

## Trace elements in the Allende meteorite—I. Coarse-grained, Ca-rich inclusions

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**Abstract**—INAA of ten coarse-grained, melilite-spinel-bearing inclusions in the Allende meteorite for Ca, Sc, Hf, Ta, W, Os, Ir, Ru, La, Ce, Sm, Eu, Tb, Dy, Yb, Fe, Co, Cr and Au reveals that all of the refractory elements are enriched by a mean factor of 18.6 relative to their concentrations in CI chondrites, consistent with a high-temperature condensation origin for the inclusions. Os, Ir and Ru were probably incorporated by the inclusions as tiny nuggets of an alloy in which they were dissolved in cosmic proportion to one another. Sc and Hf entered the inclusions in a separate phase, also in cosmic proportion, accompanied by a fraction of the REE. Bulk REE abundances are independent of the major minerals in the inclusions; yet, data from mineral separates suggest that the REE were partitioned between coexisting melilite and pyroxene according to crystal structure controls. A two-stage model is proposed in which the REE first entered the inclusions as trace, refractory condensate phases and then re-distributed themselves between the crystallizing major phases after the inclusions were melted in the nebula.

### INTRODUCTION

SEVERAL trace element studies have been made of the coarse-grained, Ca-rich inclusions in the Allende meteorite (GAST *et al.*, 1970; GROSSMAN, 1973; TANAKA and MASUDA, 1973; MARTIN and MASON, 1974; MASON and MARTIN, 1974; ONUMA *et al.*, 1974; WÄNKE *et al.*, 1974; CHOU *et al.*, 1976) and all of these have concluded that high-temperature condensation processes were involved in their origin. Among those studies, GROSSMAN (1973) did not distinguish between coarse-grained and fine-grained inclusions which appear to have markedly different origins (GROSSMAN and GANAPATHY, in press). Also, where simultaneous mineralogical data are available in the trace element studies, it appears that only the Type B inclusions, containing Ti-Al-rich pyroxenes, of GROSSMAN (1975) have been analyzed. Only the mineralogy of the Type A inclusions, melilite + spinel + perovskite, is completely consistent with the theoretically-predicted high-temperature condensates, while the origin of the Type B inclusions is more obscure (GROSSMAN, 1975). The purpose of this work is to determine the concentrations of a large number of refractory elements in a large number of coarse-grained inclusions, to see if there is any genetic relationship between Type A and Type B inclusions, to investigate the mode of incorporation of the trace elements into them and to determine whether a stage of melting is required by these data.

### EXPERIMENTAL

The sample preparation and neutron irradiation of ten

coarse-grained and ten fine-grained inclusions from the Allende meteorite were reported in GROSSMAN and GANAPATHY (in press). In that work the counting of the short-lived nuclides  $\text{Cl}^{38}$ ,  $\text{Dy}^{165}$ ,  $\text{Mn}^{56}$  and  $\text{Na}^{24}$  was described and the abundances of Cl, Mn and Na were discussed. Here we report on the results of further experiments on the same coarse-grained inclusions as in that study. The Dy data from the earlier study are also reported here. The sample numbers are the same in both papers.

Polished thin sections of 6 of these inclusions were studied by electron microprobe techniques in GROSSMAN (1975). Their approximate modal analyses are shown in Table 1 along with the correspondence between the sample numbers used here and those used in GROSSMAN (1975). Mineralogical types are classified as in that paper: Type A inclusions consist of melilite, spinel, perovskite and, rarely, a small amount of diopsidic pyroxene; Type B inclusions contain abundant Ti-rich pyroxene and spinel, along with smaller quantities of melilite and anorthite. Inclusion 7 is classified as I, or intermediate, because it contains both kinds of pyroxene. The bulk chemical compositions of these inclusions, estimated from their modes and from the electron probe analyses of their constituent phases (GROSSMAN, 1975), are also shown in Table 1.

The 10 inclusions, 3 samples of BCR-1, 2 bulk samples of the Allende meteorite (USNM Split 17, Position 25) and one bulk sample of each of the CI chondrites Orgueil and Alais were re-irradiated for 3 days at a thermal neutron flux of  $3 \times 10^{13}$  neutrons/cm<sup>2</sup> sec in the vertical thimble (VT-25 position) of the CP-5 reactor at Argonne National Laboratory. In addition to the standard pot, SP, of PERLMAN and ASARO (1969), we included many chemical standards (Ir, Os, Ru, Ag, Se, Tl, Zn, Pt, Au, Re) prepared essentially as described by KEAYS *et al.* (1971). Four portions of primary reagent grade iron wire were also included to monitor the spatial variation of the neutron flux over the cluster of sample tubes. These indicated a maximum flux difference of 1.4% and a maximum difference from the mean of 0.6%. No corrections were made for this since

Table 1. Approximate modal analyses and estimated bulk compositions of inclusions from which thin sections were made

Inclusion	Thin Section Number (Grossman, 1975a)	Type	Modal Analysis (volume %)					Estimated Bulk Composition (wt.%)				
			Melilite	Pyroxene	Spinel	Anorthite	Perovskite	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	TiO <sub>2</sub>	SiO <sub>2</sub>
1	TS22F1	B	10	40	50		trace	14	45	19	3	19
2	TS30F1	B	5	50	40	5		16	40	16	4	23
3	TS12F1	A	80		20		~1%	33	39	8	1	21
4	TS21F1	B	10	55	25	10		20	34	13	4	29
6	TS19F1	A	90		10		~1%	37	35	5	1	23
7	TS26F1	I		30	20	50		18	36	10	1	35

these variations approach our minimum uncertainties due to counting statistics. An empty supersilica sample tube was also irradiated and used as a blank.

After the irradiation, the sample tubes were washed in hot HNO<sub>3</sub> prior to counting. Initially each sample was counted for 4000 sec in the time period ranging from 2 to 4 days after the end of the irradiation in order to obtain good counting statistics for such short-lived nuclides as W<sup>187</sup>, La<sup>140</sup>, Sm<sup>153</sup> and Au<sup>198</sup>. Between 5 and 15 days after irradiation, each sample was again counted for 12–24 hr to improve the statistics for Ca<sup>47</sup> and Yb<sup>175</sup>. Finally, beginning 25 days after the irradiation, each sample was counted for 1–2 days to determine the concentrations of longer-lived nuclides.

Gamma-ray spectra were measured with a 9.6% efficiency, 50 cm<sup>3</sup> Ge(Li) detector having a PWHM of 693 eV at 121.9 keV and a PWHM of 1.73 keV at 1332.5 keV. Our system includes a 4096 channel analyser and a pulse pile-up rejector which is used to reduce count losses at high counting rates. With this system, we determined that the error due to loss of counts at 47% dead-time is <1%. All samples and standards were counted at a distance of 10 cm from the detector, resulting in dead-times between 5 and 33%. The stability of the counting efficiency of the

system was monitored weekly: the integrated photopeak of a standard Cs<sup>137</sup> source varied by <1% for a period of 3 months. Peak identification was based on both half-life and energy. Thus, we also monitored the energy vs channel calibration of our system weekly: the maximum drift observed over 3 months was equivalent to ±0.2 keV. Table 2 shows excellent agreement between the observed and reported energies for the analytical peaks that we used for each element.

