

## Trace elements in the Allende meteorite—III. Coarse-grained inclusions revisited

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**Abstract**—New RNAA determinations of Ba, Sr, Zr, U, Re, Pd, Ag, Zn and Se and INAA measurements of Lu are added to published data for 21 other elements in the same suite of ten samples. On the average, 21 refractory elements are not significantly fractionated from one another. The mean of their enrichment factors relative to C1 chondrites is  $17.5 \pm 0.4$ , indicating that the high-temperature condensate inclusions represent 5.7 wt% of the total condensable matter. Os, Ir, Ru, Re and most of the W condensed in one or more refractory siderophile element alloys along with small fractions of the Pd, Co, Au and Ag. The bulk of the Eu and Sr condensed in solid solution in melilite. Sc, Zr, Hf, Ta, U and the remaining REE condensed in a phase whose abundance in the inclusions is negatively correlated with that of melilite, either diopside or one or more minor or trace phases, including perovskite. Ba condensed in a different phase, separately from all these elements. In individual inclusions, fractionations are common between elements which were carried in by different condensate phases. Smaller fractionations are also observed for elements which condensed together. These may be due to variable proportions of them in a common condensate phase in response to different nebular equilibration temperatures or to multiple condensate phases containing different proportions of these elements. Available evidence indicates that some trace elements no longer reside in the phases which carried them into the inclusions, indicating a post-accretion thermal event which redistributed some of them. From the minimal variation of the Zr/Hf ratio in the inclusions, the solar system ratio is estimated to be  $29.6 \pm 1.8$ . From the mean U content of the inclusions and estimates of the bulk terrestrial and lunar U abundances, the Earth and Moon are estimated to contain 21% and 22–30% high-temperature condensates, respectively.

### INTRODUCTION

GROSSMAN and GANAPATHY (1976a) determined abundances of 15 refractory elements in a suite of ten coarse-grained, Ca-rich inclusions from the Allende meteorite. They discovered that enrichment factors calculated by dividing mean concentrations of refractory elements by their respective abundances in C1 chondrites are all nearly the same, indicating that these elements did not fractionate significantly from one another during high-temperature condensation in the region of the solar nebula sampled by coarse-grained inclusions. One purpose of the present study is to see if this uniformity extends to other refractory elements.

On the basis of detailed textural evidence, BLANDER and FUCHS (1975) suggested that the inclusions were once molten, although no compelling evidence exists that they condensed in this way. Oxygen isotopic evidence (CLAYTON *et al.*, 1977) indicates that they could not have been totally molten. Assuming that the inclusions accreted from solid condensates and were then partially melted while suspended in the nebula, minerals observed in them today may not necessarily be the same as those which originally accumulated to form the inclusions. Similarly, trace element ana-

lyses of mineral separates from such inclusions may yield very little information about the phases in which these elements originally condensed. Another major objective of the present study is, therefore, to use inter-element correlations for bulk inclusions to investigate the modes of condensation and incorporation of trace elements into them.

This paper adds new RNAA data for Ba, Sr, Zr, U, Re, Pd, Ag, Zn and Se and INAA data for Lu in coarse-grained inclusions to existing analyses by GROSSMAN and GANAPATHY (1975, 1976a) for 21 other elements in the same suite of samples.

### EXPERIMENTAL

#### Samples

Samples studied by RNAA in this paper are precisely the same aliquots of the coarse-grained inclusions for which INAA data were reported by GROSSMAN and GANAPATHY (1975, 1976a). Sample numbers are the same in all papers. Table 1 reviews the mineralogy of these samples as determined from approximate modal analyses of thin sections of fractions of the same inclusions analysed here or, when thin sections were not available, from X-ray powder patterns of aliquots. Also in Table 1, inclusions are classified as in GROSSMAN (1975). Type A inclusions are composed predominantly of melilite and spinel, with very small amounts of perovskite and diopside. Type B inclusions contain spinel and Ti-, Al-rich pyroxene as major phases, with lesser amounts of melilite and anorthite. Type I, intermediate, inclusions contain pyroxenes intermediate in composition between those in Type A and

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Table 1. Mineralogy of inclusions analysed in this study

Inclusion	Type	Melilite	Pyroxene	Spinel	Anorthite	Grossular	Perovskite
1	B	10	40	50			trace
2	B	5	50	40	5		
3	A	80		20			~1
4	B	10	55	25	10		
5	B	X	X	X	X	-	
6	A	90		10			~1
7	I		30	20	50		
8	B	X	X	X	-	X	
9	B	X	X	X	X	X	
10	B	X	X	X	X	X	

Numerical entries are vol% determined from thin sections. X and - denote "definitely present" and "possibly present", respectively, as determined from X-ray powder patterns.

Type B inclusions. It was difficult to tell whether an inclusion belonged to Type I or B when its mineralogy had to be determined from a powder pattern alone. In these cases, the dark color of the pyroxene seen in hand specimen was taken as an indication of a Ti-rich fassaite and its host inclusion was, therefore, classified as Type B.

#### Method

After completion of the INAA discussed in GROSSMAN and GANAPATHY (1976a), samples and standards were returned to the CP-5 reactor at Argonne National Laboratory where they received a thermal neutron flux of  $3 \times 10^{13} n/cm^2/\text{sec}$  for 10 days in the VT-25 position of the vertical thimble. The standard pot of PERLMAN and ASARO (1969) was used as a standard for Zn, U, Ba, Sr and Zr. Table 2 shows concentrations of these elements in that standard and the sources of these data. Chemical standards, prepared in essentially the same way as in KEAYS *et al.* (1974), were used for Ag, Re and Se. A Pd standard was prepared by dissolving "Specpure" Pd metal sponge in a small amount of concentrated aqua regia and diluting with 1 N HCl.

Two to three days after the end of irradiation, radiochemical separations began. Samples and standards were processed for Zn, Ag, Se and Re as in KEAYS *et al.* (1974), except that Ni crucibles were used. Because Zr, Pd, Ba and Sr were not determined by KEAYS *et al.*, details concerning radiochemical purification procedures for these ele-

ments are given here. Zr was separated from the KEAYS *et al.* rare earth fraction by the same procedure as in GANAPATHY *et al.* (1976), except that Zr was extracted into 0.4 M theonyl trifluoroacetone in benzene between two successive LaF<sub>3</sub> precipitations. Pd was separated from the KEAYS *et al.* Au fraction by repeated precipitations with dimethylglyoxime. As in LAUL and SCHMITT (1974), Ba and Sr were precipitated as sulphates from the KEAYS *et al.* AgCl fraction, were successively converted into their carbonates and nitrates and Ba was separated from Sr by precipitation as BaCrO<sub>4</sub>. We further purified Sr by precipitating it as carbonate, then nitrate and finally carbonate again. U was also determined in this fraction via its fission product <sup>140</sup>Ba, rather than through <sup>132</sup>Te as in KEAYS *et al.* Chemical yields for all elements are shown in Table 2. They were determined gravimetrically, except for Sr which was done by re-activation.

Careful re-examination of some of the spectra employed in obtaining the INAA data in GROSSMAN and GANAPATHY (1976a) revealed the presence of <sup>177</sup>Lu, a nuclide previously overlooked in that study. Thus, INAA data for Lu are also presented in this paper, based on spectra collected 5–15 days after the irradiation described in that study, over counting intervals of 12–24 hr. From the ratio of <sup>199</sup>Au counts at 158.4 keV to those at 208.2 keV measured in a pure Au standard and the count rate in our samples at 158.4 keV, it was determined that the potential interference of <sup>199</sup>Au to the <sup>177</sup>Lu peak at 208.4 keV is negligible in

Table 2. Analytical and counting information

Element	Nuclide	Energy <sup>1</sup> (kev)	Half-Life <sup>2</sup> (days)	Standard	Concentration in Standard (ppm)	Chemical Yield(%)	Counter	Counting Time
Ag	<sup>110m</sup> Ag	657.6	250.4	Chem		13 – 55	NaI	2–3 d
Ba	<sup>131</sup> Ba	123.7	11.7 <sup>3</sup>	SP	712 <sup>4</sup>	12 – 60	Ge(Li)	2–3 d
Lu	<sup>177</sup> Lu	208.4	6.71 <sup>3</sup>	SP	0.402 <sup>4</sup>	INAA	Ge(Li)	12–24 hr
Pd	<sup>103</sup> Pd	20.1	17.5	Chem		12 – 42	intr. Ge	10–16 hr
Re	<sup>186</sup> Re	137.0	3.78	Chem		25 – 40	Ge(Li)	0.5–16 hr
Se	<sup>75</sup> Se	136.0	120.4	Chem		25 – 40	Ge(Li)	1–3 d
Sr	<sup>85</sup> Sr	514.0	65.19	SP	145 <sup>4</sup>	15 – 62	NaI	1–20 hr
U	<sup>140</sup> La	487.0	12.79	SP	4.82 <sup>4</sup>	12 – 60	Ge(Li)	2–3 d
Zn	<sup>65</sup> Zn	1115.5	244.1	SP	126 <sup>4</sup>	7 – 58	Ge(Li)	2–28 hr
Zr	<sup>95</sup> Zr	756.9	63.98	SP	194 <sup>5</sup>	9 – 23	Ge(Li)	1–3 d

<sup>1</sup> PAGDEN *et al.* (1971a, b).

<sup>2</sup> Half-lives are taken from the most recent entry for each nuclide in *Nuclear Data Sheets*.

<sup>3</sup> HOLDEN and WALKER (1972).

<sup>4</sup> PERLMAN and ASARO (1971).

<sup>5</sup> GANAPATHY *et al.* (1976), using revised U fission correction.

