Trace elements in the Allende meteorite—II.
Fine-grained, Ca-rich inclusions

LAWRENCE GROSSMAN

Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago,
5734 South Ellis Avenue, Chicago, Illinois 60637, U.S.A.

and

R. GANAPATHY

Department of the Geophysical Sciences, The University of Chicago, 5734 South Ellis Avenue,
Chicago, Illinois 60637, U.S.A.

Abstract—Nine fine-grained feldspathoid-, grossular-, spinel-, pyroxene-bearing inclusions from the Allende meteorite were analysed by instrumental neutron activation analysis. On the average, these inclusions are enriched in the refractory lithophile elements Ca, Sc, Ta and the rare earths by factors of 5–30 relative to C1 chondrites but are depleted in the refractory and volatile siderophiles, Ir, Co and Au. The volatile elements Fe, Cr and Zn are present at levels of 3.38–8.51%, 326–2516 ppm and 308–1376 ppm, respectively. Textural, mineralogical and chemical data suggest that the fine-grained inclusions formed in the solar nebula by the simultaneous condensation of volatiles and refractory lithophile elements which failed to condense into the coarse-grained, high-temperature condensate inclusions. The marked differences in the enrichment factors for different refractories in the fine-grained inclusions are caused by relatively small differences in their accretion efficiencies into the coarse-grained ones. The trace element data indicate that the refractories in the fine- and coarse-grained inclusions can only be the cosmic complements of one another if the fine-grained ones represent no more than ~20% of the most abundant refractory elements.

INTRODUCTION

IN ADDITION to mineralogical and isotopic information, trace element data have been used as evidence for the high-temperature condensation origin of the coarse-grained, Ca-rich inclusions in the Allende meteorite (GAST et al., 1970; GROSSMAN, 1973; MASON and MARTIN, 1974; WÄNKE et al., 1974; GROSSMAN and GANAPATHY, 1976). Another petrographic component of this chondrite, the fine-grained inclusions, was first discovered by CLARKE et al. (1970). Their mineralogical and bulk chemical analyses, combined with scanning electron microscope (SEM) information (GROSSMAN et al., 1975) and volatile element data (GROSSMAN and GANAPATHY, 1975) suggested to the latter workers that the fine-grained inclusions formed by the simultaneous condensation of refractories and volatiles from the solar nebula. Compared to the coarse-grained inclusions, relatively few trace element studies of the fine-grained ones have appeared in the literature (TANAKA and MASUDA, 1973; MARTIN and MASON, 1974) but these have shown remarkable refractory element enrichment patterns. As part of our ongoing program aimed at understanding the behavior of the elements during the condensation of the solar nebula, we decided to investigate the trace element characteristics of a suite of these inclusions by instrumental neutron activation analysis.

SAMPLES

General identifying characteristics of what we mean by fine-grained inclusions and the preparation of the specific samples from the Allende meteorite studied herein are described in GROSSMAN and GANAPATHY (1975). The sample numbers used here are the same as in that paper.

Inclusions of this type have not been studied in detail by microprobe techniques because of their exceedingly fine grain size and because their high porosity makes their preservation improbable during the preparation of polished sections (GROSSMAN et al., 1975). Until now, the only mineralogical information reported from an inclusion described in enough detail to identify it as belonging to the class of inclusions discussed here is that in CLARKE et al. (1970). They deduced the mineralogy of a single inclusion from a combination of X-ray diffraction and bulk chemical data, reporting gehlenite, anorthite, fassaite, spinel, sodalite, nepheline and grossular. It is not clear, however, how many of these phases were actually identified from the X-ray pattern alone. In the present study, an X-ray powder pattern was made of an aliquot of each inclusion whose trace element content was determined. In addition, the white rims of inclusions 16 and 19 were X-rayed separately. The results are shown in Table 1, where all phases identified on the basis of at least one strong, characteristic, unambiguous line are listed as definitely present and those indicated by only a single weak line are listed as possibly present. Except for sample 15, all of the inclusions contain spinel and pyroxene. Sodalite, nepheline, grossular and possibly melilite are common constituents. Plagioclase and olivine are usually undetec-

Table 1. Mineralogy of samples whose trace element contents were measured in this work

