Refractory trace elements in Ca–Al-rich inclusions in the Allende meteorite

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Abstract—The condensation temperatures are calculated for a number of refractory trace metals from a gas of solar composition at 10^{-3} and 10^{-4} atm. total pressure. Instrumental neutron activation analysis of Ca–Al-rich inclusions in the Allende carbonaceous chondrite reveals enrichments of $22 \cdot 8 \pm 2 \cdot 2$ in the concentrations of Ir, Sc and the rare earths relative to Cl chondrites. Such enrichments cannot be due to magmatic differentiation processes because of the marked differences in chemical behavior between Ir and Sc, exhibited by their distributions in terrestrial igneous rocks and meteorites. All of these elements should have condensed from a cooling gas of solar composition above or within the range of condensation temperatures of the major mineral phases of the inclusions, which suggests that these inclusions are high-temperature condensates from the primitive solar nebula. Gas–dust fractionation of these materials may have been responsible for the depletion of refractory elements in the ordinary and enstatite chondrites relative to the carbonaceous chondrites.

INTRODUCTION

LORD (1965) PREDICTED that Ca–Al–Ti-rich phases will be the first minerals to condense from a cooling gas of solar composition. Since then, white inclusions containing melilite, spinel, perovskite and diopside have been reported from a number of C2 and C3 chondrites (see, for example, CHRISTOPHE, 1968; KEIL et al., 1969; FUCHS, 1969; KURAT, 1970). MARVIN et al. (1970) and LARIMER and ANDERS (1970) suggested that these aggregates were high-temperature condensates from the solar nebula based on their high concentrations of Ca, Al and Ti relative to Mg and Si. ONUMA et al. (1972) have independently arrived at the same conclusion based on the oxygen isotopic composition of the white inclusions. GROSSMAN (1972) and GROSSMAN and CLARK (1973) concluded that the mineral assemblages, textural relations and solid solution compositions of the minerals in the inclusions were formed in the solar nebula during high-temperature condensation processes.

   The purpose of this study is, first, to calculate which trace elements are so refractory that they would have condensed over the range of condensation temperatures of the major phases of the inclusions and, second, to determine if any of these trace elements are enriched in the inclusions relative to the Cl chondrites.

THEORETICAL PREDICTIONS

   CLARK et al. (1972) have discussed briefly the high-temperature condensation of a number of refractory trace metals from a gas of solar composition. The following discussion is the result of more detailed calculations for which the formation of gaseous oxides of these metals and the stabilities of some of their crystalline oxides are also considered.

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Table 1. Sources of free energy or vapor pressure data
for refractory trace metals

Gaseous species	Source	Crystalline phase	Source
Os	1	Sc_2O_3	3
Sc	1	Ta_2O_5	4, 6, 7
ScO	2	ZrO_2	8
Re	1	Y_2O_3	3
Ta	1	HfO_2	13, 4
TaO	4, 5	MoO_3	13
ZrO, ZrO_2	8	VO	14
Zr	9	VO_2	15
W	1	V_2O_3	13
WO	10, 5	ThO_2	13
Y	1		
YO	11		
Hf	1		
HfO	4, 5		
HfO_2	12		
Mo	1		
MoO	10, 5		
Ru	1		
Ir	1		
V	1		
VO	12		
Th, ThO, ThO_2	16		

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MANN et al. (1964). 12. CHANDRASEKHARAIAH (1967). 13.
ROBIE and WALDBAUM (1968). 14. GLASSNER (1957). 15. LORD
(1965). 16. ACKERMANN and RAUH (1971).

Table 1 gives the sources of thermodynamic data for all gaseous and crystalline
species considered. Free energies of gaseous VO and HfO_2 were derived from vapor
pressure data for crystalline VO and HfO_2, respectively. The vapor pressures are
order of magnitude estimates because of the uncertainties involved in the measure-
ment of very low pressures at very high temperatures, the relatively complex vapor-
ization behavior of these phases and the uncertainty in the exact molecular com-
positions of their coexisting vapors. These errors are reflected in the free energies of
the gaseous species and consequently, in their condensation temperatures. Free
energies of monatomic gaseous species were derived from vapor pressure curves
usually having pressure uncertainties on the order of 25 per cent.

Condensation temperatures for the trace metals were calculated in a similar
fashion to those of the major elements, as discussed by GROSSMAN (1972). The
partial pressure of each monatomic gaseous species as a function of temperature was
calculated from the mass balance equation for each element and from the thermo-
dynamic data for all the gaseous species considered for that element. Also required

was the temperature variation of P_0, previously computed at 10^{-3} atm. for each assemblage of major crystalline phases and found to be independent of pressure over a small pressure range (GROSSMAN, 1972). The trace elements consume completely negligible quantities of oxygen, allowing the use of these data. Given the free energies of the crystalline phases containing each element and P_0, the partial pressure of that element necessary to condense each phase can be calculated as a function of temperature and compared to its actual partial pressure in the system. The first condensate of each element is the phase which reaches saturation at the highest temperature.

These calculations are summarized in Table 2. For each element, the gaseous species are listed in the third column in order of decreasing abundance at its condensation point. Equilibrium condensation temperatures at 10^{-3} and 10^{-4} atm. total

Table 2. Molecular equilibria and condensation behavior of refractory trace metals

Element	Abundance* (Si = 10^6)	Gaseous species considered	Crystalline phases considered	First condensate	Condensation Temperature ($P_{tot} = 10^{-3}$ atm)(°K)	($P_{tot} = 10^{-4}$ atm)
Os	0·71	Os	Os	Os	1925	1840
W	0·16	WO, W	W	W	1885	1798
Zr	30	ZrO, ZrO$_2$, Zr	Zr, ZrO$_2$	ZrO$_2$	1840	1789
Re	0·055	Re	Re	Re	1839	1759
Hf	0·16	HfO $\approx$ HfO$_2$, Hf	Hf, HfO$_2$	HfO$_2$	1719	1652
Y	4·6	YO, Y	Y, Y$_2$O$_3$	Y$_2$O$_3$	1719	1646
Sc	33	ScO, Sc	Sc, Sc$_2$O$_3$	Sc$_2$O$_3$	1715	1644
Mo	2·52	Mo, MoO	Mo, MoO$_3$	Mo	1684	1603
Ir	0·43	Ir	Ir	Ir	1629	1555
Ru	1·6	Ru	Ru	Ru	1614	1541
V	900	VO, V	VO$_2$, V, VO, V$_2$O$_3$	V$_2$O$_3$	1534	1458
Ta	0·022	TaO, Ta	Ta, Ta$_2$O$_5$	Ta$_2$O$_5$	1499	1452
Th	0·034	ThO$_2$, ThO, Th	Th, ThO$_2$	ThO$_2$	1496	1429

* From CAMERON (1968).

pressure are given in the final two columns. Only those elements are listed for which a phase condensed above the temperature for diopside condensation (1450°K at 10^{-3} atm. GROSSMAN, 1972). Among the elements which condense at lower temperatures than this are U, Nb, Be, the rare earths, Rh, Pt, Pd, Au and Ag.

Gaseous and crystalline oxides of Os, Re, Ru and Ir are expected to play a minor role in the condensation behavior of these elements. Similarly, gaseous halides and hydrides of all the elements listed in Table 2 are assumed to be far less abundant than their corresponding oxides. Aside from these exceptions, the condensation temperatures listed in Table 2 may represent only lower limits because refractory carbides and nitrides of many of these elements may have higher condensation points than the phases considered here.