Table 3. Element concentrations\* in coarse-grained inclusions

Sample	Mass (mgm)	Ba	Sr	Zr	Lu (ppb)	U (ppb)	Re (ppb)	Pd (ppb)	Ag (ppb)	Zn	Se (ppb)
1	15.35	44.7±4	132±1	62.5±1.1	502±14	187±9	513±10	12.4±2.5	4.19±.20	52.9±4	93.3±.9
2	2.67	28.9±3	55.8±6	114±2	936±41	237±8	808±14	77.6±9.0	13±2	21±2	63±5
3	15.21	39.5±3	159±2	38.7±1.0	439±24	117±6	581±4	30.0±3.9	1.46±.24	37.2±2	61.5±.8
4	4.39	32.6±3	112±1	50.2±1.5	392±35	123±10	730±14	66.3±9.3	15.0±.6	486±4	
5	5.13	50.5±3	83.8±9	13.6±1.2	135±12	123±12	5.2±1.1	5.7±3.4	1.83±.35	297±1	39.9±1.8
6	2.75	48.3±6	148±1	20.3±2.0	354±15	95±14	816±10	180±20	61.0±1.8	15.7±2	349±4
7	5.22	21.4±3	89±1	41.2±.9	390±26	107±8	591±9	53.4±5.2	19.0±.9	161±1	1259±8
8	17.36	77.1±3	153±2	33.4±1.3	267±17	199±6	39.8±5	26.4±4.2	.57±.27	51.4±3	49.9±.8
9	9.03	21.2±3	186±3	17.4±1.3	198±20	65±11	329±4	59.7±4.2	1.14±.25	55.4±3	106±1
10	22.31	45.6±5	126±1	109±1	783±28	263±5	832±13		.8±.11	58.4±3	291±2

\* ppm unless otherwise indicated.

these samples. It was necessary, however, to make a Yb correction to the Lu concentrations because reactor-produced  $^{177}\text{Yb}$  decays to  $^{177}\text{Lu}$ . We used PERLMAN and ASARO's (1969) determination that Yb accounts for 2.9% of the  $^{177}\text{Lu}$  activity in SP, our standard, to correct the Lu data in all our samples according to their measured Yb contents. Because the Yb/Lu ratios in the samples are very similar to that of SP, the maximum Lu correction was <2%.

The  $^{235}\text{U}$  fission contribution to the  $^{95}\text{Zr}$  activity was calculated from the mean of the two  $^{94}\text{Zr}$  thermal neutron capture cross-sections of SANTRY and WARNER (1973) and FULMER *et al.* (1971),  $47.5 \pm 2.4$  and  $52 \pm 3$  mb, respectively, and found to be equivalent to  $11.3 \mu\text{g}$  of Zr per  $\mu\text{g}$  U.

Shown in Table 2 are the nuclides used for determination of each element, energies of their analytical peaks, half-lives employed in this work and the counting time and type of counter used for each element. The Pd precipitates were counted on a 10% efficiency, intrinsic Ge X-ray detector. A 2 in.  $\times$  2 in. NaI scintillation counter was used for the Ag and Sr precipitates. All other counting was done with a 9.6% efficiency Ge(Li) detector. Ba and U were determined in the same precipitate.

## RESULTS

Concentrations of all elements in the ten inclusions studied in this work are given in Table 3. Unfortunately, one Pd and one Zn sample were lost during radiochemical processing.

Table 4 summarizes existing literature data for these elements in Allende coarse-grained inclusions and compares them with analytical data obtained in this work. Difficulty was often encountered in determining whether an inclusion mentioned in the literature is a coarse- or fine-grained inclusion as defined by GROSSMAN and GANAPATHY (1975) or whether it is some other type of object. Samples entered on Table 4 were selected for the following reasons. The ten "group I melilite-rich chondrules" of MARTIN and MASON (1974) are obviously coarse-grained inclusions according to the GROSSMAN and GANAPATHY (1975) definition because they are described as "spherical aggregates of melilite, Ti-rich fassaite, spinel and anorthite with a coarsely crystalline igneous texture". Similar descriptions of sample WA (CHEN and TILTON, 1976), inclusion 2 of CHOU *et al.* (1976), CONARD's (1976) samples A-2, B-28, D-7 and C1-S2 by GRAY *et al.* (1973), the single inclusion analysed by MASON and MARTIN (1974) and samples N18

Table 4. Comparison of literature data for coarse-grained Allende inclusions with data obtained in this work (values in ppm unless otherwise indicated)

References	Ba	Sr	Zr	Lu(ppb)	U(ppb)	Re(ppb)	Pd(ppb)	Zn
Gast <i>et al.</i> (1970)	47.3	180						
Tanaka and Masuda (1973)	42.5	118		738				
Martin and Mason (1974)*	23-104; 57	110-200; 136	35-72; 56					
Mason and Martin (1974)	49	110	59				510	
Wanke <i>et al.</i> (1974)		130	93	500	120	730	82	82
Chen and Tilton (1976)					94			
Chou <i>et al.</i> (1976)							67, 59	
Conard (1976)*	26.5-63.7; 46.3	100-185; 144		122-630; 390		18-460; 310		34-260; 90
Palme and Wlotzka (1976)						1520		
Tatemoto <i>et al.</i> (1976)		180.9, 118.4			106, 105			
This Work*	21.2-77.1; 41.0	55.8-186; 124	13.6-114; 50.0	135-936; 440	65-263; 152	5.2-832; 525	5.7-180; 56.8	15.7-297; 105

\* Entries for this reference are the ranges of values and the means.

and N19 of TATSUMOTO *et al.* (1976) are sufficient to place all these samples in the coarse-grained inclusion category of GROSSMAN and GANAPATHY (1975). Although no textural information is given by TANAKA and MASUDA (1973), the mineralogy of their "inclusion O" seems to fit the description of a coarse-grained inclusion. No mineralogical data are given by CONARD (1976) for her inclusion from specimen NM3529, but its bulk chemical composition seems to place it in the coarse-grained category. A characteristic feature of coarse-grained inclusions, and one found in no other silicate fractions reported so far from Allende, is their exceptionally high refractory siderophile element content. Using this criterion, inclusion 1 of CHOU *et al.* (1976) and the single inclusions analysed by WÄNKE *et al.* (1974) and PALME and WLOTZKA (1976) are probably coarse-grained inclusions. The Ca-rich inclusion analysed by GAST *et al.* (1970) is included because it is enriched nearly uniformly in rare earth elements (REE) by a factor of 15–20 relative to chondritic abundances like many coarse-grained inclusions.

From Table 4, it is seen that Zn and Zr values reported here are in excellent agreement with literature data, with our ranges bracketing all previous determinations. Agreement is also good for Lu and Ba, except that CONARD (1976) found one Lu value below our range and MARTIN and MASON (1974) found some Ba concentrations above our range. Our value for Lu in BCR-1,  $485 \pm 17$  ppb, is in excellent agreement with those of CONARD (1976) and NAKAMURA (1974), 490 and 503 ppb, respectively. In the case of Sr, several of our inclusions have concentrations below 100 ppm, lower than those reported by any other laboratory. At least four inclusions in the literature are higher than 160 ppm Sr, but this is the case for only one of the ten samples studied here. This is probably due to the problem of sampling a population of objects with highly variable concentrations, rather than to analytical error, since many of our samples have Sr abundances quite close to those reported for other inclusions in the literature. Until now, only four U determinations of high accuracy existed in the literature for bulk inclusions. Several of our inclusions have U contents in good agreement with these. It is important to note, however, that several others in our suite are substantially richer in U and that these U enhancements are accompanied by enhancements in other refractory lithophiles (see Fig. 5). The Pd value of WÄNKE *et al.* (1974) is in agreement with our data, but that of MASON and MARTIN (1974) appears to be too high. The Re value of WÄNKE *et al.* (1974) is consistent with our data but that of PALME and WLOTZKA (1976) is much higher than any of ours. This is understandable considering that other refractory siderophiles in their inclusion are proportionately enriched relative to our inclusions. CONARD's (1976) INAA data for Re are consistently lower than most data from this laboratory and others. To our knowledge, Ag and Se data presented here are the only values so far reported from coarse-grained inclusions, so no comparison with other workers is possible.

## REFRACTORY ELEMENTS

### Enrichment factors

LARIMER and ANDERS (1970) and MARVIN *et al.* (1970) were the first to point out the similarity between the mineralogy of the coarse-grained, Ca-rich inclusions in the Allende meteorite and that of the earliest condensates predicted by thermodynamic calculations to crystallize from a cooling gas of solar composition. GROSSMAN (1972) showed that the mineralogy of the Type A inclusions is identical with that expected of the pre-forsterite condensates which

solidified at temperatures above  $1450^{\circ}\text{K}$  in a region of the solar nebula whose total pressure was  $10^{-3}$  atm. More recent calculations (LATTIMER *et al.*, to be published) have revised this temperature estimate to  $1437^{\circ}\text{K}$ . GROSSMAN (1973) calculated that a variety of trace elements should have condensed totally above  $1450^{\circ}\text{K}$  and showed that several of these refractory trace elements are enriched in the inclusions relative to their cosmic abundances.