Sample	Description	Spinel	Pyroxene	Sodalite	Nepheline	Grossular	Melilite	Plagioclase	Olivine
					Mineralogy*				
11	Purple-gray, unzoned	X	X	X		X	O	O	
12	Pink center with lighter pink rim	X	X	X	O	X	O		
13	Gray center, whitish yellow outer zone, gray rim	X	X	X	X	O	O		O
14	Purple-gray, unzoned	X	X	X	X		O		
15**	Beige, lumpy	O	O		X				X
16	Purple-gray core with white rim	X	X		X	X	O		
	White rim	X	X			X			
17	White with pink tint	X	X	X	X	X	O		
18	White, unzoned	X	X	X	X	X	O		
19	Purple core with white rim	X	X		X		O		O
	White rim	X	O	X	X		O		X
20	White, unzoned	X	X	X	X	X			

* X—Definitely present; O—possibly present; blank—not detected.
** Amoeboid olivine aggregate.

table but they may occasionally be present. From its texture, color and mineralogy, inclusion 15 is an amoeboid olivine aggregate (GROSSMAN and STEELE, 1976) which was mistakenly thought to be a fine-grained inclusion from its appearance on a slab surface. Its trace element data are reported here but their interpretation will be discussed in a later paper along with analyses of ten more of these objects.

Nepheline and perhaps melilite are present in the core but absent from the rim of inclusion 16. In 19, sodalite is present in the rim and not in the core but the reverse may be true for pyroxene. The olivine found in the rim of 19 is thought to be due to matrix contamination of the very small amount of material sampled for X-ray work (<0.05 mg). These appear to be the only mineralogical differences between core and rim samples. The color zoning is thus probably not due to the presence of a phase in the cores which is not present in the rims. It is more likely due to larger concentrations of colored phases in the centers of the inclusions, such as spinel or grossular doped with trace amounts of transition metals. Perhaps sodalite sometimes also plays a part in the coloration.

An estimate of the abundances of nepheline and sodalite in the fine-grained inclusions is attempted in Fig. 1. From the X-ray work, these are the only significant phases containing Na and Cl. The graphical construction in Fig.1 is based upon the assumption that the nepheline and sodalite in these inclusions have the same mean compositions as in the amoeboid olivine aggregates in Allende (GROSSMAN and STEELE, 1976). Plotting the Na and Cl contents measured in these samples by GROSSMAN and GANAPATHY (1975) on the graph shows that the ratio of nepheline to sodalite varies widely and that, together, the two phases account for 8–38% of the mass of the fine-grained inclusions. Further, the Na and Cl values

satisfy an internal check in that all the data points fall within the triangle in Fig. 1.

EXPERIMENTAL

The short neutron irradiation of 10 coarse-grained and 10 fine-grained inclusions from the Allende meteorite was reported in GROSSMAN and GANAPATHY (1975). In that work, the counting of the short-lived nuclides Cl^{38}, Dy^{165}, Mn^{56} and Na^{24} was described, and the abundances of Cl, Mn and Na were discussed. Here we report on further experiments on the same fine-grained inclusions as in that study. The Dy data from the earlier study are also reported here.

These inclusions were re-irradiated along with the 10 coarse-grained inclusions studied in GROSSMAN and GANAPATHY (1976). The irradiation conditions, standards, flux monitors and blank were thus precisely those reported in that paper. The counting equipment used, its stability, the method of data reduction and the analytical peaks employed were also the same as in that paper. The only element determined in the fine-grained inclusions which was not seen in the spectra of the coarse-grained ones was Zn. For analytical purposes, we used the Zn^{65} peak at 1115.5 keV (PAGDEN et al., 1971), having a half-life of 245 days (LEDERER et al., 1968).

Initially, each sample was counted for approximately 10^4 sec in the time period ranging from 4 to 6 days after the end of the irradiation in order to try to obtain good counting statistics for such short-lived nuclides as La^{140}, Sm^{153} and Au^{198}. Between 9 and 21 days after irradiation, each sample was again counted for approximately 1 day to improve the statistics for Ca^{47} and Yb^{175}. Beginning 45 days after the irradiation, some of the samples were counted again for 2–3 days each in order to improve statistics for the longer-lived nuclides.