The spectra were read out on magnetic tape and also on a high-speed printer. Data processing was carried out with essentially the same program used by GROSSMAN (1973). For those peaks that stood on a sloping background which varied from sample to sample, the integration was done manually. The half-lives employed are listed in Table 2, along with the standard used for each element and, when a silicate standard was used, the concentration adopted for the element in it. As shown in Table 2, the determinations of Co, Fe and Sc were each based on the average of data from two peaks. In the cases of Eu<sup>152</sup> and Ta<sup>182</sup>, the counting statistics for other peaks were too poor to permit averaging with the data for the peaks listed in Table 2, although the derived concentrations agreed within the errors. This was also the case

Table 2. Half-lives, analytical peaks and standard information for elements determined in this work

Nuclide	Half-life <sup>1</sup>	Observed	Energy (keV)	Standard	Elemental Concentration
		Energy (keV)	(Literature) <sup>2</sup>		in Standard <sup>4</sup> (ppm unless otherwise indicated)
Au <sup>198</sup>	2.697d	411.7	411.8	Chem <sup>5</sup>	
Ce <sup>47</sup>	4.535d	1297.1	1296.9	BCR-1	4.95% <sup>3</sup>
Ce <sup>141</sup>	32.5d	145.5	145.4	SP	80.3±3.9
Co <sup>60</sup>	5.263y	1173.3	1173.2	SP	14.06±0.15
		1332.5	1332.5		
Cr <sup>51</sup>	27.8d	320.3	320.1	SP	115.1±3.8
Dy <sup>165</sup>	139.2m	94.5	94.7	SP	4.79±0.19
Eu <sup>152</sup>	12.7y	1407.9	1408.1	SP	1.291±0.034
Fe <sup>59</sup>	45.6d	1099.2	1099.3	SP	1.017±0.012
		1291.7	1291.6		
Hf <sup>181</sup>	42.5d	133.1	133.0	SP	6.23±0.44
Ir <sup>192</sup>	74.2d	468.2	468.1	Chem	
La <sup>140</sup>	40.22h	1595.8	1596.2	SP	44.90±0.45
Os <sup>191</sup>	15.0d	129.5	129.4	Chem	
Ru <sup>103</sup>	39.5d	497.2	497.9	Chem	
Sc <sup>46</sup>	83.9d	889.4	889.3	SP	20.55±0.33
		1120.6	1120.5		
Sm <sup>153</sup>	46.8h	102.9	103.2	SP	5.78±0.12
Ta <sup>182</sup>	115.1d	1188.9	1189.0	SP	1.550±0.044
Tb <sup>160</sup>	72.1d	1177.9	1178.1	BCR-1	1.0 <sup>3</sup>
W <sup>187</sup>	23.9h	685.9	685.7	SP	4.2
Yb <sup>175</sup>	101.0h	396.5	396.1	SP	2.80±0.36

1. LEDERER *et al.* (1968).2. PAGDEN *et al.* (1971a, b).

3. FLANAGAN (1973). Recommended values.

4. Elemental concentrations in SP from PERLMAN and ASARO (1969) except for W which is from F. Asaro (1975, personal communication).

5. Chem indicates the use of a chemically-prepared standard, as opposed to a standard silicate.

Table 3. Comparison of literature values with elemental abundances in BCR-1 determined in this work (ppm unless otherwise indicated)

Element	This work			Flanagan (1973)	Nakamura (1974)
	Aliquot 1	Aliquot 2	Aliquot 3		
Au (ppb)	0.2±1.6			0.95(3)	
Ce	55.7±.3	53.0±.2	53.3±.2	53.9(1)	54.2
Co	37.4±.2	37.7±.2	37.4±.2	38(3)	
Cr	17±1	14±1	12±1	17.6(2)	
Eu	1.92±.02	2.03±.02	1.95±.03	1.94(1)	1.98
Fe (‰)	9.56±.06	9.53±.06	9.44±.05	9.37(1)	
Hf	4.94±.04	5.16±.07	4.85±.04	4.7(2)	
Ir (ppb)	1.2±1.5	1.3±1.5	0.9±1.6	0.004(3)	
La	25.7±.2	25.5±.4	24.6±.3	26(2)	24.4
Sc	34.5±.1	35.0±.1	34.6±.1	33(3)	
Sm	6.45±.03	6.45±.06	6.20±.03	6.6(2)	6.72
Ta	0.63±.03	0.70±.04	0.69±.02	0.91(1)	
Yb*	3.3±.1	3.5±.2	3.3±.1	3.36(2)	3.40

(1) Recommended. (2) Average. (3) Magnitude.

\* Determined via Yb<sup>169</sup>. Yb<sup>175</sup>, used for the samples, gives 2.9 ± 0.2 for aliquot

1.

Blank indicates not determined.

for Yb<sup>169</sup>, which gave poorer statistics than Yb<sup>175</sup>. For Hf<sup>181</sup>, an interference was suspected at the 136.3 keV peak so the 133.1 keV peak was used.

## RESULTS

In Table 3, we compare our results for the U.S.G.S. rock standard BCR-1 with the compilation of literature data by FLANAGAN (1973) and later rare earth data from NAKAMURA (1974). Ca and Tb are not listed because BCR-1 was used as the primary standard for these elements. We were unable to determine Os and Ru in BCR-1 because of their very low abundances and because of interferences from the 130.3 keV Yb<sup>169</sup> peak and the 496.4 keV Ba<sup>131</sup> peak, respectively. Also, BCR-1 was counted too long after the respective irradiations to detect Dy<sup>165</sup> and W<sup>187</sup>. For the elements listed, our data are usually within experimental error of the FLANAGAN (1973) values and the NAKAMURA (1974) data or only several per cent away. This reflects the high quality of SP as an INAA standard, as discussed by KATZ and GROSSMAN (in press). Our Ta data are ~25% lower than the recommended value of FLANAGAN (1973) which we believe may be in error.

Analytical data for 19 elements in Allende inclusions and bulk meteorite samples are shown in Table 4. Uncertainties quoted are based on 1σ counting statistics for both samples and standards. In general, our data for bulk Allende fall well within the ranges of literature values which are summarized by CLARKE *et al.* (1970) and GROSSMAN (1973). Our data for Orgueil are also in good agreement with the selected CI abundances shown in Table 6 and, where comparable, with values reported by SCHMITT *et al.* (1972) and PALME *et al.* as given in WÄNKE *et al.* (1974). Our data for the Allende inclusions are in general agreement with those reported by GAST *et al.* (1970), GROSSMAN (1973), TANAKA and MASUDA (1973), MARTIN and MASON (1974), MASON and MARTIN (1974) and WÄNKE *et al.* (1974), but the inclusions are so variable in composition that they do not represent a particularly good basis for comparison.

## VOLATILE ELEMENTS

Most workers now accept the theory that the coarse-grained, Ca-rich inclusions in the Allende meteorite are high-temperature condensates from the

solar nebula (MARVIN *et al.*, 1970; LARIMER and ANDERS, 1970; GROSSMAN, 1972), although some (KURAT, 1970; CHOU *et al.*, 1976) prefer the idea that they may be evaporation residues. The persistent reports of significant levels of volatile elements in them, however (CLARKE *et al.*, 1970), plagued these models from the beginning. Their presence has been attributed to co-condensation with the refractory elements under non-equilibrium conditions (ARRHENIUS and ALFVÉN, 1971), low-temperature condensation reactions between the nebular gas and the exposed surfaces of the inclusions (GROSSMAN and LARIMER, 1974), metamorphic reactions between the inclusions and the Allende matrix (GROSSMAN, 1972), nebular mixing with small amounts of lower-temperature condensates (GROSSMAN, 1975) and laboratory contamination with Allende matrix during the excavation of inclusion samples from the bulk meteorite (GROSSMAN, 1973). It appears probable that a combination of the latter three processes was involved and the presence of volatiles can now be easily reconciled with a high-temperature condensation origin.

All the inclusions analysed in this study were excavated from slab surfaces of the meteorite while they were being viewed through a stereoscopic microscope. Although very great pains were taken to avoid matrix contamination during this operation, it is virtually impossible to completely eliminate it. Visual inspection suggested that no more than 2% matrix material was present in each of our inclusion samples. In order to estimate the degree of matrix contamination in their inclusions, GROSSMAN (1973) used their Fe, Mn and Co contents and WÄNKE *et al.* (1974) used the Fe content, assuming that the inclusions contained no indigenous abundances of these elements. These estimates are upper limits, as electron microprobe analyses of individual crystals in the inclusions often

Table 4. Elemental concentrations in Ca-rich Allende inclusions, bulk Allende and