Solid solution

Solid solution effects dominate the condensation behavior of many trace elements. In the preceding calculations, the condensation point of each pure phase was calculated, i.e. each phase was assumed to condense at unit activity. It is clear, however,

that the partial pressure necessary for condensation of any metal is lowered considerably if it is allowed to form a dilute solid solution in a suitable host phase. This always leads to the initiation of condensation at a higher temperature than in the case of a pure phase and could cause elements having condensation temperatures, as pure phases, below 1450°K to condense over the same range as those of Table 2. Any element condensing at unit activity below 1758°K, the condensation point of Al_2O_3, the first major condensate at 10^{-3} atm. (GROSSMAN, 1972), can begin to condense at 1758°K as a trace constituent in Al_2O_3 if it fits into the Al_2O_3 lattice. Since the atomic ratio of Al to many of these elements is 10^5 to 10^7, this process could lead to their total removal from the gas phase.

In particular, solid solution effects can be expected to allow the condensation of the rare earths over the same temperature range as that for the condensation of some of the elements listed in Table 2. The second major phase to condense, perovskite at 1647°K, could provide lattice sites for the removal of the rare earths, as well as other trace elements (Sc, Y, Zr). Terrestrial perovskites containing up to 11 per cent rare earths by weight have been reported by BORODIN and BARINSKII (1960), demonstrating the affinity of the rare earths for the perovskite crystal structure. Condensation of the rare earth sesquioxides could thus begin at 1647°K. Since the Ti/La ratio in this system is $\sim 10^4$, a concentration of only ~ 100 ppm La_2O_3 in perovskite is required for total condensation of this element. Such a concentration could be achieved when pure La_2O_3 is still undersaturated by a factor of 10^4, which would be at about 1500°K at 10^{-3} atm. total pressure.

Although high-temperature data are lacking, the free energies of $SrTiO_3$ and $BaTiO_3$ at 298°K are very close to that of perovskite. Solid solution of these components in perovskite can be expected to cause the total condensation of Sr and Ba at temperatures in excess of 1450°K at 10^{-3} atm., well above the condensation points of the pure components.

Supersaturation

From Table 2 it is evident that lowering the total pressure by a factor of ten usually causes the condensation temperatures to fall by about 50–100°. This is equivalent to saying that the system would be supersaturated by a factor of ten with respect to these phases at 50–100° below their equilibrium condensation points. Thus, the final two columns of Table 2 can be used to estimate the degree of supersaturation of any of these elements at any temperature at 10^{-3} atm. Os, W, ZrO_2 and Re would be supersaturated by factors of 10 to 10^2 at the condensation temperature of corundum. These species could have crystallized by homogeneous nucleation from the supersaturated vapor at temperatures above 1758°K and could have served as heterogeneous nucleation sites for corundum at 1758°K. Any lower temperature condensate of the major elements could have also nucleated on grains of these refractory trace elements, on grains of corundum or on grains of those trace elements which condense between 1758°K and its condensation point.

ANALYTICAL TECHNIQUE

Sample preparation

The trace element analyses described here are part of a cooperative study of the chemistry and mineralogy of the Ca–Al-rich inclusions in Allende (KING *et al.*, 1973). At the University of

Houston, slabs of the Allende meteorite were cut with a diamond saw, using Texaco Almag lubricant. Sixteen white, subspherical to irregular, polycrystalline inclusions were located by visual inspection of the slab surfaces and were removed by Dr. E. A. King with steel needles and accessories. Individual inclusions and a sample of the bulk meteorite were pulverized with an alumina mortar and pestle and shipped to Yale in polystyrene bottles with polyethylene caps. Subsequent X-ray and microscopic inspection of the inclusions by the Houston group revealed that they were all composed predominantly of gehlenite and spinel, with varying but usually lesser amounts of perovskite, diopside, anorthite, glass and perhaps another pyroxene.

At the Smithsonian Institution, bulk samples of Allende were crushed with a hardened steel pestle on a steel plate and ground with an agate mortar and pestle. One aliquot sent to Yale by Dr. E. Jarosewich and Dr. R. S. Clarke, Jr. was used in this study.

At Yale, the 16 powdered inclusions and the bulk sample of Allende supplied by the Smithsonian were dried for one hour at 110°C and re-ground in an agate mortar. From each sample, two 25-mg aliquots were weighed into quartz irradiation vials. The vials were heat-sealed, washed in hot conc. HNO_3 and weighed.

Standards

Duplicate 25-mg aliquots of the silicate rock standards GSP-1, BCR-1, G-1 and the 'standard pot' (PERLMAN and ASARO, 1969; TUREKIAN and KHARKAR, 1970) were treated in exactly the same way as the samples and used as monitors for all elements except Ir and Au.

Twenty-mg aliquots of quartz powder were weighed into quartz irradiation vials. Standard solutions of Au and Ir were prepared from specpure gold foil and $(NH_4)_2IrCl_6$, respectively. Duplicate standards for each of these elements were made by pipetting 25 μl aliquots of these solutions on to the quartz powder substrates inside the irradiation vials in an attempt to duplicate the geometry of the samples. They contained 0·625 μg Au and 10·23 μg Ir, respectively. These standards were evaporated to dryness, heat-sealed, washed in hot conc. HNO_3 and weighed.

Throughout all subsequent irradiation and counting, an empty irradiation tube and another containing only 20 mg of quartz powder were run as blanks in parallel with all standards and samples.

Irradiation and counting

The vials were packed in an aluminum cylinder which was rotated about its axis, perpendicular to the neutron beam, at a constant speed throughout the irradiation. To further minimize any possible flux gradient perpendicular to the axis, the vials were arranged spirally such that one complete set of duplicate standards and samples was positioned closer to the cylinder axis than the other set. Since a flux gradient parallel to the axis was known to exist, all samples and standards were placed at the same height above the floor of the container.

Immediately on return to the laboratory, all vials were washed in hot conc. HNO_3 and counted on a 25 cm³ Ge(Li) diode detector in reproducible geometry at a dead time of less than 20 per cent.

Irradiations were carried out in Union Carbide's reactor at Sterling Forest, New York. The sequence of irradiations and counting periods was identical to that used by TUREKIAN and KHARKAR (1970) and KHARKAR and TUREKIAN (1971).

All spectra for blanks, standards and samples were read out on paper tape. Suitable regions of the spectra for peak and background readings were located visually. Data processing was performed on an IBM 7094/7040 computer. The gamma-ray data reduction program corrected all peaks in all samples, standards and blanks for background and decay during counting, corrected these peak areas to the same point in time, subtracted blank corrections and, finally, compared the peak area of each element in every sample to the specific activity calculated for that element in every standard used. Errors due to counting statistics were propagated through the entire sequence of calculations.

A third 25-mg aliquot of the first inclusion was selected for a fission track uranium determination using the method of BERTINE et al. (1970). A single aliquot of W-1 was used as a standard, at a concentration of 0·46 ppm U.