RESULTS

Because the samples discussed in this paper were run together with those discussed in GROSSMAN and GANAPATHY (1976), the comparison of our BCR-1 data with literature values in that paper are perfectly applicable here as well. Because the Zn/Sc ratio is considerably lower in
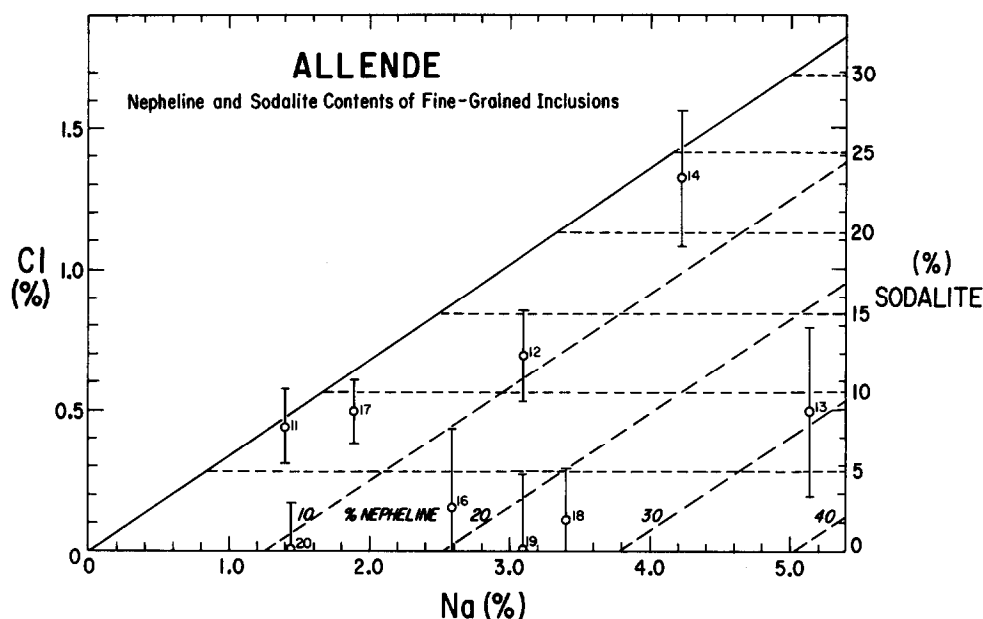
Fig. 1. The nepheline and sodalite contents of the samples studied here can be determined from the Na and Cl measurements of GROSSMAN and GANAPATHY (1975), assuming that they are the only phases present which contain these elements and that they have the same compositions as in the amoeboid olivine aggregates (GROSSMAN and STEELE, 1976).

BCR-1 than in the fine-grained inclusions, we were unable to determine Zn in the standard rock. This is also the reason why Zn was not detected in the coarse-grained inclusions. Hf, W, Os and Ru were determined in the coarse-grained inclusions but these elements were not detectable in the fine-grained ones under the conditions of this experiment.

Our analytical data for 16 elements in 10 fine-grained inclusions are shown in Table 2. Uncertainties quoted are based on 1σ counting statistics for both samples and standards. Additional uncertainties due to irradiation and counting geometry are estimated to be ±2%. Very few analysed inclusions are described fully enough in the literature to positively identify them as belonging to the fine-grained variety studied in this paper. Consequently, our ability to compare our data with literature values is limited. In general, however, where comparable, our data are in agreement with analyses reported by CLARKE et al. (1970) for an 'irregular aggregate', GRAY et al. (1973) for a 'high-Rb aggregate', TANAKA and MASUDA (1973) for their 'inclusion G' and MARTIN and MASON (1974) for their two 'Group III Ca, Al-rich aggregates' and with the range of analyses reported for their 'Group II Ca, Al-rich aggregates'. The only exceptions are that the Ca content measured by CLARKE et al. (1970) and the highest Ca content seen in the group II aggregates by MARTIN and MASON (1974) are both greater than the highest observed in this study. Also, the Fe concentrations reported by CLARKE et al. (1970) and MARTIN and MASON (1974) for group III aggregates are slightly below the lowest values seen here. The range of Fe contents reported for group II aggregates by MARTIN and MASON (1974) extends to slightly lower and slightly higher values than the range in Table 2. The inclusions are so variable in composition, however, that these discrepancies may not be particularly significant.