This work was greatly expanded by GROSSMAN and GANAPATHY (1976a) who found that Type A and Type B inclusions are similarly enriched in refractory trace elements, suggesting that both types are high-temperature condensates despite the fact that the mineralogy and major element chemistry of Type B inclusions differ from those predicted from thermodynamic calculations for the early condensates. Data for 21 elements in the same suite of ten coarse-grained inclusions from that work and the present study are summarized in Table 5. For reasons which will be discussed later in this paper, sample 5 of this collection of inclusions is ignored in the ensuing discussion. The mean concentrations of these elements in the remaining nine coarse-grained inclusions are listed in column 1 of the table along with their standard errors. Included in the table are the data of GROSSMAN and GANAPATHY (1976a) for 13 elements predicted from thermodynamic calculations (GROSSMAN, 1973; GROSSMAN and GANAPATHY, 1976a) to be totally condensed from the solar nebula at temperatures above  $1437^{\circ}\text{K}$ . Also included are new data from the present study for Lu, U, and Zr and Re which are predicted to be refractory from thermodynamic calculations in GROSSMAN and GANAPATHY (1976a), GANAPATHY and GROSSMAN (1976) and GROSSMAN (1973), respectively. Data are also presented in this table for several elements that could not have condensed totally from the solar nebula above  $1437^{\circ}\text{K}$ , either as pure oxides or in ideal solid solution in perovskite, according to existing thermodynamic data. These are the Ce and Eu data of GROSSMAN and GANAPATHY (1976a) and Sr and Ba data from the present study. In column 2 of the table are given the concentrations of all these elements in C1 chondrites along with literature sources of these data for the elements determined in the present study. Literature data used for C1 abundances of the other elements can be found in GROSSMAN and GANAPATHY (1976a). The mean enrichment factor for each element, calculated by dividing its mean concentration in the nine inclusions by its abundance in C1 chondrites, is given in the final column and illustrated in Fig. 1.

We note first from Table 5 how remarkably uniform the enrichment factors are for all 17 elements known to be refractory. The mean enrichment factor for these is  $17.4 \pm 0.4$ . As suggested by GROSSMAN (1973) and GROSSMAN and GANAPATHY (1976a), this is probably due to the fact that each of these elements condensed totally from the nebula at temperatures greater than the accretion temperature of the inclu-

Table 5. Enrichment factors relative to C1 chondrites for twenty-one refractory elements in nine coarse-grained Allende inclusions (values in ppm unless otherwise indicated)

Element	Mean Concentration	Concentration in C1 Chondrites	Enrichment Factor
Ca	17.2 ± 1.8%	0.975 %	17.7 ± 1.9
Sr	129 ± 13	8.6 <sup>1</sup>	15.0 ± 1.5
Ba	39.9 ± 5.7	2.4 <sup>2</sup>	16.6 ± 2.4
Sc	118.3 ± 23.8	6.4	18.5 ± 3.7
La	4.24 ± 0.43	0.253	16.8 ± 1.7
Ce	13.7 ± 2.2	0.645	21.3 ± 3.4
Sm	2.80 ± 0.31	0.154	18.2 ± 2.0
Eu	1.13 ± 0.07	0.0587	19.3 ± 1.3
Tb	0.60 ± 0.12	0.039	15.3 ± 3.0
Dy	4.9 ± 0.8	0.252	19.4 ± 3.2
Yb	2.7 ± 0.3	0.168	15.9 ± 2.0
Lu	0.47 ± 0.08	0.0253 <sup>5</sup>	18.7 ± 3.2
Zr	54.1 ± 11.8	3.1 <sup>3</sup>	17.4 ± 3.8
Hf	1.84 ± 0.41	0.11 <sup>3</sup>	16.7 ± 3.7
Ta	0.24 ± 0.04	0.0134	17.9 ± 2.8
W	1.88 ± 0.36	0.088	21.4 ± 4.1
U	155 ± 23 ppb	9.1 ppb <sup>4</sup>	17.0 ± 2.5
Re	582 ± 88 ppb	35.2 ppb <sup>4</sup>	16.5 ± 2.5
Ru	10.5 ± 1.7	0.69	15.3 ± 2.4
Os	8.1 ± 1.3	0.480	16.9 ± 2.6
Ir	8.16 ± 1.36	0.514	15.9 ± 2.6
Mean		17.5 ± 0.4	

<sup>1</sup> GOPALAN and WETHERILL (1971).

<sup>2</sup> REED *et al.* (1960).

<sup>3</sup> GANAPATHY *et al.* (1976).

<sup>4</sup> KRÄHENBÜHL *et al.* (1973).

<sup>5</sup> NAKAMURA (1974).

sions. Refractory trace elements must have been virtually totally scavenged from the nebular gas during accretion of the inclusions, either by incorporation of their host phases into the major mineral grains accumulating to form the inclusions or by condensing

as solid solutions in those major minerals. This results in enrichment factors relative to C1 chondrites which are nearly the same for all these elements because their relative abundances in the nebula were identical to those in C1 chondrites and the inclusions have

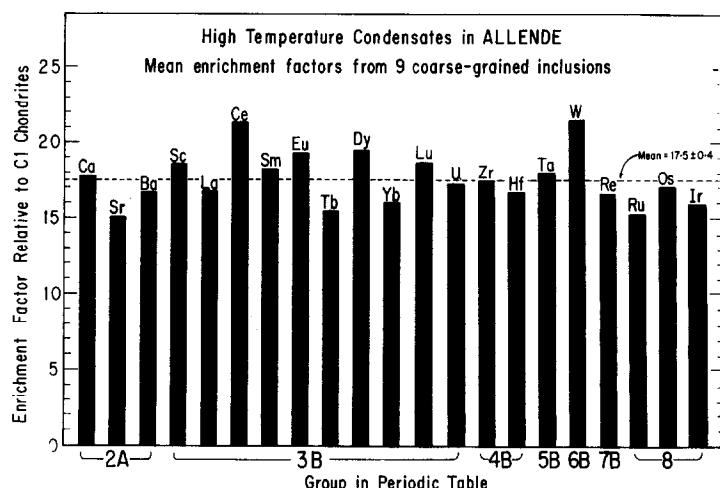


Fig. 1. Despite fractionations between different refractory elements in individual coarse-grained inclusions, refractories are not significantly fractionated from one another in the collection of inclusions as a whole. This indicates virtually total condensation of refractories above the accretion temperature of the inclusions and efficient scavenging of them by the inclusions.

incorporated them in unfractionated proportion to one another, regardless of chemical differences.

The enrichment factors for Ce(21.3), Eu(19.3), Sr(15.0) and Ba(16.6) are very similar to those of the known refractory elements. Including these four elements in the average, the mean enrichment factor for all 21 elements in Table 5 is  $17.5 \pm 0.4$ , little different from that of the 17 known refractories. Despite the fact that thermodynamic calculations have not yet shown how these four elements could have condensed totally above 1437°K, we conclude from these observations that they must have done so, perhaps as phases or solid solution components for which no thermodynamic data yet exist. More will be said of this later in this paper.

BOYNTON (1977) attempted to show that U was incompletely condensed into coarse-grained inclusions from literature data for a total of 11 such inclusions which, he claimed, showed that their mean Th/U ratio is significantly higher than the chondritic value,  $3.6 \pm 0.2$ . If his contention were true, it would manifest itself in a substantially lower enrichment factor for U than for all other refractories in this work, which is clearly not the case. Th and U were analysed in only ten of the inclusions cited by Boynton. Eight of these determinations are from the work of MASON and MARTIN (1977). The U concentrations appear to be very close to the detection limit in that work as they are quoted to only one significant figure in seven of the eight samples. In addition, the U concentrations of these seven inclusions are considerably lower than those of 12 of the 13 other inclusions reported both here and elsewhere in the literature. Boynton's conclusion is thus largely influenced by data of relatively poor quality. Of all the inclusions cited by Boynton, only the remaining two have Th/U ratios which are known with a high degree of accuracy. That analysed by CHEN and TILTON (1976) has a ratio of 7.6, higher than chondritic, while that measured by TATSUMOTO *et al.* (1976) has a ratio of 3.5, slightly lower than chondritic. A second coarse-grained inclusion studied by TATSUMOTO *et al.*, and overlooked by Boynton, has a ratio of 2.6, considerably less than chondritic. The latter three inclusions have a mean Th/U ratio of 4.6 with a standard error of  $\pm 1.5$ , which is well within error of the chondritic value. The Th/U ratio is apparently quite variable from inclusion to inclusion. This is the case for many other refractory element pairs, as discussed at length by GROSSMAN and GANAPATHY (1976a) and later in this paper. Despite these variations, however, Table 5 and Fig. 1 show that the mean ratios are always very close to their chondritic values when a sufficient number of inclusions are considered.

#### *Uniformity of enrichment factors*

Is it possible that the enrichment factors are identical for every refractory element in the high-temperature condensates? W has the largest enrichment factor, 21.4, and Sr the smallest, 15.0. The maximum

difference between enrichment factors is thus 43%. We note that C1 data used for normalization are based on only one determination each for Ba, Hf, Ta and W. The Zr concentration in C1's is based on only two data points. The C1 REE data are means of measurements of two aliquots of Orgueil which differ by 6–7% for most REE but nearly 10% for Yb (NAKAMURA, 1974). Several more high-quality determinations of these elements in C1 chondrites would greatly improve confidence in their solar system abundances and could conceivably yield mean values whose use in normalization would reduce the apparent scatter of enrichment factors about their mean in coarse-grained inclusions.

There are two types of problems associated with the data for the coarse-grained inclusions themselves that could be responsible for artificially producing enrichment factors which are more variable than may actually be the case for the high-temperature condensates. First, an undetected interference with an element's photopeak in either the sample or standard or adoption of an erroneous value for the concentration of an element in its standard will produce spuriously high or low abundances of that element in all samples. Although discrepancies between laboratories amounting to 5–10% can be interpreted to indicate effects of this sort for some elements, they are more commonly attributed to sample inhomogeneities rather than to analytical error. A large proportion of the observed scatter about the mean enrichment factor could thus be due to small, undetected analytical errors. The second problem concerns how representative this suite of coarse-grained inclusions is of the high-temperature condensates. As can be seen from Table 3 and column 1 of Table 5, the concentration of any particular refractory element varies widely from inclusion to inclusion. Because of this, even if enrichment factors are identical for all refractory elements in the high-temperature condensates, the concentration of any particular element could easily be over- or under-represented in our sample. A possible example of this was discussed earlier in this paper where it was noted that inclusions with high Sr contents are relatively rare in this collection compared to others reported in the literature, possibly accounting for the relatively low Sr enrichment factor. Another example may be the case of the siderophiles, Re, Ru, Os and Ir, which, as a group, seem to be slightly less enriched than the lithophiles. This is apparently due, however, to very low abundances of these elements in only one inclusion, sample 8, rather than to uniformly lower concentrations in all inclusions.