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RESULTS

Standards

The isotope counted and the concentration selected from the literature for each silicate standard used for each element are listed in Table 3. In the final column is given the relative

Table 3. Standards used for each element

| Element | Isotope | Concentration in silicate standards | | | | Range of specific activities (%) |
| | | BCR-1 | GSP-1 | G-1 | SP | |
		(ppm)				
Mn	Mn^{56}	1320 (2)	317·5 (2)			±4
Na	Na^{24}	24000 (2)	20616 (2)	24200 (1)	2610 (3)	±3
La	La^{140}	25·20 (2)		104 (1)	44·90 (3)	±3
Sm	Sm^{153}				5·78 (3)	±1
Au	Au^{198}					±1
Yb	Yb^{175}				2·80 (3)	±2
Ir	Ir^{192}					±1
Fe	Fe^{59}	92955 (4)	30200 (4)			±1
Sc	Sc^{46}	33·10 (4)			19·85 (4)	±1
Co	Co^{60}	35·15 (4)			13·10 (4)	±1
Eu	Eu^{152}	2·26 (4)	2·79 (4)		1·43 (4)	±3

Sources of data: (1) selected from compilation of FLEISCHER (1969).
(2) selected from compilation of FLANAGAN (1969).
(3) PERLMAN and ASARO (1969).
(4) KATZ and GROSSMAN (1973).

range of specific activities measured in the standards for each element, to the nearest per cent. For Sm and Yb, only one silicate standard was used and the differences between the specific activities of duplicate standards are largely due to counting statistics. For Mn, La and Na, for which 2, 3 and 4 standards, respectively, were used, counting statistics usually fall far short of accounting for the differences in specific activities from one standard to the next. This reflects the uncertainty in the elemental concentration of the silicate standards. For Fe, Sc, Co and Eu, however, counting statistics again account for most of the difference between the specific activities of different standards. The data for these four elements were taken from KATZ and GROSSMAN (1973), who attempted to determine concentrations of these elements which are consistent with each other in the silicate standards. Differences between duplicate Au and Ir standards represent counting uncertainty and the reproducibility of the preparation of pipetted standards. When comparing analytical data obtained in this study with those of other workers, the differing degrees of uncertainty in the concentrations of different elements in the silicate standards used here must be considered.

Where samples were compared to more than one standard for a single element, the different concentrations calculated for each sample were averaged.

Samples

All analyses are presented in Table 4. The A and B suffixes to the sample numbers denote separate 25-mg aliquots of the same inclusion or sample of the bulk meteorite. For La, Sm,

Table 4. Allende inclusions: results of instrumental neutron activation analysis.
Values in ppm unless otherwise indicated; n.d. = not detected

Sample	Fe(%)	Mn	Na	Sc	La	Sm	Eu	Yb	Co	Ir	Au
1A	8·91	608	2520	79·9	3·08	1·40	0·58	1·83	250	7·12	0·18
1B	8·89	659	2451	77·0	±0·11	±0·02	0·90	±0·30	249	7·38	±0·01
2A	4·40	306	2027	109·5	3·94	2·01	1·44	2·81	139	10·58	0·40
2B	4·44	335	2006	111·8	±0·11	±0·03	1·07	±0·35	139	10·62	±0·01
3A	6·34	420	2073	116·6	3·75	1·89	1·10	1·61	186	8·48	0·58
3B	6·53	451	2196	116·3	±0·12	±0·03	1·06	±0·36	198	8·87	±0·01
4A	9·20	690	2734	92·0	3·84	1·86	0·51	0·39	229	8·44	0·21
4B	9·37	726	2814	99·1	±0·12	±0·03	0·59	±0·34	234	7·63	±0·01
5A	3·98	276	896	119·3	2·94	1·66	0·94	2·69	149	10·69	0·17
5B	3·88	291	860	119·8	±0·10	±0·03	1·10	±0·35	151	11·85	±0·01
6A	5·46	404	8372	123·7	5·03	1·68	1·27	2·47	124	8·39	0·16
6B	5·46	432	8289	124·0	±0·17	±0·03	0·91	±0·37	123	9·05	±0·01
7A	1·45	41	677	130·1	4·60	2·40	1·49	3·21	89	9·22	0·14
7B	1·37	51	683	129·7	±0·11	±0·03	1·37	±0·37	87	8·36	±0·01
8A	6·55	740	25047	16·8	3·99	2·18	0·38	n.d.	105	0·18	0·48
8B	6·49	797	23990	16·6	±0·25	±0·02	0·31		103	0·17	±0·01
9A	4·63	417	5408	39·2	3·83	1·79	1·37	2·79	119	6·55	0·26
9B	4·48	420	5184	38·4	±0·13	±0·03	1·45	±0·26	117	6·34	±0·01
10A	9·49	722	8400	67·4	2·90	1·53	0·81	2·20	223	6·38	0·12
10B	9·40	748	13214	67·5	±0·16	±0·03	0·72	±0·32	223	4·79	±0·01
11A	8·26	644	5139	98·5	3·09	1·64	0·86	1·87	231	6·48	0·49
11B	8·33	662	17714	98·9	±0·14	±0·03	0·84	±0·36	232	6·70	±0·01
12A	7·72	638	4975	69·8	2·97	1·54	0·84	1·35	181	4·89	0·20
12B	7·69	655	4801	70·1	±0·13	±0·03	0·98	±0·31	183	5·13	±0·01
13A	2·55	189	1026	101·8	2·92	1·50	1·05	2·28	98	8·15	0·25
13B	2·57	199	1012	101·0	±0·10	±0·03	1·18	±0·35	93	7·29	±0·01
14A	3·52	292	2043	105·1	5·19	2·70	1·00	3·42	95	9·44	0·34
14B	3·63	323	1880	105·1	±0·13	±0·04	1·05	±0·37	94	10·14	±0·01
15A	5·52	514	17019	102·3	3·65	2·27	1·04	2·28	99	8·79	0·17
15B	5·31	506	16360	102·5	±0·21	±0·04	1·06	±0·38	99	8·58	±0·01
16A	8·25	563	2080	81·4			1·23		215	8·40	
16B	8·28	587	2027	81·1			1·01		215	8·93	
SAA*	23·28	1564	3668	11·6	0·47	0·22	0·15	n.d.	622	0·87	0·16
SAB	22·89	1590	3608	11·5	±0·09	±0·03	0·17		611	0·91	±0·01
KAA*	22·95	1514	3708	11·4	0·50	0·26	0·10	0·47	616	0·91	0·22
KAB	21·84	1580	3413	10·6	±0·09	±0·03	0·07	±0·29	593	0·96	±0·01
Standard deviation of differences between duplicates											
	0·14	24	1010	0·9			0·11		3	0·44	

* SA and KA are samples of the bulk meteorite.

Yb and Au, only the A aliquot was counted, so the counting uncertainty in ppm is given as the best approximation to the precision of these determinations. For the elements for which duplicate determinations are available, the standard deviation of the differences between duplicates is given in the last line of Table 4. For any element, this is a mean measure of the reproducibility of its abundance in this suite of samples and includes all contributing factors such as uncertainty in the blank correction, counting uncertainty, weighing errors and sampling errors. The data indicate severe sample heterogeneity for Na. Poorer-than-average reproducibility is indicated for Mn, Eu and Ir.

The U content of sample 1C is 30 ± 15 ppb.

The average Mn, La, Sm and Eu concentrations in the bulk sample of Allende supplied by the Smithsonian, SA, are within counting statistics of those in the sample supplied by King, KA.

Fe, Na, Sc and Co are significantly higher and Ir and Au lower in SA than in KA, although differences between duplicate samples of KA are greater than the differences between the average values of KA and SA for Fe, Na and Co.