DISCUSSION

Chemical differences between fine- and coarse-grained inclusions

Excluding sample 15, the mean concentration of each refractory element in the remaining nine fine-grained inclusions was calculated, normalized to its abundance in Cl chondrites and plotted in Fig. 2. See GROSSMAN and GANAPATHY (1976) for the Cl data used and their sources. First, it is clear that the fine-grained inclusions, like the coarse-grained ones (GROSSMAN and GANAPATHY, 1976), are significantly enriched in refractory elements relative to Cl chondrites. Unlike the coarse-grained inclusions, however, the refractory element enrichment is restricted to the lithophile elements. In the fine-grained inclusions, refractory siderophiles such as Ir are substantially depleted relative to Cl chondrites. Even among the refractory lithophile elements, large differences are observed between the coarse- and fine-grained inclusions. These elements are nearly uniformly enriched on the average in the coarse-grained inclusions (GROSSMAN and GANAPATHY, 1976), but marked variations are seen among the mean enrichment factors for different refractory lithophiles in the fine-grained inclusions. In their case, the light rare-earth elements (REE) and Ta are even more highly enriched than in the coarse-grained inclusions while the heavy REE, Ca and Sc are less enriched. The differences between the two types of inclusions are more clearly shown

Table 2. Elemental concentrations

Sample	Ca(%)	Sc	Ta	La	Ce	Sm	Eu
11	11.0±.2	25.59±.03	0.16±.03	4.64±.18	15.5±.3	3.96±.04	0.53±.02
12	6.7±.1	24.18±.03	0.43±.05	9.42±.15	24.3±.4	5.48±.04	0.36±.02
13	2.1±.1	143.1±.8	0.72±.07	12.92±.55	34.7±.6	8.75±.10	0.47±.03
14	6.3±.3	26.33±.04	0.51±.06	10.54±.14	25.1±.4	5.72±.04	0.22±.02
15*	0.92±.05	9.45±.01	0.13±.02	1.79±.04	5.2±.2	1.13±.01	0.065±.006
16	7.5±.2	4.50±.01	0.30±.05	0.72±.09	6.2±.4	1.13±.02	0.51±.03
17	7.7±.2	25.33±.05	0.47±.02	5.04±.03	19.4±.3	4.67±.03	0.35±.01
18	5.8±.2	11.88±.02	0.40±.03	7.76±.10	22.1±.3	4.95±.03	0.26±.01
19	7.0±.3	12.95±.02	0.25±.03	4.55±.07	14.6±.7	2.80±.02	0.40±.02
20	12.2±.4	21.08±.02	0.40±.02	6.21±.16	12.1±.2	3.00±.03	0.81±.02

* Sample 15 is an amoeboid olivine aggregate.
** Values in ppm unless otherwise indicated.

in Fig. 3, for which the data used for coarse-grained inclusions are the mean concentrations measured in a suite of ten inclusions by GROSSMAN and GANA-PATHY (1976). In order to understand the meaning of the highly fractionated REE pattern, it may be significant to note that this phenomenon of differential enrichment is a general one, applicable to *all* the refractory lithophile elements, not only the REE.

The uneven enrichment of light and heavy REE in fine-grained inclusions was first apparent in the data of TANAKA and MASUDA (1973) and later MARTIN and MASON (1974) and was discussed at length