Because of the uncertainties discussed above, all refractory elements could conceivably have identical enrichment factors. Because of these same uncertainties, however, real differences of as much as 20% between enrichment factors for different refractories cannot be ruled out. In the latter case, the implication would be either that different fractions of different

refractories had condensed above the accretion temperature of the inclusions or that they were not incorporated into the inclusions with equal efficiency or both.

The composition of C1 chondrites is generally believed to approximate that of the total condensable matter of the solar system. Any element concentrated totally into a smaller fraction of the condensable matter will be enriched in it relative to C1 chondrites by a factor equal to the inverse of this fraction. If all refractory elements have the same enrichment factor in coarse-grained inclusions, then they all condensed totally into the high-temperature condensates. The above argument can then be used to compute what fraction of the total condensable matter is represented by coarse-grained inclusions, simply by taking the inverse of the mean enrichment factor. For an enrichment factor of 17.5, this calculation indicates that the early condensates, as represented by coarse-grained inclusions, constitute 5.7 wt% of the total condensable matter. According to solar condensation calculations of LATTIMER *et al.* (to be published), condensation of this fraction of the total condensable matter is achieved at 1437°K, when melilite is only partially converted to diopside. This indeed seems to be the stage of condensation reached by Type A inclusions, as recorded in their mineralogy and texture (GROSSMAN, 1972). Thus, the accretion temperature of coarse-grained inclusions inferred from their mineralogy is the same as that suggested by their trace element content.

#### Concentration variations

The extreme variation often seen in the concentration of a refractory element from inclusion to inclusion was discussed by GROSSMAN and GANAPATHY (1976a) and touched upon in the previous section in relation to its effect on the uncertainties associated with values of the enrichment factors. Eu, the refractory element with the smallest concentration range, varies by a factor of 2.14. Ir shows the greatest range, varying by a factor of 21.6. The concentrations of each refractory element are distributed broadly about their mean. Eu has the smallest standard deviation, 6.6%, and Zr the greatest, 21.8%. In addition, as noted by GROSSMAN and GANAPATHY (1976a), and above for Th and U, and as discussed in greater detail later in this paper, the ratios of certain refractory elements to one another vary widely in different inclusions, often deviating markedly from their cosmic ratios. This indicates that some refractories condensed in different phases from others or in variable proportion to one another in the same phase and that individual inclusions did not sample all available condensate grains in exactly the same proportions as their relative abundances in the nebula. We have seen, however, that the mean enrichment factor relative to C1 chondrites is very nearly the same for each refractory element in the nine coarse-grained inclusions. This means that refractories are not significantly frac-

tionated from each other in the collection of inclusions as a whole, even though individual inclusions often show large fractionations between different refractory elements. The explanation is simply that a large number of inclusions is more representative of the high-temperature condensates than any single one.

#### Fine-grained inclusions

In a study of the chemistry of nine fine-grained inclusions, GROSSMAN and GANAPATHY (1976b) again found large variations in the abundances and ratios of refractory elements in individual inclusions but, in this case, even the mean concentrations of different refractories in the collection of inclusions as a whole showed that they were dramatically fractionated from one another relative to C1 chondrites. Using these data and mineralogical and textural arguments, GROSSMAN and GANAPATHY (1976b) proposed that fine-grained inclusions formed at low temperature by simultaneous condensation of volatiles and refractories. These refractories had become supersaturated when, during departures from equilibrium, they failed to condense into coarse-grained inclusions. In proposing this model, they assumed that the mean enrichment factors were *not* exactly the same for different refractories in the coarse-grained inclusions, reflecting slight variations in the fractions of each of them condensed into the high-temperature fraction. They pointed out that, if departures from total condensation into the coarse-grained inclusions were quite small, then the residual gas phase, and the fine-grained inclusions which subsequently condensed from it, would have had refractory element abundances which were severely fractionated from one another relative to C1 chondrites. GROSSMAN and GANAPATHY (1976b) noted that sample 5 of the coarse-grained inclusion set analysed by GROSSMAN and GANAPATHY (1976a) had the same fractionated REE pattern and low refractory siderophile content (see Re in Table 3) characteristic of fine-grained inclusions and proposed, therefore, that it is not a high-temperature condensate inclusion. They suggested that it may have originated as a fine-grained inclusion which had been melted and devolatilized in the nebula and had finally crystallized with a coarse-grained texture. Because its chemistry suggests that it is derived from another identifiable population of objects, we have neglected inclusion 5 thus far and will continue to do so in our discussion of high-temperature condensation.

## CONDENSATE PHASES

#### Correlation matrix

The matrix of linear, inter-element correlation coefficients for all concentration data measured in this suite of nine samples in GROSSMAN and GANAPATHY (1975; 1976a) and the present work is shown in Table 6. Numerical values for correlation coefficients appear

Table 6. Linear correlation coefficients significant at the 95% confidence level.

	Ca	Sc	La	Ce	Sm	Eu	Tb	Dy	Yb	Lu	Sr	Ba	Zr	Hf	Ta	U	
Ca	1.000		-0.689	-0.725	-0.680	0.749		-0.781		0.747		-0.728	-0.694		-0.674		
Sc		1.000	0.857	0.819	0.899	-0.821	0.761		0.790	0.963	-0.690		0.919	0.973	0.693	0.783	
La	*		1.000	0.867	0.968	-0.834	0.938	0.875	0.883	0.860		0.918	0.863	0.707	0.829		
Ce	*	*		1.000	0.796	-0.795	0.732	0.809	0.738	0.869	-0.805		0.880	0.880			
Sm	*	*	*		1.000	-0.886	0.914	0.762	0.869	0.886			0.913	0.889	0.687	0.886	
Eu	*	*	*	*		1.000	-0.741		-0.739	-0.799	0.766		-0.791	-0.837		-0.729	
Tb	*	*	*	*			1.000	0.895	0.775	0.752			0.832	0.743	0.693	0.798	
Dy	*	*	*	*				1.000	0.744	0.697			0.812		0.673		
Yb	*	*	*	*					1.000	0.805			0.913	0.845	0.816	0.936	
Lu	*	*	*	*	*				*	1.000	-0.717			0.964	0.973	0.715	0.783
Sr	*	*	*	*	*						1.000						
Ba												1.000					
Zr	*	*	*	*	*		*	*	*	*			1.000	0.960	0.798	0.867	
Hf	*	*	*	*	*				*	*	*		*	1.000	0.684	0.799	
Ta													*		1.000	0.830	
U	*	*	*	*	*		*	*	*	*			*	*	*	1.000	
Os																	
Ir																	
Ru																	
Re																	
W																	
Pd																	
Co																	
Au																	
Ag																	
Cr																	
Mn																	
Fe																	
Zn																	
Se																	
Na																	

in the upper half of the table for all element pairs whose linear correlations are significant at the 95% confidence level. Asterisks appear in the lower half of the table when these correlations are also significant at the 99% level.

#### Refractory siderophiles

The strong correlations between Os, Ir and Ru noted by GROSSMAN and GANAPATHY (1976a) are indicated in Table 6 where all possible inter-element concentration correlations among these elements and between them and Re are seen to be significant at the 99% level. That work emphasized how little fractionated the first three of these elements are from one another in each inclusion analysed. This observation, too, is extended to Re in this work, as can be seen in Fig. 2. Here, Re and Ir concentrations lie very close to a line whose slope equals the cosmic Re/Ir ratio. Such behavior on the part of Os, Ir and Ru was interpreted by GROSSMAN and GANAPATHY (1976a) to indicate that each of these elements was totally condensed above 1450°K into a common alloy phase which was incorporated in different amounts by different inclusions. From data in this paper, Re appears also to have been a constituent of this alloy.

Since the work of GROSSMAN and GANAPATHY (1976a), two studies have appeared which bear directly on this matter. Using a scanning electron

microscope equipped with a solid-state detector, WARK and LOVERING (1976) discovered alloys of Ru, Os, Ir, Pt, W, Mo, Ni and Fe as nuggets with diameters from 0.5 to 3 µm in a Type A coarse-grained Allende inclusion. In addition to these elements, high

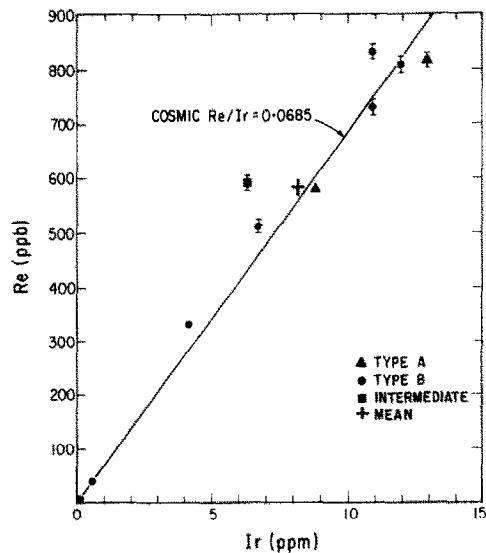


Fig. 2. Individual inclusions show little fractionation of Re from Ir, suggesting that they condensed totally into one or more alloys with other refractory siderophiles.