Sample Inclusions:	Mineralogical Type	Ca (%)	Hf	Ta	W	Sc	La	Ce	Sm	Eu
1	B	16.1 <sup>±</sup> 0.2	2.07 <sup>±</sup> .13	0.25 <sup>±</sup> .04	1.08 <sup>±</sup> .16	131.3 <sup>±</sup> .3	4.17 <sup>±</sup> .10	13.5 <sup>±</sup> 0.8	2.82 <sup>±</sup> .02	1.01 <sup>±</sup> .02
2	B	10.3 <sup>±</sup> 0.6	4.43 <sup>±</sup> .35	0.31 <sup>±</sup> .13	3.73 <sup>±</sup> .38	275.4 <sup>±</sup> .5	6.54 <sup>±</sup> .19	26.6 <sup>±</sup> 2.2	4.58 <sup>±</sup> .04	0.66 <sup>±</sup> .05
3	A	23.6 <sup>±</sup> 1.0	1.07 <sup>±</sup> .11	0.19 <sup>±</sup> .03	1.37 <sup>±</sup> .15	99.8 <sup>±</sup> .2	4.35 <sup>±</sup> .09	12.6 <sup>±</sup> 0.7	2.84 <sup>±</sup> .02	1.14 <sup>±</sup> .02
4	B	18.3 <sup>±</sup> 1.1	1.63 <sup>±</sup> .23	0.27 <sup>±</sup> .08	2.98 <sup>±</sup> .22	102.8 <sup>±</sup> .1	4.34 <sup>±</sup> .11	16.3 <sup>±</sup> 1.6	2.38 <sup>±</sup> .03	1.25 <sup>±</sup> .05
5	B	8.6 <sup>±</sup> 0.4	0.79 <sup>±</sup> .12	0.74 <sup>±</sup> .07	1.33 <sup>±</sup> .23	80.1 <sup>±</sup> .2	16.0 <sup>±</sup> .15	36.7 <sup>±</sup> 0.9	9.96 <sup>±</sup> .05	0.64 <sup>±</sup> .03
6	A	26.0 <sup>±</sup> 0.5	1.15 <sup>±</sup> .28	0.20 <sup>±</sup> .14	2.73 <sup>±</sup> .20	92.6 <sup>±</sup> .1	2.23 <sup>±</sup> .06	4.9 <sup>±</sup> 1.9	1.67 <sup>±</sup> .02	1.41 <sup>±</sup> .05
7	I	11.2 <sup>±</sup> 1.0	1.43 <sup>±</sup> .16	0.09 <sup>±</sup> .07	1.23 <sup>±</sup> .50	61.4 <sup>±</sup> .2	3.46 <sup>±</sup> .16	15.0 <sup>±</sup> 1.1	2.24 <sup>±</sup> .03	1.10 <sup>±</sup> .14
8	B	16.2 <sup>±</sup> 0.7	1.07 <sup>±</sup> .06	0.23 <sup>±</sup> .02	0.44 <sup>±</sup> .12	79.0 <sup>±</sup> .2	4.15 <sup>±</sup> .10	6.3 <sup>±</sup> 2.4	2.96 <sup>±</sup> .02	1.12 <sup>±</sup> .07
9	B	21.2 <sup>±</sup> 1.1	0.57 <sup>±</sup> .07	0.14 <sup>±</sup> .03	2.08 <sup>±</sup> .16	41.2 <sup>±</sup> .1	3.19 <sup>±</sup> .10	9.3 <sup>±</sup> 0.5	1.91 <sup>±</sup> .02	1.40 <sup>±</sup> .02
10	B	12.3 <sup>±</sup> 0.5	3.12 <sup>±</sup> .09	0.48 <sup>±</sup> .03	1.28 <sup>±</sup> .23	181.0 <sup>±</sup> .1	5.71 <sup>±</sup> .10	18.9 <sup>±</sup> 0.6	3.79 <sup>±</sup> .03	1.10 <sup>±</sup> .02
Bulk Allende						11.64 <sup>±</sup> .02	0.53 <sup>±</sup> .04		0.303 <sup>±</sup> .009	0.120 <sup>±</sup> .006
Bulk Allende						11.73 <sup>±</sup> .06	0.63 <sup>±</sup> .05		0.32 <sup>±</sup> .01	0.109 <sup>±</sup> .004
CI Chondrites:										
Orgueil						6.38 <sup>±</sup> .03	0.20 <sup>±</sup> .06		0.12 <sup>±</sup> .01	0.051 <sup>±</sup> .003
Alais						1.61 <sup>±</sup> .04	0.28 <sup>±</sup> .07		4.53 <sup>±</sup> .03	1.10 <sup>±</sup> .02

Blank indicates not determined.

\* 2 $\sigma$  upper limit.

show moderate amounts of FeO (GROSSMAN, 1975).

In Table 5, we have normalized our volatile element data from Table 4 (Fe, Co, Cr, Au) and the Na and Mn data for these same inclusions from GROSSMAN and GANAPATHY (in press) to their respective abundances in the bulk meteorite as determined in our laboratory. In this way, we can determine upper limits to the amount of matrix contamination and tell which volatiles have large indigenous abundances if we assume that the contaminant has the composition of the bulk meteorite. It is seen that a very wide range of Allende-normalized values may be obtained for different volatile elements in the same inclusion. For each inclusion, the element with the lowest normalized abundance gives the upper limit to the per cent matrix contamination. Higher normalized data are possible for other elements if, in addition to the amounts of them present due to the admixture of matrix, additional indigenous amounts are also present. The final column in Table 5 gives the upper limits to the amounts of matrix contamination, allowing for moderate heterogeneity in the composition of the contaminant. Because of the extreme care which we exercised in sampling the inclusions, we believe that

the upper limits derived for inclusions 2 and 7 far exceed the actual contamination levels and that these particular inclusions contain exceptionally high levels of indigenous volatiles. Because the matrix contamination usually amounts to <2%, we have not corrected any of the refractory element data in this paper for this dilution effect.

Examination of Table 5 shows that the indigenous volatile component in the inclusions is particularly rich in Cr, Au and Na and less rich in Fe, Co and Mn compared to the bulk meteorite. GROSSMAN and GANAPATHY (in press) discussed the origin of indigenous Na, Mn and Cl at great length and concluded that they were metasomatic. More will be said of this later in this paper.

## REFRACTORY ELEMENTS

### Enrichment factors

In Table 6, the mean concentration and enrichment factor relative to CI chondrites is given for each refractory element in each mineralogical type of inclusion. Also listed are the CI values used for normalization and the literature sources for these data. For

Table 5. Allende-normalized volatile element abundances in the inclusions and estimates of the degree of matrix contamination

Inclusion	Fe	Co	Mn	Cr	Au	Na	Upper Limit to Amount of Matrix Contamination (%)
1	.0188	.0110	.0304	.1507	.0741	.3766	2
2	.1272	.0976	.1191	.4289	.3210	.1814	13
3	.0148	.0354	.0147	.0350	.7284	.4021	2
4	.0594	.0518	.0641	.4523	2.49	.4457	6
5	.0603	.0164	.0517	.3326	.0370	.4797	2
6	.0251	.3167	.0124	.2167	4.72	.0793	2
7	.1464	.1081	.2795	1.02	.3519	2.44	11
8	.0123	.0145	.0134	.1626	.2346	.2643	2
9	.0347	.0126	.0471	.0188	.6296	1.38	2
10	.0087	.0563	.0062	.2135	1.79	.1662	1

the CI chondrites Alais and Orgueil (ppm unless otherwise indicated)

Tb	Dy	Yb	Os	Ir	Ru	Fe	Co	Cr	Au (ppb)
0.73±.05	5.5±0.3	2.9±0.2	6.8±0.2	6.71±.02	9.0±0.7	4440±110	7.16±0.07	568±3	12±2
1.11±.16	7.2±1.0	4.0±0.4	12.1±0.5	11.99±.03	16.9±2.0	3.01±.03%	63.5±0.6	1617±9	52±10
0.68±.04	5.4±0.3	1.9±0.2	8.7±1.9	8.82±.02	11.6±0.5	3490±110	23.0±0.2	132±2	118±5
0.49±.10	5.7±0.7	3.0±0.3	10.5±0.4	10.95±.03	10.8±1.1	1.40±.02%	33.7±0.3	1705±9	403±9
1.61±.08	8.8±0.7	0.9±0.1	0.26±0.18	0.162±.006	0.82±0.87	1.42±.02%	10.7±0.1	1254±6	6±4
±0.29*	0.06±1.0	1.5±0.2	11.9±0.6	12.98±.03	15.9±1.3	5940±200	206±1	817±6	765±5
0.24±.10	3.8±0.9	2.3±0.2	7.9±0.3	6.31±.02	10.6±0.8	3.46±.02%	70.3±0.4	3844±18	57±8
0.60±.18	3.3±0.3	3.0±0.3	0.58±0.10	0.602±.018	1.1±0.4	2900±280	9.4±0.3	613±8	38±4
0.51±.03	4.5±0.5	1.3±0.2	4.2±0.2	4.15±.01	5.4±0.4	8190±70	8.2±0.1	71±1	102±6
1.01±.04	8.6±0.4	4.2±0.3	10.3±0.2	10.95±.03	13.5±0.5	2050±140	36.6±0.2	805±4	290±6
				0.766±.003		23.74±.11%	653±3	3813±38	151±3
				0.780±.003		23.50±.20%	648±3	3727±37	173±4
		0.54±.18	0.473±.003			18.90±.10%	478±3	2883±15	124±4
	4.07±0.9	1.84±.15	0.03±.05	0.234±.002		8.10±.04%	124.1±.5	1041±5	63±3