by BOYNTON (1975). The pink aggregate, inclusion G, studied by TANAKA and MASUDA (1973) exhibits a marked negative Eu anomaly and a marked positive Yb anomaly superimposed upon a pattern of rapidly decreasing enrichment of the other REE with increasing atomic number. Hereafter, such inclusions will be called the 'Tanaka–Masuda type'. MARTIN and MASON (1974) found five fine-grained inclusions with such patterns, their 'group II aggregates', and two others with sharp negative anomalies for both Eu and Yb, their 'group III aggregates'. In the latter two samples, the enrichments increase from Gd to Ho and the mean enrichment for the elements Gd through Tm is similar to that for La through Sm. Such inclusions will be referred to as the 'Martin–Mason type' in this paper. REE patterns for all inclusions examined in the present study are shown in Figs. 4 and 5. The C1 data used for normalization are the same
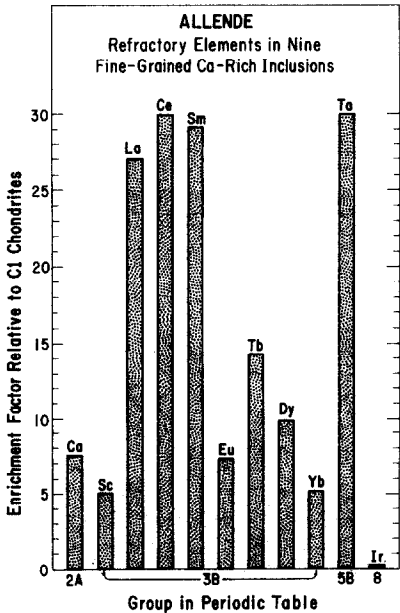

Fig. 2. The fine-grained inclusions possess a severely fractionated refractory element enrichment pattern relative to C1 chondrites.
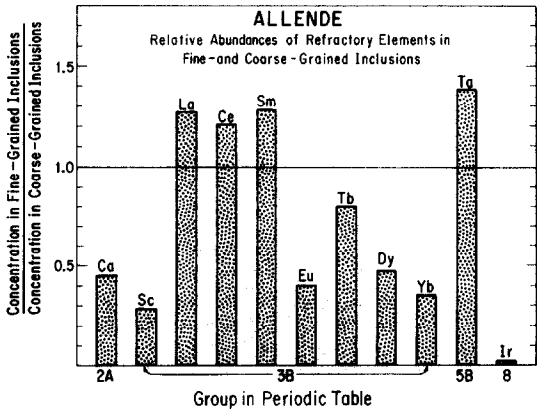

Fig. 3. The fine-grained inclusions contain severely fractionated refractory element abundances compared to the coarse-grained inclusions (GROSSMAN and GANAPATHY, 1976).

in fine-grained Allende inclusions**

Tb	Dy	Yb	Ir(ppb)	Fe(%)	Co	Cr	Au(ppb)	Zn
0.16±.04	1.7±.6	0.96±.07	32±2	4.65±.03	23.5±.2	456±3	20±8	667±3
0.53±.05	2.0±.6	0.68±.13	137±3	5.10±.03	20.5±.2	1661±9	19±6	1210±5
1.55±.08	10.5±1.2	0.05±.13	28±5	7.60±.04	39.3±.3	631±4	42±25	1376±9
0.73±.08	2.6±.7	0.50±.07	7±3	8.51±.05	31.2±.2	822±5	3±4	1027±6
0.18±.04	0.7±.5	0.15±.03	4±1	7.17±.04	11.1±.1	1800±10	9±2	104±2
<0.09	<0.8	1.79±.06	253±2	7.12±.04	54.1±.3	747±5	22±2	1026±5
0.59±.12	1.6±.3	0.49±.03	7±1	3.38±.02	9.9±.1	647±4	3±1	553±2
0.35±.04	1.9±.4	0.50±.04	6±1	6.28±.04	24.6±.2	2516±14	3±2	1124±3
0.90±.43	0.7±.7	1.64±.06	332±2	6.92±.05	25.0±.1	1723±10	27±2	962±3
0.25±.06	1.5±.5	1.34±.10	189±1	5.37±.03	32.6±.2	326±2	15±7	308±2

as in GROSSMAN and GANAPATHY (1976). In order to establish which of our inclusions have which of the two types of REE patterns noted previously, it is necessary to compare the Tb and Dy enrichments with those of the light REE because we were unable to obtain data for Ho, Er, Tm and Lu. Thus, inclusions 11, 12, 14, 17, 18 and possibly 20 belong to the Tanaka–Masuda type and inclusion 13 resembles the Martin–Mason type. From Table 1, the only mineralogical difference between 13 and 14 is that