Asterisks indicate inter-element correlations significant also at the 99% level

Re, Co and Rh contents were found by PALME and WLOTZKA (1976) in a similar metal particle, 20  $\mu\text{m}$  in diameter, from another Allende inclusion in a combined INAA and electron microprobe study. It is tempting to use such observations as confirmation of models which predict these elements to condense as metals (GROSSMAN, 1973) and in a solid solution with one another (PALME and WLOTZKA, 1976) above the accretion temperature of the inclusions. One of the exceptional features of the grains described so far is that their compositions are variable and often highly fractionated compared to cosmic abundances. For example, while the Os/Ir ratio only varies from 0.92 to 1.25 for bulk coarse-grained inclusions, it ranges from 0.86 to  $>13$  in the metal grains. The cosmic ratio is 0.93. This could mean that different nuggets were removed from equilibrium with the gas at different temperatures, either because they grew so large that diffusion into their centers was slow compared to the cooling rate or because they were incorporated by growing crystals of major condensate phases. Alternatively, because of the possibility of unmixing and compound formation, it is certainly conceivable that several different refractory siderophile phases could be stable condensates in this eleven-component system and many of these would have had to change their equilibrium composition as the surrounding gas cooled. The fact that the Os/Ir ratio is so close to

cosmic in each bulk inclusion means that both elements must be totally condensed above 1437°K and that compositional differences between different metal condensate grains are averaged out in some process accompanying formation of each inclusion. To have escaped detection in many petrographic studies, the mean radius of the metal grains must be <0.25 μm. In order to account for the mean Os content of a 0.5 cm diameter coarse-grained inclusion, more than  $10^7$  such metal grains must be present. Apparently, the averaging process was simply the incorporation of vast numbers of alloy grains by each inclusion. Such inferences, though interesting, cannot be made if compositions and textures of the metal nuggets were altered or established during post-condensation events which heated or partially melted the inclusions. Under these circumstances, perhaps a less ambiguous source of information about refractory siderophile element condensation are chemical data for bulk inclusions.

Although W is predicted to be one of the highest-temperature condensates both as a pure metal (GROSSMAN, 1973) and as a constituent of a siderophile element alloy (PALME and WLOTZKA, 1976), it is less strongly correlated with Os, Ir, Ru and Re than are these four elements with one another. Its correlation with the former two is significant at the 95% level but not at the 99% level. It fails to correlate

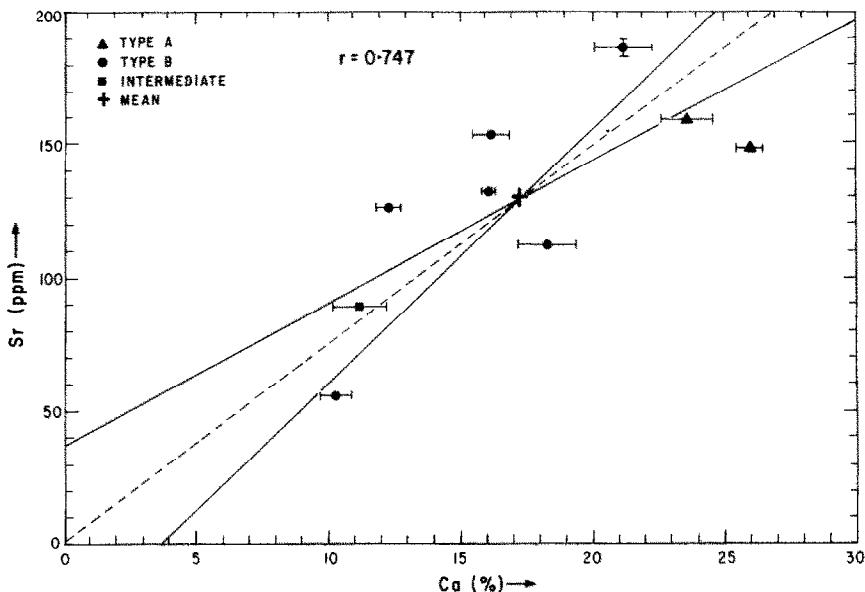


Fig. 3. The strong Sr-Ca correlation extends to Ca contents as high as 26%, indicating that most of the Sr condensed in melilite.

with the latter two at the 95% level but does so at the 90% level. W probably condensed as a component of the refractory siderophile alloy. Its failure to correlate with the other components at the 99% level may be related to the greater analytical uncertainty for W due to its poorer counting statistics. An equally plausible explanation is that a fraction of the W may have condensed in the alloy and another fraction in some other form. Significant amounts of W were seen in the metal nuggets by WARK and LOVERING (1976) and PALME and WLOTZKA (1976), but it is not known how much of this W was present in the original metal condensate and how much was added during a latter recrystallization event.

#### Refractory lithophiles

**Ca, Eu and Sr.** The correlation coefficients pres-

ented in Table 6 for the element pairs Ca-Eu, Ca-Sr and Eu-Sr show that these elements are positively correlated with one another at the 98% confidence level. At least some of the Eu and Sr must have been brought into the inclusions with a major, Ca-bearing phase. PALME *et al.* (1975) also reached this conclusion for Eu from its positive correlation with Ca in their suite of inclusions. In order to learn more about the condensation behavior of Sr and Eu, their concentrations are plotted against those of Ca in Fig. 3 and 4, respectively. The two least squares regression lines for each element pair, as well as the average line computed from these, are shown on each graph. For each element pair, the data points scatter so widely that its two regression lines have significantly different slopes and intercepts from one another. These two lines can be considered as probable error limits about their mean.

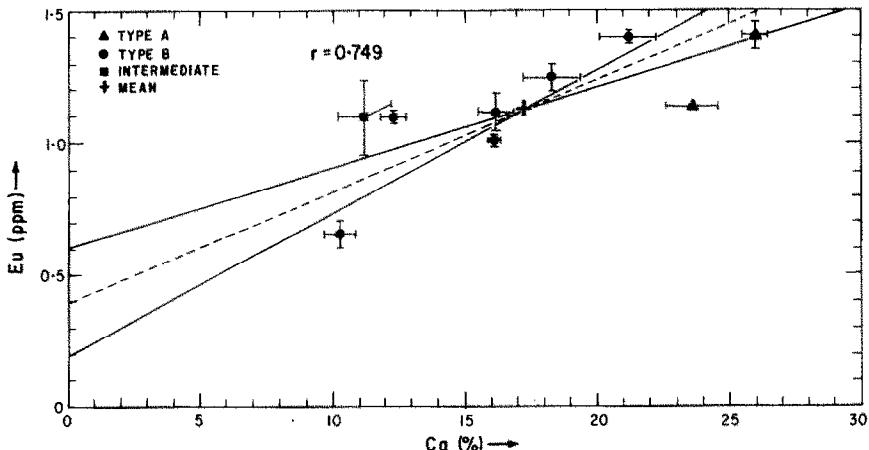


Fig. 4. Eu is strongly correlated with Ca and Sr, indicating that the bulk of it also condensed in melilite. The non-zero intercept of the Eu-Ca correlation implies that a significant fraction of the Eu condensed in another phase.

If the coarse-grained inclusions were melted after they condensed, the minerals and their relative proportions seen in thin section today are not necessarily the same as those which accreted together to form the inclusions. We must thus rely on condensation theory to tell us what phases could have carried trace elements into the inclusions. Allowing for the possibility of incomplete reaction of early-formed condensates with the vapor, the original major phases of the inclusions could have been corundum or hibonite, perovskite, melilite, spinel and diopside (GROSSMAN, 1972). Because the correlations extend to 26% Ca, the Sr-Eu-rich end-member must contain at least this much Ca. This eliminates corundum and spinel because they contain no Ca and hibonite and diopside because they contain too little Ca, 6.0% and 18.5%, respectively. The only remaining candidates are perovskite and melilite, both with ~29.3% Ca. Because the maximum Ti content observed in coarse-grained inclusions is only 1.65% (CONARD, 1976), the maximum perovskite content is more than an order of magnitude too low to account for the Ca content of any of the inclusions studied here. Melilite is thus the Sr-Eu-rich carrier. This does not necessarily mean, however, that Sr and Eu condensed in melilite. Instead, they may have condensed in a trace phase which was preferentially incorporated by melilite, but there is no reason to prefer this extra complicating factor.

As seen in Fig. 3, no other Sr-containing component is required by the data because the most probable intercept of the Sr-Ca correlation is very close to zero, 1.4 ppm Sr. In this case, the scatter of data about the mean regression line could be caused by a variable Sr content in the melilite which in turn, could reflect differences in the nebular equilibration temperature of the melilite. Another component with the same mean Sr/Ca ratio as the melilite, but lower Ca content, cannot be ruled out but is not required by the data. The uncertainty in the regression line is large enough, however, to allow an additional Sr carrier with either a higher or lower Sr/Ca ratio than the melilite. In this case, the scatter could be caused by the mixing of both Sr carriers with Ca-Sr-free phases, such as spinel, in addition to variations in end-member compositions.

The Eu-Ca data, Fig. 4, require a second Eu carrier with a higher Eu/Ca ratio than melilite because the intercept of their regression line is  $0.4 \pm 0.2$  ppm Eu. A large fraction of the Eu in these samples was contributed by a phase other than melilite. Here again the scatter could be caused by variable end-member compositions and by mixing with Eu-Ca-free phases.