Ca, we averaged all the CI data from MASON (1962), NICHIPORUK *et al.* (1967), AHRENS *et al.* (1969), VON MICHAELIS *et al.* (1969) and WÄNKE *et al.* (1974). For Sc, we took the mean of all CI data in HASKIN *et al.* (1966), SCHMITT *et al.* (1972), WÄNKE *et al.* (1974) and our data in Table 4. In the case of the rare earths, we selected the Orgueil values of NAKAMURA (1974) except for Tb which he did not determine. NAKAMURA's Gd and Dy abundances in Orgueil are 0.739 and 0.735 when normalized to his data for the average of ten ordinary chondrites. We calculated a CI Tb concentration by multiplying the mean of these values, 0.737, by the average Tb concentration in the 9 ordinary chondrites measured by HASKIN *et al.* (1966).

All of the refractory elements are substantially enriched relative to their abundances in CI chondrites in each mineralogical type of inclusion. Because of the wide concentration range observed for each of these elements in the Type B inclusions and because

of the fact that only one intermediate and only two Type A inclusions were analysed, little significance can be attached to apparent elemental abundance differences between the different mineralogical types, as given in Table 6. It can be concluded, however, that the Type A inclusions are significantly richer in Ca than the others since this is a direct consequence of the greater abundance of melilite and the absence of pyroxene in the Type A's, which is the basis of the mineralogical classification. It is also noteworthy that the Ca data in Table 4 are within error of the CaO contents estimated from the modal analyses of thin sections of the samples listed in Table 1, except for inclusions 1 and 4. This suggests that the samples used for trace element work usually, but not always, have nearly the same mineralogical compositions as those fractions of the samples visible in thin section.

From the last column of Table 6 and Fig. 1, it is apparent that this population of 10 inclusions is, on the average, rather uniformly enriched in all of

Table 6. Average concentrations and enrichment factors of refractory elements in coarse-grained inclusions relative to CI chondrites

Element	Concentration (ppm unless otherwise indicated)				Enrichment Factor			
	CI chondrites	Mean Type A Inclusion	Mean Type B Inclusion	Mean of All Inclusions	Intermediate Inclusion	Mean Type A Inclusion	Mean Type B Inclusion	Mean of All Inclusions
Ca	0.975%(7)	24.8%	14.7%	16.4%	11.5	25.4	15.1	16.8
Hf	0.10(3)	1.11	1.95	1.73	14.3	11.1	19.5	17.3
Ta	0.0134(2)	0.20	0.35	0.29	6.7	14.6	25.8	21.6
W	0.088(2)	2.05	1.85	1.83	14.0	23.3	21.0	20.7
Sc	6.4(7)	96.2	127.3	114.5	9.6	15.0	19.9	17.9
La	0.253(1)	3.29	6.30	5.41	13.7	13.0	24.9	21.4
Ce	0.645(1)	8.8	18.2	16.0	23.3	13.6	28.3	24.8
Sm	0.154(1)	2.26	4.06	3.52	14.5	14.6	26.3	22.8
Eu	0.0587(1)	1.28	1.03	1.08	18.7	21.7	17.5	18.4
Tb	0.039(7)	0.34	0.87	0.70	6.2	8.7	22.2	17.9
Dy	0.252(1)	2.7	6.2	5.3	15.1	10.8	24.7	21.0
Yb	0.168(1)	1.7	2.8	2.5	13.7	10.1	16.4	14.9
Os	0.480(4)	10.3	6.4	7.3	16.5	21.5	13.3	15.3
Ir	0.514(5)	10.9	6.5	7.4	12.3	21.2	12.6	14.3
Ru	0.69(6)	13.8	8.2	9.6	15.4	19.9	11.9	13.9
Mean					13.7	16.3	20.0	18.6

(1) NAKAMURA (1974). (2) WÄNKE *et al.* (1974). (3) EHMANN and CHYI (1974). (4) MORGAN (1971). (5) KRÄHENBÜHL *et al.* (1973). (6) CROCKET *et al.* (1967). (7) See text.

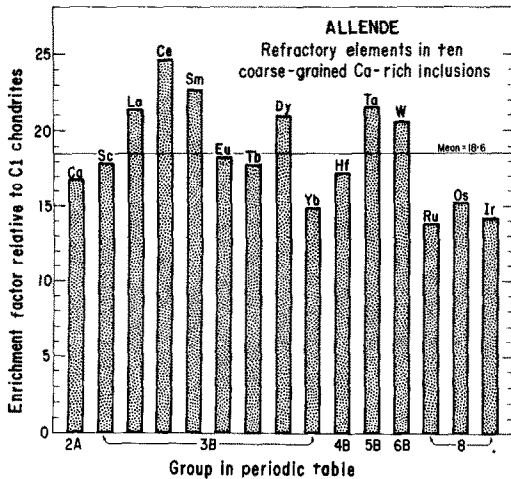


Fig. 1. In spite of widely-differing chemical properties and geochemical behavior, all refractory elements are nearly uniformly enriched in these inclusions relative to their abundances in C1 chondrites. The mean enrichment factor of 18.6 indicates that the inclusions represent about 5.4 wt % of the total condensable matter of the solar system.

the refractory elements determined in this work relative to C1 chondrites. The siderophile elements, Ru, Os, Ir, all seem to be enriched by lower factors than the lithophiles but this is due largely to the very low concentrations of these elements in inclusions 5 and 8, as seen in Table 4. Yb also seems to be a bit low compared to the others but this is not because it is consistently lower. It is again due, rather, to particularly low concentrations in only 2 or 3 inclusions. As will be discussed later in this paper, individual inclusions sometimes show markedly noncosmic proportions of some refractories relative to others. Thus, some of the variability in the enrichment factors for different elements is probably due to the small number of inclusions sampled in this study. Had many more samples been analysed, we suspect that much of the variability would have disappeared. Another possible source of differing enrichment factors are the C1 abundances themselves, which are often based on only single determinations. Given all these possible sources of scatter, the uniformity of enrichment is truly remarkable, particularly in view of the wide range of geochemical behavior represented by these elements. The only thing in common to these chemically-diverse elements is that they all condense from a gas of solar composition in the range of the condensation temperatures of the major phases of the inclusions (GROSSMAN, 1973), accounting for their coexistence and great abundance in them. Furthermore, these elements should all be *totally* condensed in this temperature range, 1442–1742°K at  $10^{-3}$  atm total pressure (GROSSMAN, in press), resulting in their occurrence in near-cosmic proportion to one another and, hence, in the near-uniformity of their enrichment relative to C1 chondrites.

The phenomenon of uniform enrichment was noted by GROSSMAN (1973) for 6 refractory elements in 16

inclusions and by WÄNKE *et al.* (1974) for 29 refractories in one inclusion and both studies concluded that this was very strong evidence for the high-temperature condensation origin of the inclusions. Neither of those studies, however, reported the mineralogy of the analysed samples so it is not known which of those inclusions were Type A or Type B. GROSSMAN (1975), in distinguishing between Type A, Type B and intermediate inclusions, noted that only the Type A's possess the theoretically predicted high-temperature (> 1440°K) condensate mineral assemblage: melilite + spinel + perovskite ± diopside. The data presented here show for the first time that the Type A inclusions also contain the enhanced refractory trace element contents that would be expected if they are truly samples of the high-temperature condensates.