Accuracy

The concentrations of all 11 elements determined here in the bulk samples of Allende from both sources are compared to those reported for the Allende meteorite by other workers in Table 5. In the final column, the first line of data for each element applies to SA and the second

Table 5. Comparison of analyses of the Allende meteorite.
Values in ppm unless otherwise indicated. n.d. = not detected

Element	KING (1969)	EMERY et al. (1969)	MORGAN et al. (1969)	WAKITA and SCHMITT (1970)	CLARKE et al. (1970)	WARREN (1971)	BAEDECKER (1972)	GILLUM and EHMANN (1971)	This work
Mn	1300	1700		1450 ± 40	1400	1450			1564, 1590 1514, 1580
Na	3000		3300 ± 100	3370 ± 100	3300	3400			3668, 3608 3708, 3413
Co	700	600	684 612	640 ± 20	600	640			622, 611 616, 593
Fe	23·6%	27·8%	24·4 ± 0·4%	21·9 ± 0·4%	23·85%	23·9%			23·28%, 22·89% 22·95%, 21·84%
Sc		10	12·2 ± 0·2	11·0 ± 0·5	11	11			11·6, 11·5 11·4, 10·6
Ir			0·71 ± 0·03			0·71	0·78, 0·80, 0·81		0·87, 0·91 0·91, 0·96
Au			0·26 ± 0·01					0,21	0·16 0·22
La				0·44 ± 0·02	0·7				0·47 0·50
Sm				0·29 ± 0·01	0·5	0·31			0·22 0·26
Eu				0·107 ± 0·005	0·1	0·113			0·15, 0·17 0·10, 0·07
Yb				0·32 ± 0·02	0·4				n.d. 0·47

to KA. The Mn, Co, Fe, Sc, La, Yb and Eu determinations of this work are all within counting statistics of the ranges of values reported for these elements in the literature. Three of the Na values reported here and all the Ir determinations are slightly higher than the concentrations of these elements reported in the literature. One Sm and one Au value are significantly lower than those of other workers. The Na and Sm discrepancies may be related to uncertainties in the concentrations of these elements in the silicate standards, discussed above.

As far as the inclusions themselves are concerned, very little analytical data have appeared in the literature. GAST et al. (1970) have reported rare earth abundances in a 'Ca-rich inclusion' from Allende. These data appear in Table 6 where they are compared with the ranges of concentration found in the suite of inclusions of the present study. It is evident that the inclusion of GAST et al. (1970) is relatively rare earth-rich, having La and Eu abundances near the upper end of the ranges determined here and Sm and Yb values lying above the ranges reported here, but just within or slightly beyond the ranges of uncertainty due to counting statistics. The slightly lower Sm and Yb concentrations found in this study may be due to the adoption of low concentrations of these elements in the silicate standards.

CLARKE et al. (1970) have described gehlenite–spinel–perovskite-bearing chondrules from Allende. In a systematic study of the abundances of 15 elements in 61 individual Allende chondrules, WARREN (1971) has analyzed one containing 17·4 per cent Al, 12·1 per cent Ca and 1·25 per cent Ti (A in Table 6 of this study) and another containing 13·6 per cent Al, 19·7 per cent Ca and 0·74 per cent Ti (B in Table 6). In a similar study of the compositions of 36 Allende chondrules, MENNINGA (1971) found one containing 8·71 per cent Al, 2·5 per cent Ca and 0·5 per cent Ti (C in Table 6). Although no mineralogical analyses are available for any of these,

Table 6. Comparison of analyses of Ca-rich inclusions in the Allende meteorite. Values in ppm unless otherwise indicated

	GAST et al. (1970)	WARREN (1971) A	B	MENNINGA (1971) C	This work
La	4·63 ± 0·19				2·90–5·19
Sm	2·82 ± 0·11	3·0	3·4		1·40–2·70
Eu	1·30 ± 0·05	1·3	1·15	0·31 ± 0·04	0·31–1·49
Yb	3·96 ± 0·16				0·39–3·42
Na		1·53%	0·16%	1·84 ± 0·02%	0·07%–2·50%
Sc		117	133	64·2 ± 0·2	16·6–130·1
Mn		360	26	0·073 ± 0·002%	41–797
Fe		5·8%	0·37%	9·65 ± 0·08%	1·37%–9·49%
Co		76	8	282 ± 2	87–250
Ir		5·6	5·8	3·63 ± 0·03	0·17–11·85
Au				0·094 ± 0·01	0·12–0·58

they almost certainly contain gehlenite, spinel and perovskite. Eu, Na, Sc and Ir abundances in all of these chondrules lie within the concentration ranges for these elements determined in the present study. One Fe, one Co and the Sm values lie slightly above the range reported here, but one Mn, one Fe, the Au and two Co determinations are lower than the lowest concentrations found here. It will be shown that a wide range of Fe, Co and Mn concentrations may be expected, depending on the degree of contamination of the inclusions by matrix material. Again, the Sm data of this study are slightly lower than those of other workers. This may be related to uncertainty in the concentration of this element in SP.

DISCUSSION

The data presented in Table 4 allow the elements considered in this study to be classified into three categories. Fe, Mn and Co fall into the first group of elements which are depleted in all of the inclusions relative to the bulk meteorite. The second class consists of the elements Sc, La, Sm, Eu, Yb and Ir which are enriched in all of the inclusions relative to the bulk meteorite (except for Ir in 8). In the final group are Na and Au which may have concentrations in the inclusions less than, equal to or greater than their respective abundances in the bulk meteorite. Furthermore, the three elements in group one display strong positive correlations with one another, as demonstrated by the Fe–Mn plot of Fig. 1. The elements of group two also show marked positive correlations with each other as shown for Sc–Ir in Fig. 2 but, in contrast, they each exhibit striking negative correlations with all of the elements of the first group. Finally, the elements of group three do not correlate positively or negatively with each other or with any of the elements of the other groups.

Table 7 is the correlation matrix for the 17 samples in which all 11 elements were determined. Table 8 is the correlation matrix of all 36 samples for which complete analytical data were available for only 7 elements. For 17 samples, a correlation coefficient greater than 0·56 is required for 99 per cent confidence that the pair of elements in question are correlated. For 36 samples, this critical value is 0·39. Comparison of Tables 7 and 8 reveals that, in nearly every case, increasing the number of samples strengthens positive and negative correlations but results in lower correlation coefficients for pairs of elements which showed insignificant correlation in 17 samples.
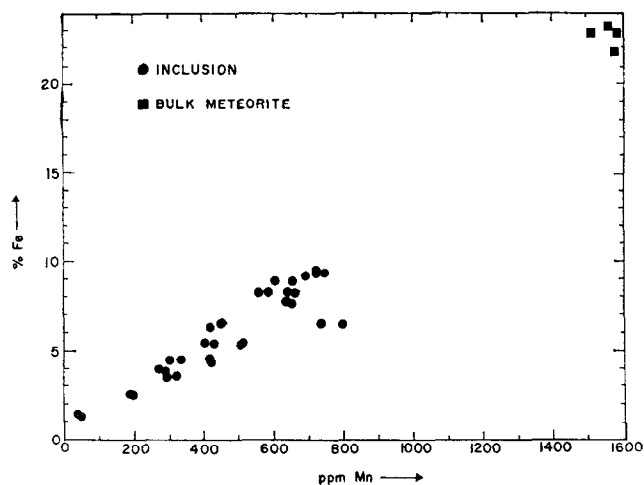
2