*Condensation of Eu and Sr.* As pointed out above and in GROSSMAN and GANAPATHY (1976a), the condensation behavior of Eu is somewhat of a mystery. Eu shows a normal enrichment factor in coarse-grained inclusions, indicating its total condensation above their accretion temperature. Yet, the calculations of GROSSMAN and GANAPATHY (1976a), which

assume ideal solution of  $\text{Eu}_2\text{O}_3$  in perovskite, show that only <40% of the total Eu could condense above 1437°K. The situation is improved if  $\text{Eu}_2\text{O}_3$ ,  $\text{Eu}_3\text{O}_4$  and  $\text{EuO}$  are all allowed to dissolve in both perovskite and melilite. In this case, ~90% of the Eu condenses above 1437°K. Thus, the magnitude of the Eu enrichment factor can be accounted for only marginally, at best, by these calculations. This is not the only problem. These three Eu oxides are the only reasonable candidates for solar nebular condensates for which thermodynamic data are available. In BOYNTON (1975) and GROSSMAN and GANAPATHY (1976a), crystalline  $\text{Eu}_2\text{O}_3$  is found to be more stable than  $\text{Eu}_3\text{O}_4$  or  $\text{EuO}$  in the solar nebula below 1650°K, leading necessarily to the conclusion that Eu condenses predominantly as a trivalent ion when these species are used as solid solution components. The oxygen fugacity of the nebula is  $\sim 10^{-17}$  atm. at 1600°K and only  $\sim 10^{-23}$  atm. at 1500°K. The problem is that experiments conducted by DRAKE (1975) show conclusively that Eu is predominantly divalent over this temperature range in both plagioclase and a basaltic andesite melt at oxygen fugacities as high as  $10^{-12.5}$  atm. This suggests that Eu was probably divalent when it condensed in solution in melilite. Our use of Eu oxides as solid solution components in silicates such as melilite, and perhaps even in perovskite, is a gross over-simplification and leads to demonstrably incorrect results. To do the calculations properly will require thermodynamic data for more relevant components, such as  $\text{Eu}_2\text{Al}_2\text{SiO}_7$  and  $\text{EuTiO}_3$ .

A similar difficulty is encountered in the case of Sr. Its enrichment factor in coarse-grained inclusions is also normal, again indicating nearly total condensation above 1437°K. With data for only one crystalline phase,  $\text{SrO}$ , calculations show that only ~10% of the total Sr can condense in ideal solution in melilite above this temperature. Thermodynamic data are obviously needed for such species as  $\text{Sr}_2\text{Al}_2\text{SiO}_7$ .

DRAKE and WEILL (1975) showed that, as the oxygen fugacity is decreased, the distribution coefficient for Eu between plagioclase and silicate melt rises above that for adjacent REE and approaches a value similar to that for Sr. This is a consequence of the fact that ionic radii of  $\text{Sr}^{2+}$  and  $\text{Eu}^{2+}$  are almost identical to one another, regardless of coordination number (WHITTAKER and MUNTUS, 1970). The fact that Sr and some of the Eu entered the inclusions together in melilite and were not accompanied by the bulk of the remaining REE is further evidence that Eu was divalent when it condensed from the solar nebula.

*The second component.* One of the striking features of Table 6 is the array of strong positive inter-element correlations among Sc, La, Ce, Sm, Tb, Dy, Yb, Lu, Zr, Hf, Ta and U and strong negative correlations between each of these elements and Ca, Eu and Sr. Examples of these positive correlations were shown by GROSSMAN and GANAPATHY (1976a) for the pairs

Hf–Sc and Sm–Sc, although it must be borne in mind that data for inclusion 5 are plotted in that work but are not used here in the computation of the correlation coefficients in Table 6. Further examples, using data obtained in the present study, are shown in Fig. 5, U vs Sm, and in Fig. 6, Zr vs Hf.

An example of one of the negative correlations is shown in Fig. 7 where La is plotted against Eu. It is seen here that the negative correlation is largely controlled by the data point for sample 2 at 0.66 ppm Eu. Because this sample is unusually rich in REE and possesses a large negative Eu anomaly (GROSSMAN and GANAPATHY, 1976a), it plays a significant role in all negative correlations between Eu and the remaining REE. Since there is no continuum of data points between this sample and the others in Fig. 7, it could be argued that this sample belongs to a different population of objects and, therefore, should be rejected when computing correlation coefficients. In fact, though, inspection of a thin section of sample 2 reveals that it is a perfectly normal Type B inclusion in both mineralogy and texture. Also, its refractory siderophile element content is not unusual compared to those of other inclusions in this group. Finally, even if sample 2 is removed from consideration, the remaining eight data points still define a negative correlation between La and Eu which is significant at the 93% level.

The simplest explanation of the array of positive correlations is that the bulk of each of the refractory lithophiles except Ca, Eu, Sr and Ba was carried into the inclusions by the same mineral. The negative correlations with Ca, Eu and Sr indicate, first, that the mineral is not melilite, second, that it is poorer in

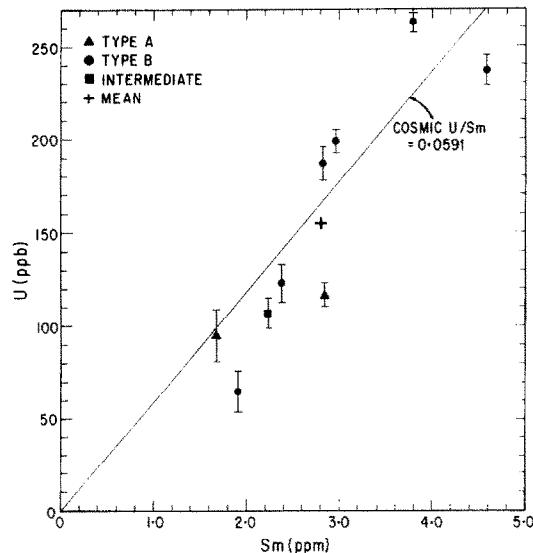


Fig. 5. Except for Ca, Sr, Eu and Ba, all refractory lithophiles are strongly positively correlated with one another. Data for element pairs scatter along lines whose slopes equal their cosmic ratios. Small fractionations between these elements, such as seen here for U and Sm, are due to variable composition of their host phase or a multiplicity of host phases.

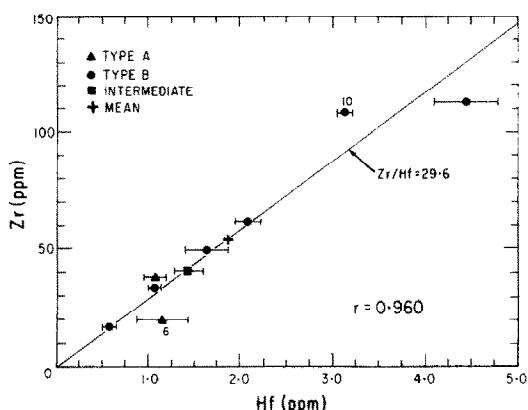


Fig. 6. Zr and Hf are strongly correlated in coarse-grained inclusions. Two samples, 6 and 10, have Zr/Hf ratios distinct from the mean value,  $29.6 \pm 1.8$ .

Ca, Eu and Sr and richer in the other refractory lithophiles than melilite and, third, that the abundance of this component increases in the inclusions as that of the melilite component decreases. The latter conclusion suggests that this component may be a major phase. Addition of increasing amounts of such a phase to melilite would lower the concentrations of Ca, Eu and Sr and increase those of the remaining elements, Sc, La, Zr, etc. Of the major phases which accreted to form the inclusions, possible carriers are corundum or hibonite, spinel and diopside. Neither corundum nor spinel can tolerate the required concentrations of REE in their structures, but diopside and probably hibonite can.

From abundance variations of refractory lithophiles, it is thus seen that melilite and clinopyroxene

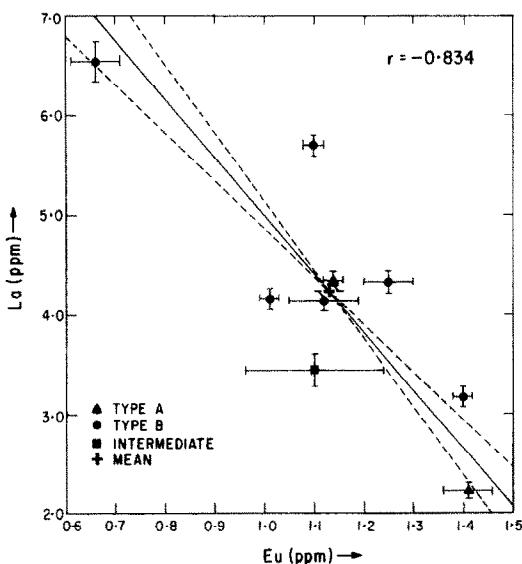


Fig. 7. As is the case for most other refractory lithophiles, La is strongly negatively correlated with Eu and Sr. The abundance of the carrier phase of the former elements increases as the abundance of the melilite component decreases.

could have been the phases responsible for carrying the bulk of these elements into the inclusions. But these are the major phases now observed in thin sections of the inclusions, aside from spinel whose structure cannot tolerate significant quantities of large-ion lithophiles. Could the mineral grains seen in the inclusions today be the actual condensates which accreted to form them? Trace element studies of mineral separates from inclusions show that melilite is enriched in Eu by a factor of 2.5–4.0 (MASON and MARTIN, 1974; ONUMA *et al.*, 1974; NAGASAWA and JAHN, 1976; NAGASAWA *et al.*, 1977) and in Sr by a factor of ~5 (MASON and MARTIN, 1974; NAGASAWA and JAHN, 1976) relative to coexisting clinopyroxene. Also, pyroxene is consistently richer in heavy REE than its coexisting melilite. These are precisely the chemical characteristics required of the melilite and pyroxene which are postulated to have carried trace elements into the inclusions and, at first sight, this is a strong argument that we are observing the actual condensate grains. This seems to be ruled out, however, by the distribution of La. Its strong negative correlation with Eu (Fig. 7) and Ca (Table 6) in bulk inclusions suggests that it must have been one of the elements depleted in the melilite carrier relative to the pyroxene carrier. The chemical studies of mineral separates cited above show, however, that melilite either has the same La content as coexisting pyroxene or is up to 75% richer in La. Thus, if the second carrier was pyroxene, we have one more argument based on REE, in addition to that presented by GROSSMAN and GANAPATHY (1976a), that trace elements were redistributed between major phases after accretion of the inclusions, perhaps during a heating or partial melting episode. U is another element expected to be depleted in the melilite carrier relative to the pyroxene carrier. DROZD *et al.* (1977), using a neutron-induced fission track technique, showed, however, that melilite is 50% richer in U than its coexisting pyroxene. This is further evidence for element redistribution after accretion.