The origin of the Type B inclusions is more obscure because of their mineralogy. While it is true that they contain spinel, usually 10–15% melilite and, very rarely, perovskite, they are dominated by a Ti–Al-rich pyroxene whose thermodynamic properties are unknown. Whether this phase could be a high-temperature condensate is, therefore, also unknown, although GROSSMAN and CLARK (1973) suggested that it might be the condensate equivalent of the diopside predicted by GROSSMAN (1972) to have formed in the nebula at 1450°K at  $10^{-3}$  atm total pressure. In addition, the Type B inclusions contain significant amounts of anorthite which could have formed in the nebula by the reaction of spinel with diopside only at temperatures below the condensation points of forsterite and metallic nickel–iron which have only rarely been reported from these inclusions. The intermediate inclusion contains 50% anorthite and no melilite at all.

High concentrations of refractory trace elements have been reported from the following Type B inclusions: the Ca–Al-rich chondrule and inclusion O of TANAKA and MASUDA (1973), the single inclusions studied by MASON and MARTIN (1974) and ONUMA *et al.* (1974), the group I melilite-rich chondrules of MARTIN and MASON (1974) and inclusion 2 of CHOU *et al.* (1976). These workers all concluded that the inclusions were formed by high-temperature condensation processes. The trace element data presented in this paper confirm their results for the Type B inclusions and show that there is a strong link between them, the intermediate inclusion and the Type A inclusions. Just as the Type A inclusions are samples of high-temperature condensates, so also are these other kinds of inclusions.

GROSSMAN (1973) found that the mean enrichment factor for Ir, Sc, La, Sm, Eu and Yb in 16 inclusions was 22.8 relative to C1 chondrites. When those data are normalized to the same C1 values used in this paper, the enrichment factor becomes 19.5. The difference between that determination and 18.3, the mean value for the same six elements as determined in this work, is presumably related to the highly variable concentrations of these elements in different inclu-

sions (see Table 4). The enrichment factors are calculated relative to C1 chondrites because it is believed that the composition of those meteorites approaches the mean composition of the total condensable matter of the solar system. Assuming that the refractory trace elements were scavenged from the nebula with 100% efficiency by the major phases of the inclusions, GROSSMAN (1973) reasoned that the inclusions represent  $100/22.8 = 4.4\%$  of the total condensable matter of the solar system. Based on the 15 refractories determined in this paper and improved C1 data, we estimate that the different mineralogical types of inclusions, considered as a single population, represent  $100/18.6 = 5.4\%$  of the total condensable matter of the solar system, a value close to that predicted from condensation calculations (GROSSMAN, 1973).

#### Mechanisms of incorporation

GROSSMAN (1973) showed that Os, Ir, Ru and W could have condensed as pure metals and Hf, Ta and Sc as pure oxides in the same temperature range as the major phases in the inclusions, or higher. It was suggested in that paper that the rare earths could have also condensed in that temperature range by forming solid solutions with perovskite.

The abundances of two refractory siderophile elements, Os and Ir, from Table 4, are plotted against one another in Fig. 2. No distinct separation is obvious between inclusions of different mineralogical type. The abundances of these two elements correlate very strongly with one another in the inclusions and lie very close to a line whose slope equals the cosmic Os/Ir ratio. A similar result is obtained when our Ru data are plotted against the data for either of these two elements. W, Co and Au, however, show little tendency to correlate with the platinum metals, although the highest concentrations of these elements tend to be found in inclusions with relatively high abundances of Os, Ir and Ru. This could be fortuitous.

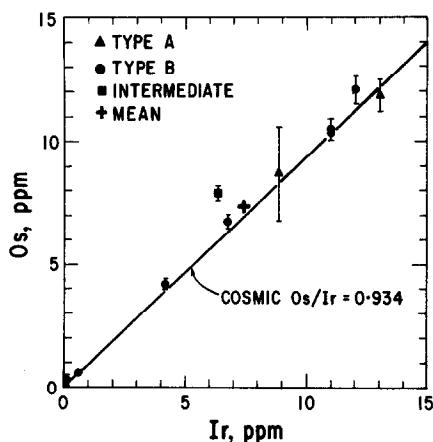


Fig. 2. Refractory siderophile elements occur in nearly cosmic proportion to one another in each inclusion, indicating that they condensed totally in a single component, rather than as two, separate, pure phases.

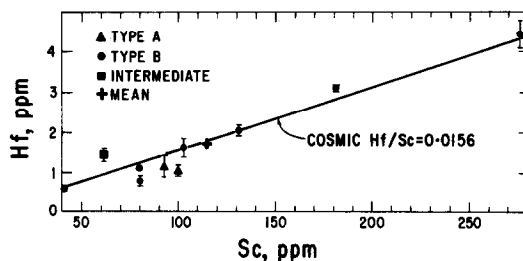


Fig. 3. Hf and Sc probably also condensed into a single phase in which they occurred in cosmic proportion to one another.

The strong correlations observed between Os, Ir and Ru can be explained if these three elements were incorporated by the inclusions in a single component which contained these elements in cosmic proportion to one another and if that component were added in varying amounts to the different inclusions. The Os, Ir and Ru may have condensed totally into solid solution with one another, rather than condensing as three separate, pure, metallic phases. Thus, the component may have been submicron nuggets of a refractory platinum metal alloy which acted as condensation nuclei for the major phases or vice versa.

Our data for two refractory lithophile elements, Sc and Hf, are plotted against one another in Fig. 3. Again, no major difference is evident between inclusions of different mineralogical types. The abundances of Hf and Sc are strongly correlated with one another and lie close to a line whose slope equals the cosmic Hf/Sc ratio. As in the case of the platinum metals, both elements might have entered the inclusions as a single component in which they occurred in cosmic proportion to one another. Both elements might have condensed totally by dissolving in a major, minor or trace silicate or oxide phase, rather than as separate grains of  $\text{HfO}_2$  and  $\text{Sc}_2\text{O}_3$  as suggested by GROSSMAN (1973). Again, if these elements condensed in a phase distinct from the major silicates or oxides, their coexistence with such phases could be due to their interdependence for condensation nuclei.

Ir is plotted against Sc in Fig. 4. The total lack of correlation between the concentrations of these two

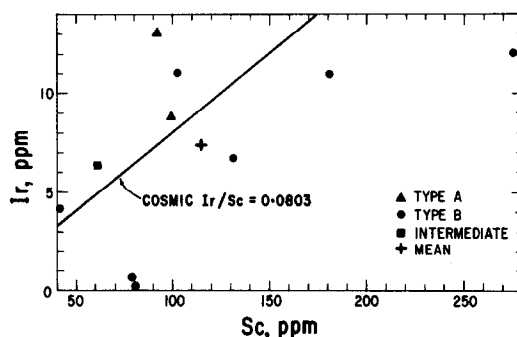


Fig. 4. Ir and Sc condensed in different components whose abundances in any particular inclusion are unrelated to one another.

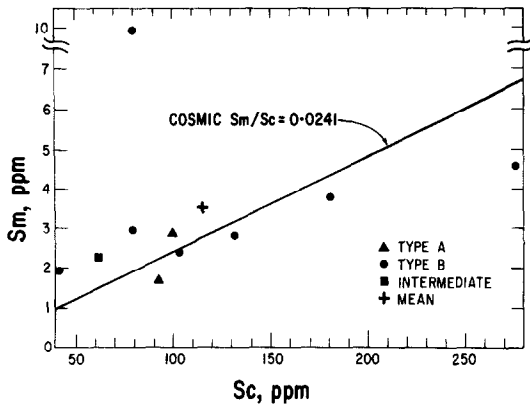


Fig. 5. Sm and Sc entered the inclusions in at least two components: one in which the Sm/Sc ratio was variable, but close to cosmic; the other was greatly enriched in Sm relative to Sc compared to C1 chondrites.

elements indicates that they entered the inclusions in different components whose abundances in any particular inclusion are not related to one another. In spite of this, the point representing the mean composition of the 10 inclusions falls remarkably close to the cosmic line, in accord with the near-uniformity of C1-based enrichment factors discussed above.