Fig. 1. The Fe–Mn correlation in the Ca-rich inclusions from Allende. The pure inclusions contain very little Fe or Mn. Their concentrations in these samples may be proportional to the degree of contamination of the pure inclusions by the meteorite matrix. Symbols are larger than the error bars due to counting statistics.
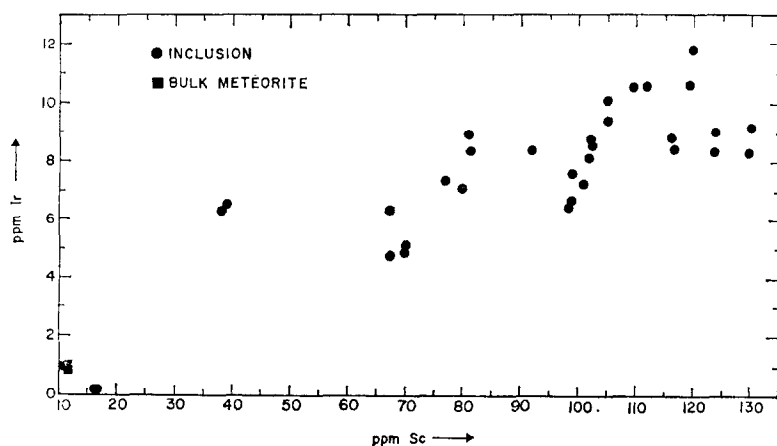

Fig. 2. The Ir–Sc correlation in the Ca-rich inclusions from Allende. The bulk meteorite contains very small amounts of Ir and Sc. In general, the samples least contaminated by matrix material are most enriched in Sc and Ir. Symbols are larger than the error bars due to counting statistics.

The simplest interpretation of the Fe–Mn–Co correlations is that their covariance plots represent two-component mixing lines where the high-iron end-member is the bulk meteorite and the low-iron component is the actual pure Ca-rich inclusion. Such mixing may have occurred by contamination of the inclusions with the meteorite matrix material at the time they were removed from the meteorite in the laboratory. Such reasoning implies that the pure inclusions contain ≤46 ppm Mn, ≤1·4 per cent Fe and ≤88 ppm Co, the lowest concentrations found. KURAT (1970) has

Table 7. Inter-element correlation coefficients for 17 samples*

	Na	Mn	Sc	La	Sm	Eu	Yb	Co	Ir	Au
Fe	−0·018	0·922	−0·687	−0·811	−0·827	−0·770	−0·681	0·924	−0·699	−0·164
Na		0·148	−0·348	0·126	0·197	−0·207	−0·327	−0·174	−0·417	0·152
Mn			−0·765	−0·778	−0·776	−0·815	−0·749	0·874	−0·777	−0·114
Sc				0·617	0·579	0·689	0·663	−0·613	0·864	0·034
La					0·867	0·674	0·570	−0·833	0·598	0·203
Sm						0·622	0·554	−0·851	0·584	0·264
Eu							0·811	−0·716	0·731	0·069
Yb								−0·607	0·753	−0·104
Co									−0·621	−0·172
Ir										−0·045

* 99 per cent confidence level is 0·56.

reported the results of microprobe analyses of gehlenite-bearing inclusions from Lancé. His Fe (0·16 per cent) and Mn (<400 ppm) data confirm the relatively low abundances of these elements in the pure inclusions inferred from the present study. CLARKE et al. (1970) described a similar inclusion in Allende which contains 1·8 per cent Fe, undetectable Mn and <100 ppm Co as well as a gehlenite-bearing chondrule containing only 0·29 per cent Fe, 160 ppm Mn and <100 ppm Co. Since these data are based on physically separated samples, they may suffer from the same contamination problem reported here. The Fe analyses of Table 4 thus indicate that most of the inclusion samples are contaminated with between 10 and 25 per cent matrix material, not an unreasonable amount considering that their total masses are sometimes less than 100 mg and their average diameter is only 6–7 mm. Although no smooth trend of increasing contamination with decreasing sample size is present, it is worthy of note that the highest Fe content (9·45 per cent) is in the smallest inclusion (72 mg) and the lowest Fe (1·41 per cent) is found in an inclusion weighing 259 mg.

Similarly, the marked negative correlations of group two elements with those of group one can also be interpreted as mixing curves, with the concentrations of Sc, Ir and the rare earths decreasing with increasing dilution of the inclusions by matrix material. The scatter of the data observed in the correlation plots for group two elements (Fig. 2, for example) may indicate that the pure inclusions themselves, though all enriched in these elements, contain variable concentrations of them, perhaps correlating with the abundance of one or two of the minerals of the inclusions.

Table 8. Inter-element correlation coefficients for 36 samples*

	Na	Mn	Sc	Eu	Co	Ir
Fe	−0·011	0·951	−0·704	−0·796	0·954	−0·699
Na		0·158	−0·312	−0·267	−0·160	−0·425
Mn			−0·786	−0·850	0·900	−0·785
Sc				0·682	−0·627	0·880
Eu					−0·734	0·751
Co						−0·616

* 99 per cent confidence level is 0·39.

In the same way, the scatter observed in the plots for the first group of elements suggests that the meteorite matrix is also inhomogeneous in composition.

Figure 3 is a plot of the Fe concentrations in the inclusions versus the Na contents. ,KURAT'S (1970) microprobe data show <1500 ppm Na and <400 ppm Na
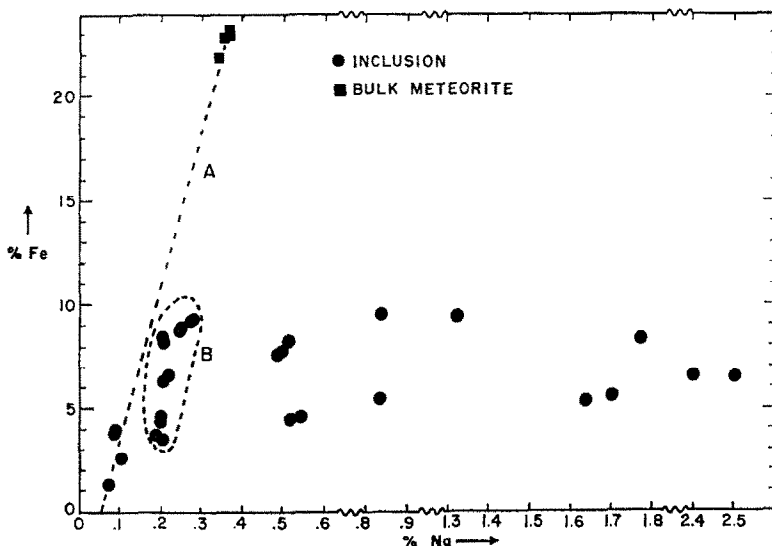

Fig. 3. Na and Fe abundances in the Ca-rich inclusions from Allende. There is some suggestion of mixing between a Na–Fe-rich bulk meteorite component and a Na–Fe-poor inclusion component, but many samples show evidence of the addition of a third Na-rich component. Symbols are larger than the error bars due to counting statistics.

for two Lancé inclusions, significantly lower Na abundances than most of the analyses of Table 4. If the inclusions of this study were contaminated with matrix material, the points in Fig. 3 should plot along a line such as that labelled 'A', connecting the bulk meteorite (∼3600 ppm Na) composition with one representing the average pure inclusion (<0·5 per cent Fe, <1000 ppm Na). There is only a slight suggestion that such a linear array exists, with the cluster of points 'B' appearing to have a relatively small excess of Na over that expected from their Fe content. The remaining one-third of the Na analyses are greater than 4500 ppm and bear no relationship to the Fe contents. Among these are inclusions 10 and 11, for which duplicate Na analyses differ by factors of >2 and >3, respectively, indicating the possible presence of a poorly-sampled, trace, Na-rich mineral suggestive of the rare occurrence of nepheline and other feldspathoids in similar inclusions (CHRISTOPHE, 1969; FUCHS, 1969; MARVIN et al., 1970; CLARKE et al., 1970). Thus, in order to account for the Na content of these samples, a third component must be present, in addition to the primitive inclusion component and the meteorite matrix component.