Another important result emerges from the foregoing discussion. Suppose, in an extremely oversimplified example, that all inclusions accreted with the same bulk major and trace element composition, that they all underwent partial melting which resulted in the same proportions of constituent phases, and that the bulk of the large-ion lithophiles found their way into melilite and clinopyroxene. During incomplete extraction of inclusions for analysis, melilite could have been preferentially sampled relative to pyroxene in the case of some inclusions and the opposite may have occurred in the case of others. Thus, it could be argued that the array of positive and negative correlations observed for the refractory lithophiles has nothing to do with condensation, but, instead, merely represents an artificial mixing line, produced during sampling in the laboratory. Fortunately, again because La does not correlate positively with Ca, Sr and Eu, such an artifact cannot be dominant in this suite of samples. This effect could contribute signifi-

cantly, however, to the scatter about the correlation lines in this work and may be the cause of the apparent positive correlation between La and Eu in the set of coarse-grained inclusions analysed by MASON and MARTIN (1977).

Until now, we have considered only the possibility that the carrier of all refractory lithophiles except the bulk of the Ca, Sr, Eu and Ba was a major phase. GROSSMAN (1973) suggested that REE would have condensed in solid solution in perovskite. GROSSMAN and GANAPATHY (1976a) noted that two Type A inclusions, whose melilite/spinel ratios are the only visible mineralogical difference between them, have completely different REE patterns. Although other interpretations are possible, they proposed that REE, Sc and Hf were carried into the inclusions in minor or trace phases and suggested as candidates perovskite and at least one other phase, a trace mineral rich in rare refractory elements. LOVERING *et al.* (1976b) observed several such trace phases in a coarse-grained inclusion, but caution must be exercised in assuming these are condensate phases if the inclusions were indeed melted after they condensed. If more than one carrier is involved, the positive correlations between REE, Sc, Zr, Hf, Ta and U suggest that all such carriers had to enter the inclusions together.

We have already concluded that the total amount of perovskite which entered the inclusions was very minor. How could progressive addition of such minor or trace carrier phases cause the Ca content of the inclusions to decrease by more than a factor of two? It obviously cannot; however, the inclusions might have accreted in such a way that the amount of perovskite and trace carrier phases is inversely related to the Ca content. For example, suppose such a phase, or phases, were present in more or less constant proportion to spinel, diopside and corundum or hibonite prior to addition of melilite. Progressive addition of melilite would cause an increase in Ca, Sr and Eu contents and, because it is a major phase, a decrease, due to dilution, in the concentrations of all other elements present in the pre-melilite mixture. Because they are neither positively nor negatively correlated with Ca, refractory siderophiles must have been added as an independent component, either in highly variable proportion to the pre-melilite mixture or throughout the accretion history of the inclusions.

An alternative suggestion is that, before they were added to the inclusions, grains of perovskite and trace carrier phases were preferentially incorporated by a phase with lower Ca, Sr and Eu contents than melilite. Progressive addition of such a phase, either spinel, diopside, corundum or hibonite, to melilite-rich assemblages would thus cause Ca, Sr and Eu contents to fall as the concentrations of the other refractory lithophiles increase. In this way, perovskite and trace minerals are condensate hosts for these elements but it is a major mineral that actually carries them into the inclusions. Independent textural evidence may exist for such a process. In a petrographic

study, GROSSMAN (1975) noted that perovskite is commonly associated with surfaces of spinel crystals in Type A inclusions. Using a scanning electron microscope, HUTCHEON (1976) found epitaxial growths of perovskite on surfaces of spinel crystals from Types A and B inclusions. These textural features suggest that perovskite may have nucleated on spinel crystals during condensation and that it was thus carried into the inclusions with spinel. If perovskite was a major contributor of REE to the inclusions, however, the fact that the bulk of these elements now resides in melilite and clinopyroxene argues that perovskite lost its REE to these phases since accretion, probably during heating or partial melting events. It seems doubtful, then, that the epitaxial growths of perovskite are an original condensation feature because, as such, they would have had to survive thermal events which caused nearly complete removal of REE from its structure.

*Other components.* One hundred and five correlations are possible between the 15 refractory lithophile elements which we have been discussing. Inspection of Table 6 shows that 87 of these are significant at the 95% level. At the 90% level, 95 significant correlations are found; the only possible correlations which are not significant are Ta with Ca, Sr, Eu and Ce, Sr with Tb, Dy and U, Ca with Sc and Tb and Ce with U. This could be interpreted as an indication that some Ta, Sr and Ca entered the inclusions in components other than those discussed so far. We have already seen that some Ca and Sr could have been carried into the inclusions in a component other than melilite and that this component need not be the carrier of REE, Sc, Zr, etc. The missing correlations with Ta may be related to the relatively large analytical uncertainties for this element.

Ba. An amazing feature of Table 6 is the complete absence of significant correlations between Ba and any other element. Ba has a mean enrichment factor of 16.6 (Table 5), leaving little doubt that it is a refractory element. Yet, it must have been carried into the inclusions independently of all other elements here. Therefore, it must have condensed in a phase other than melilite or the Sc-, REE-, Zr-bearing condensate. So far, theory has provided little help in identifying a refractory Ba-containing condensate. Again with data for only one crystalline phase, BaO, thermodynamic calculations show that less than 1% of the Ba can condense in ideal solid solution in perovskite and melilite above the accretion temperature of the inclusions. This is another case where thermodynamic data are needed for more likely condensate phases, such as  $\text{Ba}_2\text{SiO}_4$ ,  $\text{BaTiO}_3$  or  $\text{BaAl}_2\text{Si}_2\text{O}_8$ . A Ca-bearing variety of celsian, the latter phase, was discovered in a coarse-grained inclusion by LOVERING *et al.* (1976a) and  $\text{BaTiO}_3$  was reported in the matrix of Allende by MASUDA and TANAKA (1977).

#### Refractory element fractionations

The elements we have discussed so far fall into four

groups. The refractory siderophiles, group one, were carried into the inclusions together in one or more alloys. Group two consists of Ca, Eu and Sr; the bulk of each of which was carried into the inclusions in melilite. The bulk of each of the group three elements, Sc, Zr, Hf, Ta, U and the REE except Eu, was carried into the inclusions in a different phase from the other refractory lithophiles. Ba is the only member of group four, requiring a carrier phase separate from the other three. As pointed out by GROSSMAN and GANAPATHY (1976a), it is easy to see how large fractionations could have been produced in individual inclusions between elements in different groups. Such elements were present in different condensate phases and individual inclusions were simply unable to sample all available phases in exactly the same proportions as their relative abundances in the nebula. As discussed above, such elements show no fractionations when analyses of a large number of inclusions are averaged together because a larger sample is more representative of the high-temperature condensates.

Another type of fractionation exists, however; that between elements in the same group. Such fractionations were discussed above for groups one and two and were attributed either to multiple condensate phases with different compositions or to variable concentration ratios in a single condensate phase. Similar explanations are required to explain fractionations within group three as well. In addition to showing that REE, Sc and Hf are correlated with one another, GROSSMAN and GANAPATHY (1976a) pointed out that, when concentrations of any pair of these elements are plotted against each other, the data points scatter about a line whose slope equals their cosmic ratio. This is also true for correlations between those elements and Zr, Lu and U, the group three elements whose abundances were determined in the present study (see Fig. 5). There are several possible explanations for the fractionations represented by this scatter. Two elements with non-coincident condensation curves will be present in variable proportion to one another if their common carrier phase was isolated from the gas at different nebular equilibration temperatures. Similarly, if several carriers were involved, each may contain an element ratio greatly different from the others. Although deviations of data points from cosmic lines tend to be relatively small, individual inclusions were apparently unable to sample all available carrier compositions in exactly the same proportions as their relative abundances in the nebula. For any pair of group three elements, however, the mean data point falls very close to the cosmic line, a reflection of the similarity of their mean enrichment factors which, in turn, implies virtually total condensation and efficient accretion of both elements into the population of inclusions as a whole. This situation is completely analogous to that of the refractory siderophiles, except that inter-element correlation coefficients for lithophiles tend to be smaller than those for siderophiles (see Table 6). If single

carriers are involved in both cases, this observation indicates better sampling of the siderophile carrier by the inclusions and/or less variability in its composition. The latter explanation may imply a closer approach to equilibrium condensation for siderophiles. If multiple carriers are involved, the poorer correlations among lithophiles suggest for these elements more carriers, greater element fractionations between carriers, poorer sampling of available carriers by inclusions or a combination of these factors.