When Sm is plotted against Sc (Fig. 5) the data points scatter around a cosmic line and do not deviate greatly from it, except for one inclusion. This could imply that the rare earths are associated with the Sc-rich component but that they occur in it in variable proportion to Sc. Alternatively, the scatter may imply the presence of an additional REE component, independent of the Sc component. This is one obvious explanation for inclusion 5 which has a much greater than cosmic Sm/Sc ratio. At least two different Sm carriers are required to explain all the data. Note again, however, that the mean of the 10 inclusions plots rather close to the cosmic line. Sc shows a similar relationship to Ta and inclusion 5 again has a

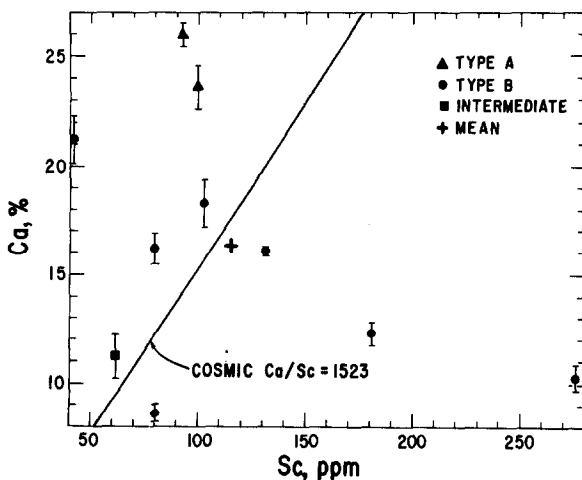


Fig. 6. In spite of huge variations in the Ca/Sc ratio from inclusion to inclusion, the mean Ca/Sc ratio of all ten inclusions is very close to the cosmic ratio.

much higher than cosmic Ta/Sc ratio. W is not correlated strongly with either Sc or Ta.

Figure 6 shows that strong correlations do not always exist between pairs of refractory lithophile elements. Individual inclusions display marked positive or negative deviations from a cosmic Ca/Sc ratio; yet the mean of the 10 inclusions again plots very close to the cosmic line. This phenomenon, also seen in Fig. 4, suggests that individual inclusions may not have compositions particularly representative of the high-temperature condensates but that the mean composition of a large number of inclusions is a much better sample. This is because some refractory elements entered the inclusions in different components from others and there is no necessary reason for every inclusion to have sampled an identical fraction of each available component. A collection of inclusions, however, is a larger sample of the condensate and may be expected to be more representative.

At first sight, the lack of correlation between Ca and Sc suggests that the Sc-bearing component is not one of the major phases but this conclusion cannot be deduced from these data alone since the Ca content of an inclusion is a complicated function of the mineralogy due to the large number of Ca-rich phases. FRONDEL (1970) noted that the distribution of Sc in nature seems to be related to its affinity for the crystal structure of pyroxene. Thus, if Sc entered the inclusions in solid solution in one of the major phases, pyroxene is the likely candidate. The Type A inclusions, however, devoid of pyroxene, have greater Sc concentrations than four pyroxene-rich inclusions. It appears that pyroxene cannot be the only Sc carrier.

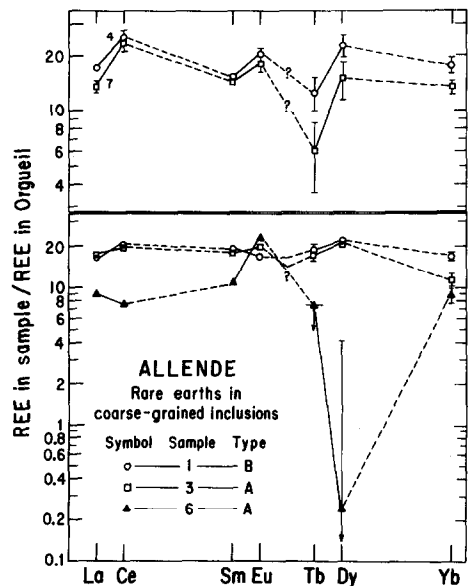


Fig. 7. Despite major mineralogical differences, inclusions 4 and 7 have very similar REE patterns. Inclusions 1 and 3 have totally different mineralogical compositions but nearly identical REE patterns. 3 and 6 have very similar mineralogy and remarkably different REE patterns. Note that the Tb value in inclusion 6 is a  $2\sigma$  upper limit.



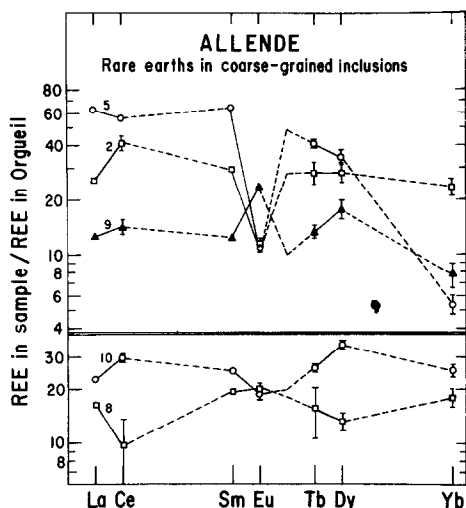


Fig. 8. Type B inclusions display a wide range of different REE patterns. Inclusions 10 and 8 show sympathetic REE patterns.

#### The rare earth elements

Figures 7 and 8 show Orgueil-normalized REE patterns for the 10 inclusions studied here. Most published REE patterns for coarse-grained Allende inclusions have small Eu excesses (GAST *et al.*, 1970), except for the one given by WÄNKE *et al.* (1974) which shows no Eu anomaly and inclusion O of TANAKA and MASUDA (1973) which has a negative Eu anomaly and is very similar to our inclusion 2. Inclusions 1 and 3 in this work show no Eu anomaly. Eu excesses are evident in our inclusions 4, 7 and 9 which also show increasing enrichment from Tb to Dy, similar to the data of MARTIN and MASON (1974), MASON and MARTIN (1974), OSBORN *et al.* (1974) and the Ca-Al-rich chondrule measured by TANAKA and MASUDA (1973). The patterns for the two Type B inclusions 8 and 10 appear to be sympathetic with one another such that, if they were averaged together, a nearly flat pattern would result. Inclusions 5 and 6 are unique. Inclusion 5, a Type B, is the most highly enriched in rare earths of those samples studied here. It has a striking Eu depletion, steadily decreasing enrichments of the heavy rare earths and many similarities to the remarkable pattern found in a fine-grained inclusion by TANAKA and MASUDA (1973). Inclusion 6, a Type A, has a Eu excess, very low enrichments of Tb and Dy and a 'normal' Yb enrichment.

We wish to call the reader's attention to several specific features of the patterns in Fig. 7. Inclusions 1 and 3 have nearly identical absolute and relative REE abundances, except for a tiny difference at Eu and a slight difference at Yb. Inclusion 3 is a Type A, containing about 80% melilite, 20% spinel and ~1% perovskite. Inclusion 1, a Type B, has a radically different mineralogical composition: 10% melilite, 50% spinel, 40% Ti-Al-rich pyroxene and a trace of perovskite. Likewise, inclusions 4 and 7 have very similar REE patterns in spite of considerable differ-

ences in mineralogy (see Table 1). Note also the extreme differences in both the absolute amounts and the relative abundances of REE between inclusions 3 and 6. The Tb datum for inclusion 6 is a  $2\sigma$  upper limit. Yet, the mineralogy of inclusion 6 is nearly identical with that of 3: 90% melilite, 10% spinel. In summary, there appears to be no relationship between the REE patterns and the major mineral phases which we observe in the inclusions today.

We expect that each of these phases has different preferences for different REE because of their different crystal structures. If all of these phases condensed from the nebula and partitioned the condensing REE between themselves according to crystal-chemical controls, we should have observed some correlation between the REE patterns and the mineralogy. From the absence of such a correlation, we conclude that the bulk of the REE did not condense in solid solution in the major mineral phases which then accreted to form the inclusions. Rather, we believe that the REE condensed in solid solution in perovskite and/or in one or more trace, submicron, refractory phases which have not yet been discovered.