13 may contain some olivine and grossular which are not present in 14. Sample 19 is difficult to classify because Tb is so much more enriched than Dy. It may contain olivine, unlike 14. Sample 16 has a REE pattern unlike any other so far reported from a fine-grained inclusion. But for the absence of sodalite in 16, its mineralogy is like that of 17. Thus, the mineralogical differences are rather minor between inclusions 13, 16 and 19 and examples of the Tanaka–Masuda type.
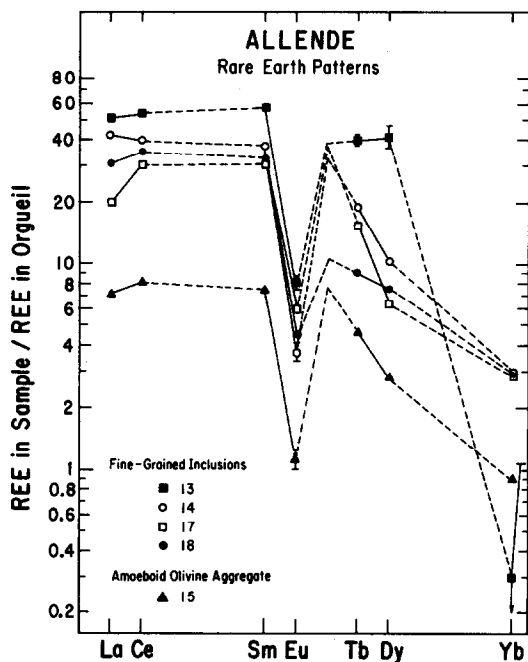

Fig. 4. Rare earth patterns in fine-grained inclusions often exhibit marked Eu depletions. Some are also depleted in Tb and Dy relative to the light REE but sample 13 is not.
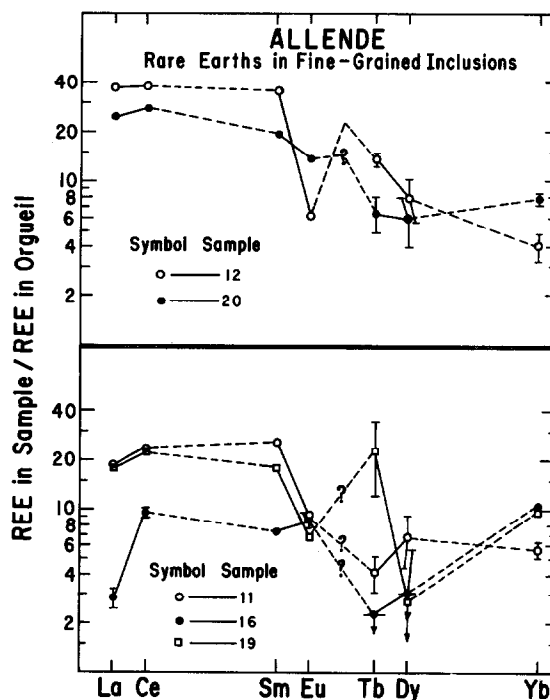

Fig. 5. Fine-grained inclusions exhibit a variety of different REE patterns. Tb and Dy values in sample 16 are 2σ upper limits.

Partially reflecting the major mineralogical differences between the coarse- and fine-grained inclusions and in addition to the aforementioned refractory element differences, their volatile element concentrations are also quite distinct, as seen in Fig. 6. In this figure, the coarse-grained inclusion data are again the averages from GROSSMAN and GANAPATHY (1976), except for Cl and Zn which are based on single determinations by WÄNKE et al. (1974). The volatile lithophile elements and Zn are enriched in the fine-grained inclusions by factors of 4-14 relative to the coarse-grained ones. Again the siderophiles, this time Co and Au, are strongly depleted in the fine-grained inclusions. Cr, which may show both lithophile and siderophile tendencies during condensation, shows little preference for either type of inclusion.

Textural and mineralogical constraints on origin

In an SEM study of a fine-grained pink inclusion, GROSSMAN et al. (1975) found it to be a delicate, cavernous aggregate of beautiful, well-formed crystals. The large volume of void space between the crystals and their euhedral forms strongly suggest that the fine-grained inclusions are aggregates of solid condensates from the solar nebula. In fact, the textural evidence for the direct condensation of the fine-grained inclusions is more compelling than in the case of the coarse-grained ones (GROSSMAN, 1975).