The Au concentrations bear no relationship to the abundances of any other element determined (see Table 7). They vary from 0·12 ppm to 0·58 ppm, whereas the average Au content of the bulk meteorite is 0·19 ppm (see Table 4). Since Au

does not correlate with Na, it could only have entered the inclusions with the Na-rich component if this third component had a variable Au/Na ratio. Since it does not correlate with any of the elements of group one, it could only be associated with the matrix contamination if the matrix is much more heterogeneous with respect to Au than to Fe, Co and Mn. That such heterogeneities do indeed exist in Allende is supported by the data of WARREN (1971) which show that the Au/Fe ratio can vary from 1.04×10^{-6} to 2.54×10^{-5} from chondrule to chondrule in Allende. MENNINGA (1971) found this ratio to vary from 1.13×10^{-7} to 4.3×10^{-6} in his study of individual Allende chondrules. It appears then that the rather wide range of Au values found here could have been generated by varying degrees of contamination by a matrix exceedingly heterogeneous with respect to Au.

If we correct the Ir, Sc, La, Sm, Eu and Yb concentrations of all inclusions for matrix contamination, assuming that the pure inclusions contain no Fe, Co or Mn, we can compare them to the abundances of these elements in the Cl's Ivuna and Orgueil in order to better understand the condensation process. The data so corrected and compared appear in Table 9 where it can be seen that the pure inclusions are enriched in these elements by factors of 18·3 to 25·7 relative to Cl's. It will be shown that such high concentrations of these elements are unlikely to have resulted from magmatic differentiation but are quite consistent with an origin for these inclusions by condensation processes.

Table 9. Average elemental concentrations in Ca-rich inclusions, corrected for matrix contamination, and enrichment factors relative to Cl's

	Average concentration in pure Ca-rich inclusions (ppm)	Average concentration in Orgueil and Ivuna (ppm)	Enrichment factors*
Ir	10·9	0·45[1]	24·1 ± 4·6
Sc	128·1	5·6[2]	22·9 ± 5·1
La	4·9	0·19[2]	25·7 ± 4·7
Sm	2·4	0·133[2]	18·3 ± 3·0
Eu	1·4	0·053[2]	25·6 ± 4·9
Yb	2·8	0·137[2]	20·4 ± 6·7

Sources of Cl abundance data:

1. Average of EHMANN et al. (1970) and CROCKET et al. (1967).
2. SCHMITT et al. (1964).

   * Enrichment factor = average concentration in Ca-rich inclusion/average concentration in Orgueil and Ivuna.

Ir and Sc in terrestrial igneous rocks

Although a search of the literature reveals little detailed understanding of the behavior of Ir during terrestrial magmatic differentiation, the following general observations have been made. CROCKET (1969) has confirmed that the platinum metals, as a group, are enriched in terrestrial basic and ultrabasic rocks relative to granites. In particular, GREENLAND (1971) has found that the Ir concentrations in a differentiated tholeiitic intrusion decrease from 0·25 ppb in the mafic zone to 0·006 ppb in the salic zone. In the same study, a close correlation was evident between Ir and Cr concentrations, perhaps related to crystallochemical similarities between Ir^{4+} and Cr^{3+}. This correlation was obscured only in the zone of sulphide precipitation, where Ir was enriched relative to Cr. RAZIN et al. (1965), in a study of the distribution of the platinum metals in the Inaglinsk Massif, discovered 200–900 ppb Ir in chrome-spinel-bearing

dunites and only 0·4–40 ppb in the associated pyroxene-bearing rocks. They also found that chrome-spinel contained an average of 30 times more platinum metals than coexisting olivine. During the normal course of terrestrial magmatic differentiation, it appears that the depletion of Ir in acidic rocks relative to basic ones is related to its strong fractionation into high-temperature chromite crystals and sulphide liquids.

In terrestrial igneous rocks, the distribution of Sc is controlled primarily by its affinity for the crystal structures of pyroxene and amphibole. The summary by FRONDEL (1970) shows that Sc rarely exceeds 10 ppm in dunites and peridotites and 50 ppm in basalts and gabbros. On the other hand, pyroxenites and hornblendites may have Sc contents up to 200 ppm while the Sc concentration in andesites and granites is usually less than 20 ppm.

It seems that the only product of normal terrestrial magmatic processes which could potentially concentrate both Ir and Sc would be a chromite- or sulphide-bearing pyroxenite. Although it can be argued that the gehlenite–spinel–perovskite-bearing inclusions in the C3's commonly contain a mineral having the spinel structure and often contain pyroxene, the omnipresent gehlenite and perovskite, if magmatic in origin, would indicate a substantially different and more complex pre-crystallization history than a chromite–pyroxenite. Sulphides have only rarely been observed inside the inclusions. Microprobe analyses of spinels in the Lancé inclusions (KURAT, 1970) show that their compositions are very close to the Mg–Al end-member, containing 0·1 to 8 per cent FeO and a maximum of only 0·3 per cent Cr_2O_3, much lower than Ir-enriched terrestrial spinels. Also, the Ca–Al-rich inclusions never contain olivine, not even as an accessory mineral, unlike Ir-enriched, spinel-bearing terrestrial ultrabasic rocks.

Ir and Sc in meteorites

The Ir content of carbonaceous, enstatite and ordinary chondrites usually lies between 0·2 and 0·9 ppm while that of achondrites is as much as 100 times lower (EHMANN and REBAGAY, 1970; CROCKET et al., 1967; MÜLLER et al., 1971). The Ir concentrations in ordinary chondrites are related to their metallic iron contents, the H group containing 0·7–0·8 ppm and the L group 0·4–0·5 ppm (MÜLLER et al., 1971). The metal phase of the Eagle Station pallasite was found to contain 2·81 ppm Ir while the silicate phase contains only 0·13 ppb (BAEDECKER, 1967), demonstrating the siderophile behavior of Ir. Meteoritic metal usually contains 10–40 times more Ir than coexisting sulphides (EHMANN et al., 1970). Meteoritic silicates containing more than 1 ppm Ir are extremely rare, but iron meteorites often have Ir concentrations between 1 and 60 ppm (COBB, 1967; WASSON, 1969).

Because of the siderophile behavior of Ir, processing of metal-bearing meteoritic matter seems insufficient to concentrate Ir to the levels observed in the metal-free Ca-rich inclusions. That their Ir concentrations are not associated with metal or sulphide grains is confirmed by the strong negative correlation of Ir with both Fe and Co.