#### Condensation of the rare earths

At what temperatures and in what forms could the REE have condensed from the solar nebula without forming solid solutions with the major phases? First, let us examine the condensation temperatures of the crystalline rare earth oxides. Following GROSSMAN (1973), we assume that the only abundant gaseous species of the rare earths are the monatomic elements themselves and their monoxides, except for Ce where we found  $\text{CeO}_2$  to be in greater abundance than CeO. Free energies of formation for the gaseous monoxides were calculated from the data of AMES *et al.* (1967) and taken from HULTGREN *et al.* (1964 and later) for the gaseous elements, ACKERMANN and RAUH (1971) for gaseous  $\text{CeO}_2$ , the JANAF Tables (1974) for gaseous monatomic O, and GSCHNEIDER *et al.* (1973) for the crystalline oxides.  $P_{\text{O}}$  as a function of temperature was taken from the programs used to compute the condensation sequence at  $10^{-3}$  atm total pressure in GROSSMAN (in press). The abundances of the REE are from CAMERON (1973a). The method of calculation is the same as that outlined in GROSSMAN (1973). The temperature of first appearance of each rare earth oxide at  $10^{-3}$  atm total pressure is given in the third column of Table 7. These temperatures have uncertainties on the order of  $\pm 20^\circ$ , on the basis of  $\pm 2$  kcal/mole uncertainties in the free energies of the solid oxides.  $\text{Eu}_2\text{O}_3$  was found to have a higher condensation point than either  $\text{Eu}_3\text{O}_4$  or  $\text{EuO}$  and  $\text{Ce}_2\text{O}_3$  condenses before  $\text{CeO}_2$ .

Even from this simple calculation, it is evident that all the REE except Eu should have condensed from the solar nebula above  $1300^\circ\text{K}$  and that all REE heavier than Eu, except for Yb, should have condensed before forsterite,  $1430^\circ\text{K}$  (GROSSMAN, in press). The presence of pyroxene in the inclusions suggests

Table 7. Condensation of rare earth oxides from a gas of solar composition of a total pressure of  $10^{-3}$  atm

Element	Condensation as Pure Oxide		Condensation in Solid Solution in Perovskite Percent Condensed		
	Phase	Condensation Temperature ( $^{\circ}$ K)	1600 $^{\circ}$ K	1500 $^{\circ}$ K	1400 $^{\circ}$ K
La	La <sub>2</sub> O <sub>3</sub>	1339	46	95	100
Ce	Ce <sub>2</sub> O <sub>3</sub>	1312	31	86	99
Pr	Pr <sub>2</sub> O <sub>3</sub>	1319	64	97	100
Nd	Nd <sub>2</sub> O <sub>3</sub>	1353	54	96	100
Sm	Sm <sub>2</sub> O <sub>3</sub>	1342	65	98	100
Eu	Eu <sub>2</sub> O <sub>3</sub>	1140	<1	3	40
Gd	Gd <sub>2</sub> O <sub>3</sub>	1462	99	100	100
Tb	Tb <sub>2</sub> O <sub>3</sub>	1439	100	100	100
Dy	Dy <sub>2</sub> O <sub>3</sub>	1519	100	100	100
Ho	Ho <sub>2</sub> O <sub>3</sub>	1497	100	100	100
Er	Er <sub>2</sub> O <sub>3</sub>	1590	100	100	100
Tm	Tm <sub>2</sub> O <sub>3</sub>	1439	100	100	100
Yb	Yb <sub>2</sub> O <sub>3</sub>	1319	15	90	100
Lu	Lu <sub>2</sub> O <sub>3</sub>	1548	100	100	100

that they continued to accrete condensates until the temperature fell to at least as low as 1442 $^{\circ}$ K (GROSSMAN, in press) but the absence of forsterite (GROSSMAN, 1975) indicates that they stopped accreting above 1430 $^{\circ}$ K. Thus, although the REE are refractory, if each one condensed as the pure oxide, the inclusions would be devoid of Yb and the REE lighter than Gd, but enriched in all the others. This is clearly not the case.

GROSSMAN (1973) suggested that the REE might have condensed in solid solution in perovskite whose crystal structure is known to be receptive to REE (BORODIN and BARINSKII, 1960). Following this idea, BOYNTON (1975) calculated the relative proportions of the rare earths condensed in perovskite but he was unable to compute these as a function of temperature. He assumed that the REE formed non-ideal solutions in this phase and calculated what the activity coefficients would have to be in it in order for his model to explain a fractionated REE pattern in a fine-grained Allende inclusion. In our opinion, this fractionation pattern could have resulted from any number of processes since the origin of the fine-grained inclusions is extremely obscure (GROSSMAN and GANAPATHY, in press). We are not convinced that the computations of BOYNTON (1975) give the true activity coefficients of the REE in perovskite so, in the absence of these, we have calculated REE condensation curves assuming ideal solution in this phase. Although the latest published calculations (GROSSMAN, in press) show perovskite condensing at 1632 $^{\circ}$ K at  $10^{-3}$  atm total pressure, unpublished work based on updated thermodynamic data for gaseous TiO raises this temperature to 1680 $^{\circ}$ K. Under these conditions, Ti is more than 97% condensed in the temperature range of our REE calculations whose results are shown in the final three columns of Table 7. These data show that, although considerable opportunity for fractionation of the REE from one another exists

at high temperature, all of the REE are virtually totally condensed at temperatures greater than the inferred accretion temperatures of the inclusions, 1430–1440 $^{\circ}$ K, except for Eu. Because all of the inclusions do not have Eu depletions, perovskite cannot be the only rare earth carrier.

In spite of the fact that neither of the two simple models presented in Table 7 can account in detail for the REE patterns observed in the inclusions, the calculations do demonstrate the refractory behavior of the REE in the solar nebula. The precise mode of condensation of the REE is still unknown; however, we might imagine that the highly variable and irregular patterns in Figs. 7 and 8 were perhaps produced by the addition of several condensate phases containing REE in solid solution, such as mixed oxides of the REE, perovskite, hibonite, ZrO<sub>2</sub> or Sc<sub>2</sub>O<sub>3</sub>. Another possibility is that the REE condensed as several unknown, exceedingly stable, very rare, oxide or silicate compounds with other refractory elements, such as Sc and Hf (see Figs. 3 and 5).

#### *Rare earths in separated phases*

MASON and MARTIN (1974) and ONUMA *et al.* (1974) prepared density separates of pyroxene-rich and melilite-rich fractions from Type B inclusions and measured the abundances of REE in both fractions. Both studies yielded similar results. Melilites had large Eu excesses superimposed on a trend of decreasing enrichment of REE with increasing atomic number while the coexisting pyroxenes had large, sympathetic Eu depletions and a trend of increasing enrichment of the heavier REE. The similarity of these distributions to one another suggests that the REE are actually in the crystal structures of the two phases, supporting our earlier contention that melilite and pyroxene show preferences for different REE. If, rather, trace amounts of REE-rich oxide grains were mechanically mixed into the fractions, it would be diffi-

cult to explain why, each time, the Eu-rich oxide phase contaminated the melilite fraction and the Eu-poor phase the pyroxene fraction. Furthermore, both such oxide phases would be expected to be concentrated in the denser, pyroxene-rich fraction because they would probably be denser than pyroxene. Also, there is a marked resemblance between the REE patterns in the coexisting melilites and pyroxenes in these inclusions and the patterns of coexisting plagioclases and clinopyroxenes from basaltic igneous rocks (SCHNETZLER and PHILPOTTS, 1971). On the basis of these considerations, we believe that the most likely explanation of the melilite/pyroxene data is that these two phases partitioned the REE between themselves by crystal structure control (MASON and MARTIN, 1974; ONUMA *et al.*, 1974). This is *not* in conflict with our earlier conclusion that the *bulk* REE patterns of the inclusions were not established by nebular partitioning of the REE into the major phases. It does require, however, that the distribution of the REE between the major phases took place *after* the accretion of the inclusions. The most likely mechanism is by crystallization of the melilite and pyroxene from molten inclusions (MASON and MARTIN, 1974; ONUMA *et al.*, 1974).