The coarse-grained inclusions are thought to be high-temperature condensates from the solar nebula because some of them, the Type A inclusions (GROSSMAN, 1975), are composed of such phases as melilite, spinel, perovskite and diopside which equilibrium calculations predict would condense from a gas of solar composition between 1680 and 1440°K at 10^{-3} atm total nebular pressure (GROSSMAN, 1972; GROSSMAN and GANAPATHY, 1976). In spite of the fact that they are also enriched in refractory elements, the fine-
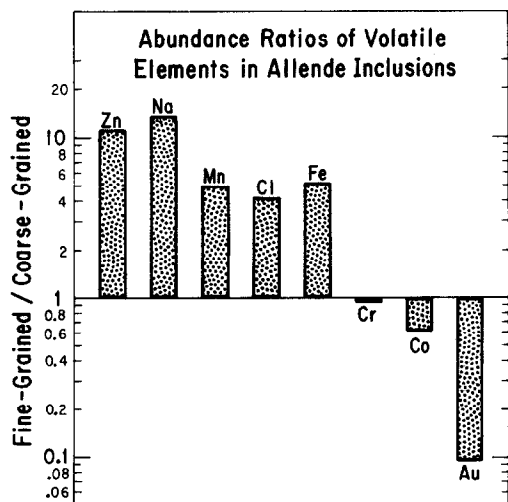

Fig. 6. The fine-grained inclusions are enriched in volatile lithophiles but depleted in volatile siderophiles compared to the coarse-grained inclusions.

grained inclusions contain little obvious mineralogical evidence of being high-temperature condensates. Perovskite has never been detected in them and melilite could not be identified with certainty in any of our X-ray patterns. The crystal structure of the pyroxene is also unknown as is its TiO_2 and Al_2O_3 contents. Spinel is a high-temperature condensate phase but both it and the pyroxene must be rich in FeO because of the high mean Fe content (6.1%) of the fine-grained inclusions and the absence of metallic nickel-iron and troilite from their X-ray patterns. High FeO contents are indicative of low solar nebular equilibration temperatures (~ 800°K). Grossular, a major component of some inclusions, does not condense at high temperatures because of the greater stability of several other Ca-Al-rich phases but it could conceivably form and persist metastably under certain non-equilibrium conditions. Nepheline and sodalite together make up 20% by mass of the fine-grained inclusions, on the average. As pointed out by GROSSMAN and STEELE (1976), it is not known whether equilibrium calculations would predict either of those phases to condense from a gas of solar composition but, if so, their condensation temperatures would be below 1000°K at 10^{-3} atm. It is evident that few mineralogical similarities between fine- and coarse-grained inclusions are demonstrable at the present time. Significant differences certainly exist, however, as the coarse-grained inclusions only occasionally contain grossular, nepheline and sodalite and then only as accessory phases.

Mixing model

The high concentrations of both refractory and volatile elements in the fine-grained inclusions suggest that they may be mixtures of high- and low-temperature condensates which formed when late-accreting, Ca-Al-rich refractory phases reacted with low-temperature (<1000°K) nebular gases to form Na- and Cl-rich feldspathoids. GROSSMAN and GANAPATHY (1975) rejected this idea for two reasons. At temperatures intermediate between the condensation points of the refractory elements and the inferred temperature of appearance of the feldspathoids, the bulk of the condensable matter of the solar system should have crystallized in the form of forsterite and metallic nickel-iron; yet, no trace of either of these mineral phases is observed in the inclusions. Another important observation was made in the SEM study of GROSSMAN et al. (1975). The alkali-bearing aluminosilicates often occur in the form of euhedral crystals intimately intergrown with the Ca-rich phases, suggesting simultaneous condensation of refractory and volatile elements. Furthermore, Al should have been virtually totally condensed above 1600°K at 10^{-3} atm pressure, leaving a vanishingly small amount in the gaseous state at the temperature of feldspathoid formation. One would then expect the feldspathoids to have derived their Al from pre-existing condensed phases, forming crusts, coatings or rims on them.