Sc concentrations in meteorites have been summarized by FRONDEL (1970). The abundance of Sc seldom exceeds 10 ppm in chondrites, but usually falls between 25 and 50 ppm in achondrites. Sc concentrations in excess of 100 ppm are very rare in meteoritic materials and could only be produced from them via severe fractionation processes.

The mineralogy and trace element content of the Ca-rich inclusions thus appear to rule out their origin by normal magmatic differentiation processes acting on observed meteoritic starting materials.

Condensation of the refractory elements

On the other hand, the condensation of a cooling gas of solar composition is expected to result in the enrichment of the early condensate phase assemblage in the elements of Table 2. At a total pressure of 10^{-3} to 10^{-4} atm., Sc, Ir and the rare earths condense over the same temperature range as corundum, perovskite, melilite and spinel. CROCKET *et al.* (1967) were the first to point out the high condensation temperature of Ir. LARIMER and ANDERS (1970) and EHMANN and GILLUM (1972) suggested that the least volatile siderophile elements may have been fractionated with the refractory lithophile elements.

Many workers have noted relatively high concentrations of some of the other refractory elements in Ca-rich inclusions similar to those studied here. KURAT (1970) has described perovskite containing 2·2 per cent ZrO_2 and 1·1 per cent Y_2O_3 from a Lancé inclusion whose overall Zr and Y concentrations were calculated to be ~1500 ppm and ~800 ppm, respectively. These represent substantial enrichments relative to their concentrations in C3's, 9–12 ppm Zr and 2–3 ppm Y (CLARKE *et al.*, 1970). EHMANN and REBAGAY (1970) have reported average Zr and Hf concentrations in 'white inclusions' from Allende of 24 ppm and 0·36 ppm, as compared to abundances in the black matrix of 1·6 ppm and 0·14 ppm, respectively.

If the major condensates began to nucleate only on pre-existing refractory grains of Os, W, ZrO_2 and Re, a very large fraction of each of these trace metals may have been physically trapped inside corundum, perovskite and melilite crystals. Similarly, once condensation of these major phases had begun, their crystals could have provided suitable substrates for the condensation of the remaining refractories, HfO_2, Y_2O_3, Sc_2O_3, Mo, Ir, Ru, V_2O_3, Ta_2O_5, ThO_2 and the rare earths and any supersaturated, uncondensed, higher-temperature refractories, either by providing heterogeneous nucleation sites for them or by providing crystal structures suitable for the formation of solid solutions with some of them. The crystallization of the major phases probably was a very efficient mechanism for the scavenging of the trace metals from the vapor.

That these high-temperature condensates have also been involved in the chondrule-forming process is indicated by the high refractory element concentrations in some Allende chondrules reported by WARREN (1971) and MENNINGA (1971), as seen in Table 6. In addition, two other Ca–Al–Ir-rich Allende chondrules reported by WARREN (1971) contain 980 and 710 ppm V while normal chondrules contain only 100–200 ppm V. OSBORN (1971) reported a chondrule from the C4 Karoonda which contains 22·5 per cent Al, 87 ppm Sc and 24 ppm Ir and OSBORN *et al.* (1973) have discovered Ir–Al and Ir–Sc correlations in chondrules from ordinary chondrites.

The Na-*rich component*

The high Na concentrations sometimes observed in these Ca–Al-rich inclusions are probably related to the presence of small quantities of feldspathoids such as nepheline ($NaAlSiO_4$) and sodalite ($3NaAlSiO_4 \cdot NaCl$) which have sometimes been reported as accessory phases in similar inclusions in Allende and other C3 chondrites (see references above). These minerals are probably also the hosts for high concentrations of K (GAST *et al.*, 1970), I and Xe^{129} (PODOSEK and LEWIS, 1972). Equilibrium calculations show that both of these minerals could only condense from

a gas of solar composition at temperatures below 1000°K and they probably would not appear even then due to the removal of Na from the vapor by feldspars above 1100°K. Such phases are thus completely out of condensation equilibrium with the major minerals of the inclusions, which are stable condensates in equilibrium with the gas between 1750° and 1450°K at 10^{-3} atm.

ARRHENIUS and ALFVÉN (1971) and ARRHENIUS (1972) have proposed that this apparently anomalous coexistence of Ca–Al-rich refractory compounds with alkali-halogen-rich volatile minerals can be explained by condensation of low-temperature grains from a very low-pressure, high-temperature plasma. In this model, ionization effects control the condensation sequence, with Ca, Al and Ti only becoming neutral at gas temperatures between 5000° and 6000°K, when Na also becomes available for condensation. They claim that grains forming at these plasma temperatures have temperatures below the condensation points of both feldspathoids and Ca–Al silicates and, consequently, they condense together. But Ir becomes neutral at 10,000°K, when grain temperatures are below its condensation point. Similarly, Mg and Si are neutral at 8000°K, when grain temperatures are below the condensation temperatures of forsterite and enstatite, even at the extremely low pressures envisioned by these workers. It is difficult to understand why these inclusions contain Ir, having high neutralization and condensation temperatures, and feldspathoids, having low neutralization and condensation temperatures, while the common meteoritic magnesium silicates, with intermediate temperatures, are absent (FUCHS, 1969). The ionization-controlled condensation model fails to account for these observations.

The author has previously suggested (GROSSMAN, 1972) that the feldspathoids in the inclusions have little to do with condensation processes, but are the result of later, secondary reactions between high- and low-temperature condensates in the meteorite parent bodies. The necessity of a third, extraneous, Na-rich component to account for the Na abundances in the samples studied here is in agreement with this hypothesis. The I–Xe data of PODOSEK and LEWIS (1972) show that the I and therefore probably the Cl, were emplaced in the inclusions at an early date. The data also suggest that the feldspathoids may have formed over a 4 m.y. time span, which is probably 10 to 100 times longer than the condensation time of the solar system (CLARK et al., 1972).

Enrichment factors

At complete equilibrium, the condensate phase assemblage at 1450°K and 10^{-3} atm. total pressure contains 100 per cent of the total TiO_2, Al_2O_3 and CaO as well as 10 per cent of the MgO and 14 per cent of the SiO_2 in the system. This temperature is thought to be close to that at which reaction ceases between vapor and the high-temperature condensate phase assemblage of the Ca–Al-rich inclusions (GROSSMAN, 1972). If it is assumed that the average analyses of the Orgueil and Ivuna Type I carbonaceous chondrites (WIIK, 1956) are representative of the mean composition of the condensable matter of the solar system, one can calculate that the 1450°K equilibrium condensate assemblage would have consumed 8·03 weight per cent of the total condensable matter. If the refractory trace metals were each scavenged from the vapor by these high-temperature condensates with 100 per cent efficiency,

they should show concentration enrichments of $100/8\cdot03 = 12\cdot48$ relative to their mean concentrations in Orgueil and Ivuna. Such enrichments are approximately a factor of two lower than those actually observed (see Table 9). KURAT (1970), however, reported that the diopside forms narrow rims surrounding the inclusions in Lancé, indicating that most of the melilite did not take part in the reaction to form diopside and that equilibrium was not attained at 1450°K (GROSSMAN, 1972). If the formation of diopside at this temperature is neglected, the condensate phase assemblage is calculated to have consumed $5\cdot59$ wt. % of the condensable matter, leading to an enrichment factor of $17\cdot9$, which is much closer to the observed enrichment factors of $18\cdot3$ to $25\cdot7$ seen in Table 9. Consideration of the fact that much high-gehlenite melilite also remains preserved in the cores of the inclusions suggests that they contain only about $4\cdot46$ wt. % of the condensable matter. This leads to an enrichment factor of $22\cdot4$ in the range of those observed. Alternatively, if the trace refractories were scavenged from the vapor with less than 100 per cent efficiency, the observed enrichments can be explained if the solar system is richer in the refractory elements than is indicated by their abundances in Cl chondrites. The high-temperature inclusions, having concentrated the trace refractories, may have then been fractionated from the material which was ultimately incorporated into the Cl chondrites. Preservation of the smoothness of the curve of elemental abundance versus mass number is still possible even if the true solar system abundances of the trace refractories are a factor of $1\cdot5$ higher than those given by CAMERON (1968), as suggested by ANDERS (1971).