#### *Origin of the inclusions*

GROSSMAN and CLARK (1973) showed that inclusions of these compositions could have condensed in a partially molten condition at equilibrium if the total nebular pressure were greater than several millibars, but they ruled this possibility out on the basis of the absence of certain critical phase assemblages which would have resulted from crystallization of these liquids. BLANDER and FUCHS (1975) proposed that the inclusions condensed completely as metastable, sub-cooled liquid droplets in the same pressure range where GROSSMAN (1972) showed that Ca–Al-rich phases would condense as solids under equilibrium conditions. A third possible mechanism for the production of molten inclusions is through a secondary event which caused aggregates of solid condensates to melt while they were still suspended in the nebula. Such events could be high-energy impacts between aggregates, such as have been proposed by WHIPPLE (1972), CAMERON (1973b) and LANGE and LARIMER (1973) for the production of ferromagnesian chondrules.

In the model of BLANDER and FUCHS (1975), a sub-cooled liquid droplet condenses whose chemical composition varies with falling nebular temperature in a way very similar to the bulk composition of the solid condensates, as calculated by GROSSMAN (1972). Ultimately, the droplet cools to the point where the once-homogeneous liquid phase crystallizes to a mixture of Ca–Al-silicate and oxide phases. CLAYTON *et al.* (in press) showed that the different mineral phases separated from a single inclusion had not had their oxygen isotopic compositions homogenized, contrary to

what would be expected if they crystallized together from a common melt. BLANDER and FUCHS (1975) and CHOU *et al.* (1976) suggested that the isotopic heterogeneity was produced after the inclusions crystallized and by a mechanism involving the different diffusion rates of oxygen isotopes into the different mineral phases. This model collapses when it attempts to explain why spinel from inside melilite crystals has the same isotopic composition as spinel from inside pyroxene crystals when the melilite is far less enriched in  $O^{16}$  than the pyroxene (CLAYTON *et al.*, in preparation), suggesting that it exchanged its oxygen more readily than the pyroxene.

As far as the trace elements are concerned, they should have the same solubility in any two Blander–Fuchs droplets of the same composition at any temperature. The differences in bulk chemical composition between inclusions 3 and 6 (see Table 1) are very slight, certainly not great enough to produce the vastly different REE patterns observed between them. From this evidence alone, we conclude that *at least* the REE would have to be added to the inclusions in the solid form if the Blander–Fuchs model were correct.

The model we believe holds most promise of explaining all the data is one in which condensation of the major crystalline phases occurs as outlined in GROSSMAN (in press) down to the temperature range 1430–1440°K at  $10^{-3}$  atm. The refractory trace elements condense as an alloy in the case of the platinum metals and as several refractory oxide or silicate phases in the case of the REE, Hf, Sc and Ta. The grain sizes of the major phases may have been in the micron range as in the fine-grained Allende inclusions (GROSSMAN *et al.*, 1975), but the condensation of mm-sized crystals is also a distinct possibility at these temperatures. The refractory trace element carriers were probably grains much less than a micron in size. They may have been condensation centers for the major phases or vice versa. Also present in the nebula were refractory interstellar grains with non-solar oxygen (CLAYTON *et al.*, 1973) and magnesium (LEE and PAPANASTASSIOU, 1974) isotopic compositions. These could have provided condensation nuclei for both the major and the trace phases. The various types of grains often stuck to one another as they came in contact, forming aggregates several mm in size. Further condensation may have taken place on these nuclei, helping to cement the grains together. Occasionally, grains of lower-temperature condensates such as olivine, troilite or metallic nickel–iron, carried from lower-temperature regions of the nebula, were also incorporated by the aggregates. Then the aggregates were partially melted, perhaps during mutual, hypervelocity impacts. In many cases, depending on the temperatures reached, the REE carriers dissolved in the melt and the REE partitioned themselves between the crystallizing major phases. Other trace element-rich phases may have had such high melting points that they did not go into solution in the melt. These have not yet been observed in the

inclusions because of their exceedingly fine grain size. Just as they escaped vaporization during the high-temperature stage of the nebula, some of the interstellar grains must have escaped melting during this secondary heating event. They would have maintained substantially different isotopic compositions from other phases in the inclusions as long as they were hot for too short a time to allow complete isotopic exchange with the melt. Some of the interstellar material could be a fraction of one of the high-melting major phases, such as spinel.

Depending on the relative proportions of the phases which accreted together to form the inclusions, there is no need for any particular one to have the mean composition of the condensed fraction of the solar system at any specific temperature. Thus, Type B inclusions, though rich in SiO<sub>2</sub>, do not have cosmic Ca/Al ratios (see Table 1). The melting model suggests that the phases observed in the inclusions today are not all necessarily condensate phases. Thus, the Ti-rich pyroxene in the Type B inclusions may have nothing to do with condensation but may simply be a crystallization product of melts having a certain composition range. This could also be the case for anorthite, which does not appear as an equilibrium condensate phase until the temperature falls well below the point where magnesium silicates condense. Small amounts of lower-temperature condensates added as contaminants to the inclusions before they melted could account for the occasional presence of forsterite (BLANDER and FUCHS, 1975) and nickel-iron (GROSSMAN, 1975) in them. If a small amount of FeO-rich olivine were added, it could have reacted with the melt without re-precipitating as olivine and the FeO would reappear in solid solution in other phases. This can explain the presence of small quantities of FeO in fresh, unaltered grains of pyroxene and spinel (GROSSMAN, 1975) and perhaps some of the other volatiles (Co, Au, Mn, Cr) as well (KURAT *et al.*, 1975), although textural and isotopic evidence suggests that some of the alkalis entered the inclusions during metamorphism of the parent body (GROSSMAN and GANAPATHY, in press).

### Alais

During the course of this work, we analysed 24 mg of the Alais CI chondrite (FMNH Me 1486) in the form of two small lumps. From Table 4, it can be seen that this specimen yielded elemental abundances greatly different from our Orgueil data and average CI values in the literature. Specifically, the refractory lithophile elements are considerably enriched relative to CI chondrites, but not uniformly. Both refractory and volatile siderophile elements (Fe, Co, Au, Ir, Os) are depleted in our Alais sample by factors of two to four relative to Orgueil, as are the volatile lithophiles Na and Mn (GROSSMAN and GANAPATHY, in press). It is difficult to see how this complex enrichment and depletion pattern could be caused by laboratory or museum contamination. Furthermore, Zr and Hf in another Alais sample from the Field Museum analysed by us were found to be ~30 times higher than in Orgueil. SCHMITT *et al.* (1972) reported a Sc value for Alais (source unknown) which is 50% higher than their average CI data,

although the sample from the Paris Museum studied by KRÄHENBÜHL *et al.* (1973) appears normal for all the elements studied by them. We suggest that this matter be investigated more thoroughly, as potentially valuable information may exist in Alais if these abundance variations are real.

### CONCLUSIONS

1. Ten coarse-grained, spinel-bearing inclusions in the Allende meteorite are enriched in the 15 refractory elements Ca, Sc, Hf, Ta, W, Os, Ir, Ru, La, Ce, Sm, Eu, Tb, Dy and Yb by a mean factor of 18.6 relative to their abundances in CI chondrites, supporting the contention that they are samples of high-temperature condensates from the solar nebula.

2. The refractory siderophile elements Os, Ir and Ru were probably incorporated by the inclusions as tiny nuggets of an alloy in which they were dissolved in cosmic proportion to one another.

3. The refractory lithophile elements Sc and Hf entered the inclusions in a phase in which they were present in cosmic proportion to one another. A fraction of the REE was probably also present in this phase, although there is some indication of at least one other REE-rich phase.

4. Absolute concentrations and relative proportions of REE are independent of the identity of the major minerals in the inclusions, suggesting that the REE were not carried into the inclusions via condensation in solid solution in the major phases. Neither the condensation of their pure oxides nor their condensation in solid solution in perovskite can account fully for the observed REE abundances.

5. The distribution of REE between coexisting melilite and pyroxene in the inclusions appears to have been caused by the partitioning of the REE between these phases according to crystal structure controls. This occurred after accretion of the inclusions, probably during a stage of partial melting and rapid recrystallization without complete homogenization of isotopic compositions.

6. Some of the indigenous volatiles could have been introduced as small amounts of lower-temperature condensates before the inclusions were melted.

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