#### *The Zr/Hf ratio of the solar system*

GANAPATHY *et al.* (1976) proposed that the Zr/Hf ratio of the solar system is  $28.2 \pm 3.9$  based on one Hf and two Zr determinations on the Orgueil C1 chondrite. This ratio is in disagreement with the value of  $52 \pm 7$  determined for Orgueil by EHMANN and CHYI (1974). Evidence has been presented herein that refractory elements are not significantly fractionated from one another relative to their solar system abundances in this population of nine coarse-grained inclusions. An independent estimate of the solar system Zr/Hf ratio is thus possible, simply by dividing the mean Zr concentration in these Allende inclusions by their mean Hf content (see Table 5). The result is  $29.4 \pm 9.2$ . The reason for the large uncertainty is that the standard errors of the Zr and Hf data about their means are both large. Fortunately, using the same data base, it is possible to make another estimate with much greater precision. We have seen that concentrations of refractory lithophile elements in group three are strongly correlated with one another in coarse-grained inclusions. Concentration data for all other pairs of these elements fall along lines whose slopes equal their respective solar system ratios. This should also be the case for Zr and Hf. As can be seen from Fig. 6 and Table 6, they are positively correlated and have an unusually high correlation coefficient, indicating very little fractionation of Zr from Hf during condensation of their carrier phase or phases. The solar system Zr/Hf ratio determined by taking the mean and standard error of the Zr/Hf ratios of the nine inclusions is  $29.6 \pm 1.8$ . This value is in excellent agreement with the GANAPATHY *et al.* (1976) ratio and disagrees considerably from the EHMANN and CHYI (1974) value.

Small, but real, variations in the Zr/Hf ratio do appear to exist in these samples. Although seven of the nine inclusions have ratios within  $2\sigma$  counting uncertainties of the derived solar system value, inclusions six and ten have Zr/Hf ratios of  $17.6 \pm 9.3$  and  $34.9 \pm 2.2$ , respectively. Thus, occasionally even Zr and Hf were fractionated slightly from one another during condensation of the carrier, or carriers, of the elements in group three.

#### *Volatile elements*

Volatile elements are defined in this paper as those which are unable to condense completely above  $1437^{\circ}\text{K}$  at  $10^{-3}$  atm. total pressure. They fall into two

distinct groups in Table 6. The first group consists of Pd, Co, Au and Ag. The first three of these elements correlate strongly with one another, but do not correlate with any other volatile or refractory elements at the 95% level. At the 90% level, however, 4 of the 15 possible correlations between these elements and the refractory siderophiles W, Os, Ir, Ru and Re are significant. Nine of the remaining 11 possible correlations are significant at the 80% level. At the 80–90% level, Ag correlates significantly with Co, Pd and all refractory siderophiles. Thus, it appears that small amounts of Pd, Co, Au and Ag condensed into the refractory siderophile element alloy. The reason why these elements correlate less strongly with refractory siderophiles than do the latter elements with one another is that significant fractions of the Pd, Co, Au and Ag in our samples are present in components other than the siderophile alloy, such as those discussed below.

Enrichments of Co and Au were found by PALME and WLOTZKA (1976) in a refractory metal-rich fraction of a coarse-grained inclusion relative to the bulk inclusion. Assuming that it is not the result of later element redistribution, this association provides further evidence for co-condensation of refractory and volatile siderophiles. Although calculations show that Co (GROSSMAN and OLSEN, 1974), Ag (GROSSMAN and LARIMER, 1974), Au and Pd (PALME and WLOTZKA, 1976) were unable to condense completely above  $1437^{\circ}\text{K}$ , PALME and WLOTZKA calculated that small fractions of volatile siderophiles could have condensed above the accretion temperature of the inclusions into an alloy in which W, Os, Ir, Ru and Re were totally condensed. The abundances of volatile siderophiles suggest that this was the case. Even if it is assumed that the *total* amount of Pd, Co, Au and Ag present in our samples condensed with the refractory siderophiles, their mean enrichment factors relative to C1 chondrites, 0.13, 0.11, 1.34 and 0.14, respectively, are still very low compared to 17.5, the value expected for total condensation. Pd, Co and Ag appear to be  $<1\%$  condensed, while Au may be as much as 7.5% condensed. The marked contrast between the enrichment factors of refractory siderophiles and those of volatile siderophiles is an extremely powerful argument that chemical fractionations observed in coarse-grained inclusions were controlled by differences in volatility, rather than by differences in geochemical behavior.

The second group of volatiles in Table 6 consists of Cr, Mn, Fe, Zn, Se and Na. Of the ten inter-element correlations possible between the first five of these elements, nine are significant at the 95% confidence level. The strong positive correlations between these elements suggest that the bulk of each of them was added to these samples in a common component. The negative correlations of Cr, Fe, Zn and Se with Sr, the negative correlations of Zn with Ca and Eu and the positive correlation of Zn with Ce all seem to be accidental. The two samples richest in volatiles

just happen to be poorest in Ca, Sr and Eu. The correlations disappear when these two samples are omitted from consideration. As discussed by GROSSMAN and GANAPATHY (1976a), several sources are possible for the volatiles. During extraction of inclusions from the meteorite in the laboratory, it is almost impossible to avoid contaminating them with small amounts (<2%) of Allende matrix material. This cannot be the only source, however, because microprobe analyses of spinels and pyroxenes in coarse-grained inclusions reveal the presence of small, but significant, amounts of Cr and Fe in their crystal structures (GROSSMAN, 1975). Observed concentrations of these elements in these phases are too high to be accounted for by equilibrium condensation above 1437°K. Perhaps small amounts of volatiles were added to the inclusions as grains of lower-temperature condensates and were redistributed into refractory phases during a later stage of partial melting. Na fails to correlate with Cr, Fe, Zn and Se at the 95% level, but does so at lower confidence levels. Although Na undoubtedly could have entered the inclusions with the other volatiles in either of the modes suggested above, the fact that it is less strongly correlated with the other volatiles than the latter elements are with one another suggests that a significant fraction of the Na was added to the inclusions in a different way. GROSSMAN and GANAPATHY (1975) reviewed evidence for alkali metal addition during metamorphic reactions in the parent body, but new petrographic evidence (WARK and LOVERING, 1977) suggests that alkalies were added prior to the assembly of the Allende meteorite. This suggests that some Na in coarse-grained inclusions may owe its origin to reactions between the surfaces of the inclusions and the nebular gas at temperatures far below the condensation temperatures of the major phases in the interiors of the inclusions.

#### *High-temperature condensates in the Moon and Earth*

Carbonaceous chondrites are apparently accumulations of various solar nebular condensate components. One of these, preserved as the coarse-grained inclusions in Allende, contains all refractory elements in cosmic proportion to one another, on the average, and seems to be the major source of refractories in Allende (GROSSMAN and GANAPATHY, 1976b). If planets formed from the same components as carbonaceous chondrites, a knowledge of the abundance of one refractory element in a planet is sufficient to calculate global concentrations of all other refractories. GANAPATHY and ANDERS (1974) made use of this approach, taking advantage of lunar heat-flow measurements to estimate that the Moon's U content is 59 ppb. Assuming a theoretical high-temperature condensate component, HTC, representing 4.62 wt% of the total condensable matter, they calculated that the mean refractory element enrichment factor in HTC is  $100/4.62 = 21.6$ , which implies a U content of 197 ppb. From this and the Moon's U content, they estimated that the Moon contains 30% HTC.

Re-evaluation of both terrestrial (LANGSETH *et al.*, 1976) and lunar (KEIHM and LANGSETH, 1977) heat-flow measurements suggests, however, that the Earth contains 32 ppb U and the Moon only 35–46 ppb. The latter value implies that a substantial reduction is necessary in the GANAPATHY and ANDERS (1974) estimate of the lunar HTC content. If, on the other hand, the chemical composition of all HTC which formed in the solar nebula is taken to be identical to that of coarse-grained inclusions, a large correction is necessary in the opposite direction. This stems from the fact that the mean refractory element enrichment factor in coarse-grained inclusions is only 17.5, implying that they represent 5.7 wt% of the total condensable matter. Combining the revised heat-flow data with our estimate of the U content of HTC, 155 ppb, gives 23–30% HTC in the Moon and 21% in the Earth. The Earth and Moon are quite similar in their contents of refractory elements. Both, however, are substantially enriched in refractories relative to C1 chondrites which contain only 5.7% HTC.

#### CONCLUSIONS

Several different phases must have carried refractory elements into the coarse-grained inclusions. Os, Ir, Ru, Re and most of the W were brought in by one or more refractory siderophile element alloys, along with small amounts of Pd, Co, Au and Ag. Melilite appears to have been the carrier for the bulk of the Sr and Eu. The bulk of each of the Sc, Zr, Hf, Ta, U and the other REE was probably carried in by diopside or one or more minor or trace phases, including perovskite. Ba entered in a separate phase, distinct from the carriers of the other elements. In individual inclusions, fractionations between elements brought in by different carriers are common, presumably because each inclusion did not sample all available condensate phases in exactly the same proportions as their relative abundances in the nebula. Smaller fractionations are seen in individual inclusions for elements which condensed together. Such elements may have been in solid solution in a single condensate phase in which their relative proportions varied, depending on the temperature at which the phase stopped equilibrating with the nebular gas. Alternatively, they may have condensed in more than one phase, each with different proportions of these elements. Despite these fractionations in individual inclusions, however, the mean concentration of each refractory element in the nine coarse-grained inclusions, divided by its abundance in C1 chondrites, is very nearly the same,  $17.5 \pm 1.8$ . This indicates virtually total condensation of refractory elements above the accretion temperature of the inclusions and very efficient scavenging of them by the inclusions. A large number of inclusions is apparently a far more representative sample of the high-temperature condensates than any single one. Finally, the present-day distribution of trace elements between coexisting melilite and

pyroxene was not established during accretion of the inclusions but, instead, must reflect a post-condensation thermal event which redistributed them internally.

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