Rare earths

The rare earth abundances of four typical inclusions and the bulk meteorite have been normalized, element by element, to their abundances in a composite of nine chondrites (HASKIN et al., 1968) and plotted in Fig. 4 as a function of atomic number. Despite the large uncertainties in the concentrations of Eu and Yb, it is clear that the bulk meteorite is enriched in the rare earths by about 40–50 per cent relative to the chondrite composite, probably due to the high content of Ca-rich inclusions, which are highly enriched in the rare earths. The most striking feature of the rare earth pattern of these inclusions is the significant Eu excess, like that in 2A and 6A, found in about 75 per cent of those examined. This type of pattern, with similar enrichments relative to chondrites, has been reported in a 'Ca-rich inclusion' from Allende by GAST et al. (1970). Four of the inclusions exhibit patterns similar to that of 1A and 14A, where the normalized Eu abundance is within error of that of Sm.

The relative abundances of the rare earths expected in the condensates have purposely been ignored in previous discussions since existing thermodynamic data for the gaseous rare earth oxides are very poor and those for important crystalline species such as EuO are lacking entirely. The observed rare earth patterns can be rationalized, at least qualitatively, in the following manner. In the highly reducing environment of a high-temperature solar gas, solid solutions of the most easily reduced metals are the most stable. Since Eu displays a much more extensive chemical behavior in the +2 state than the other rare earths, it might be expected to concentrate in the very early condensates relative to them. Other inclusions,
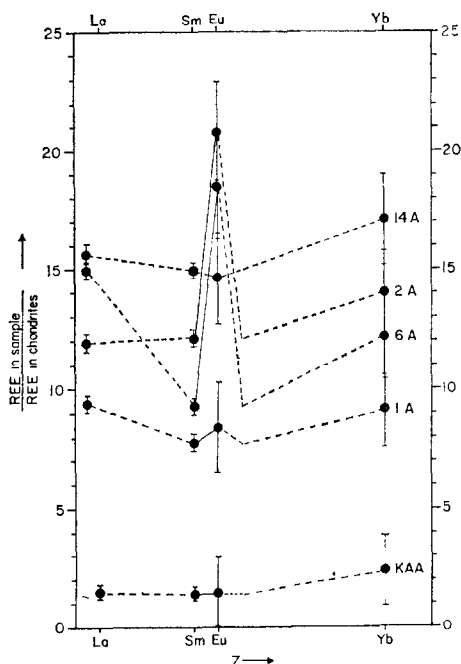
Fig. 4. Chondrite-normalized rare earth abundances for the Ca-rich inclusions from Allende and the bulk meteorite. The inclusions are enriched in all the rare earths relative to the bulk meteorite. Some show Eu excesses, perhaps due to the condensation of Eu in the $+2$ state.

representing more advanced stages of condensation would show no preferential uptake of Eu since this element would have been joined by the other rare earths by this time. KURAT's (1970) description of the Zr–Y-rich perovskite in Lancé suggests that perovskite may also be the host for the rare earths.

It is interesting to note that terrestrial perovskites, many from highly differentiated igneous rocks, show a completely different rare earth pattern from that observed here (BORODIN and BARINSKII, 1960). They are all enriched in the light rare earths relative to the heavy ones and show slight Eu depletions. This is a fairly general pattern observed among differentiated continental igneous rocks and is exhibited by these perovskites because they probably represent the dominant sink for the rare earths in their host rocks.

Refractory element fractionations in chondrites

In their study of chemical fractionations in meteorites, LARIMER and ANDERS (1970) pointed out that Ca, Al and Ti were depleted in ordinary and enstatite chondrites relative to carbonaceous chondrites and attributed this fractionation to loss of an early high-temperature condensate from a gas of solar composition. They also noted parallel depletion trends for Hf, La, Sc, Y and Zr. This study shows that the early Ca–Al–Ti-rich condensates should indeed be enriched in these elements also. GROSSMAN (1972) showed that the mineralogical compositions, textural relations and major element abundances in the white achondritic inclusions in the C3's are those expected of the primitive condensates and of those phases whose removal from a gas of Cl composition is presumed to have caused the refractory

element depletion of the ordinary and enstatite chondrites relative to the Cl's. The work of LARIMER and ANDERS (1970) shows that the depletion factors of most of the refractory elements are roughly constant in the ordinary chondrites (0·69) and in the enstatite chondrites (0·50) relative to the carbonaceous chondrites, despite the fact that many of the analyses have come from different laboratories employing different analytical techniques on different meteorites and in spite of the notorious sample heterogeneity problem associated with meteorite analysis. This means that, if these fractionations were indeed produced by removal of high-temperature condensates from a gas having Cl composition for all but the most volatile elements, the fraction removed must contain the refractory elements in the same relative proportions as the starting material, with only minor fractionations relative to one another. The trace element data presented in Table 9 thus indicate that the inclusions in the C3's fulfil one more requirement of the removed material, since they are enriched in each of the refractory elements La, Sm, Eu, Yb, Sc and Ir relative to the Cl's by approximately the same factor, 18·3 to 25·7. If 100 per cent of each of these refractory elements and 100 per cent of the Ca, Al, Ti, Hf, Y, Zr and Th were condensed into assemblages like the inclusions in the C3's, only 1·3 per cent and 2·1 per cent of the mass of the total condensable matter (23 and 38 wt.% of the high-temperature condensate) must be lost in the form of these aggregates during the accretion of the ordinary and enstatite chondrites, respectively, in order to account for the observed depletions.

CONCLUSIONS

The Ca–Al-rich inclusions in the Allende carbonaceous chondrite are enriched in Sc, Ir and the rare earth elements by factors of 22·8 ± 2·2 relative to Cl chondrites. The chemical behavior of Ir is totally unlike that of Sc and the rare earths: in terrestrial igneous rocks, Ir is concentrated into the accessory chromite and sulphides of ultrabasic rocks while Sc enters the crystal structures of pyroxene and amphibole; in meteorites, Ir is usually siderophile and Sc is lithophile. Thermodynamic calculations show, however, that all these elements could have condensed from a cooling nebula of solar composition above or within the range of condensation temperatures of the major phases of the inclusions. Large enrichments of these refractory trace elements in the Ca–Al-rich inclusions thus provide further strong evidence that they are high-temperature condensates from the solar nebula. Differing degrees of fractionation of such crystalline materials from the vapor in different regions of the nebula could have generated the refractory element depletions of the ordinary and enstatite chondrites relative to the carbonaceous chondrites.

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