAROSEWICH E. (1971) Chemical analysis of the Murchison meteorite. Meteoritics 6, 49-52.

Keil K., Huss G. I. and Wiik H. B. (1969) The Leoville, Kansas meteorite: a polymict breceia of carbonaceous chondrites and achondrites. Abstract. In *Meteorite Research*, (editor P. M. Millman), p. 217. Reidel.

- Krähenbühl U., Morgan J. W., Ganapathy R. and Anders E. (1973) Abundance of 17 trace elements in carbonaceous chondrites. *Geochim. Cosmochim. Acta* 37, 1353-1370.
- Kurat G. (1970) Zur Genese der Ca-Al-reichen Einschlüsse im Chondriten von Lancé. Earth Planet. Sci. Lett. 9, 225-231.
- LARIMER J. W. and Anders E. (1967) Chemical fractionations in meteorites—II. Abundance patterns and their interpretation. *Geochim. Cosmochim. Acta* 31, 1239-1270.
- LARIMER J. W. and Anders E. (1970) Chemical fractionations in meteorites—III. Major element fractionations in chondrites. *Geochim. Cosmochim. Acta* 34, 367–387.
- MARVIN U. B., WOOD J. A. and DICKEY J. S., JR. (1970) Ca-Al-rich phases in the Allende meteorite. Earth Planet. Sci. Lett. 7, 346-350.
- McKay D. S., Clanton U. S., Morrison D. A. and Ladle G. H. (1972) Vapor phase crystallization in Apollo 14 breccia. In Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 3, pp. 739-752. M.I.T. Press.
- OLSEN E., Fuchs L. H. and Forbes W. C. (1973) Chromium and phosphorus enrichment in the metal of Type II (C2) carbonaceous chondrites. *Geochim. Cosmochim. Acta* 37, 2037-2042.
- Onuma N., Clayton R. N. and Mayeda T. K. (1972) Oxygen isotope cosmothermometer. Geochim. Cosmochim. Acta 36, 169-188.
- OSBORN E. F., DEVRIES R. C., GEE K. H. and Kraner H. M. (1954) Optimum composition of blast furnace slag as deduced from liquidus data for the quaternary system CaO-MgO-Al₂O₃-SiO₂. Trans. AIME **200**, 33-45.
- RICHARDSON F. D. and JEFFES J. H. E. (1948) The thermodynamics of substances of interest in iron and steel making from 0°C to 2400°C, I: oxides. J. Iron Steel Inst. 160, 261–270.
- Scott E. R. D. (1972) Chemical fractionation in iron meteorites and its interpretation. *Geochim. Cosmochim. Acta* 36, 1205–1236.
- Turekian K. K., Clark S. P., Jr., Davis A. and Grossman L. (1973) Heterogeneous accumulation revisited. (Abstract) *Meteoritics* 8, 77-78.
- WÄNKE H., BADDENHAUSEN H., DREIBUS G., QUIJANO-RICO M., PALME H., SPETTEL B. and TESCHKE F. (1973) Multielement analysis of Apollo 16 samples and about the composition of the whole moon. Abstract. In *Lunar Science IV*, (editors J. W. Chamberlain and C. Watkins), pp. 761-763. Lunar Science Institute.
- Wood J. A. (1967) Chondrites: their metallic minerals, thermal histories and parent planets. *Icarus* 6, 1-49.