Rather, the SEM work shows that they exist as discrete crystals and grains, suggesting a primary origin in which both Al and Na condensed directly and simultaneously from the vapor phase to form the nepheline and sodalite.

One more major objection to the mixing model is brought out in the present study. Theoretically, the >1440°K high-temperature condensate fraction should contain all the refractory elements in Table 2 in cosmic proportion to one another because each of them was virtually totally condensed above this temperature, according to equilibrium calculations. Experimental measurements on coarse-grained inclusions (GROSSMAN, 1973; GROSSMAN and GANAPATHY, 1976) demonstrate that their trace element contents satisfy this important constraint. If some of this material did not accrete until the nebular temperature was much lower, the refractory elements would be expected to remain in cosmic proportion to one another, although they would all be diluted by the addition of volatile elements. This assumes that low-temperature condensation reactions did not result in the net release of selected refractory elements back into the vapor. As seen in Figs. 2 and 3, however, the refractory lithophile elements are severely fractionated from one another relative to their abundances in C1 chondrites and in the coarse-grained inclusions. Thus, the chemistry of the fine-grained inclusions cannot be the result of simple addition of volatile elements to a previously unaccreted fraction of the coarse-grained inclusions.

Incomplete condensation

The presence of the coarse-grained inclusions in Allende shows that the refractory elements did not fractionate appreciably from one another during condensation or accretion. This makes it difficult to explain the occurrence of condensate assemblages in Allende with fractionated refractory element abundances. Very few possibilities exist. The one that appears to hold the most promise is incomplete, non-equilibrium condensation.

In this model, the coarse-grained inclusions condensed above 1440°K, leaving a small amount of each refractory element behind in the gaseous state. In contrast to the equilibrium model which predicts total condensation of the refractories in this temperature range, this model proposes non-equilibrium, *incomplete* condensation. As a result of burial of early-formed phases and/or a cooling rate which was rapid compared to diffusion and reaction rates, elements which must condense by entering into solid solution in pre-existing grains or into phases which form by reactions between such grains and the gas could have failed to condense completely. Hereafter in this paper, the terms 'accretion efficiency' and 'condensation efficiency' are used to designate the fraction of any refractory element which *was* incorporated into the coarse-grained inclusions in spite of these processes which could have occurred during the latter stages

of their accretion. The high-temperature condensate grains were then efficiently removed from this part of the nebula by a process such as gravitational settling toward the median plane. Following this, metallic nickel–iron and forsterite condensed in the same region between 1475 and 1400°K. The appearance of the metal phase triggered the condensation of siderophile trace elements, including any residual refractory siderophiles which had been left behind after the formation of the coarse-grained inclusions. Gravitational settling of condensate grains continued and the region of interest was swept clean of condensed forsterite and nickel–iron and the accompanying siderophile trace elements. Again, some Fe, Mg and Si remained behind in the gaseous state because of non-equilibrium effects. Because the Al partial pressure would have been higher than in the equilibrium case, the temperatures of feldspathoid formation were elevated by as much as 100–200°, but not high enough for Na-rich silicates to appear before nickel–iron or forsterite. Consequently, at temperatures below 1200–1000°K, nepheline and sodalite condensed directly from gaseous Na, Al, Si, Cl and O, forming primary euhedral crystals along with other Ca-, Al-rich silicates and oxides, such as pyroxene, spinel and grossular. These phases accreted together to form the fine-grained inclusions. The much smaller grain size in them compared to the coarse-grained ones suggests that the density of condensation nuclei was much higher for the fine-grained inclusions, perhaps a result of more rapid cooling (MARTIN and MASON, 1974) and/or greater supersaturation at this stage of nebular evolution.

This model has several distinct advantages over the mixing model outlined above. First, it readily explains why the feldspathoids occur as primary, rather than secondary, phases. Second, the mixing model was never able to explain why forsterite and metallic nickel–iron are absent from the fine-grained inclusions because high-temperature condensate *grains* had to react with the nebular gas at temperatures below the condensation points of those phases. No process could be found to separate intermediate-temperature silicate grains from high-temperature silicate grains. In this model, *all* previously condensed grains are removed and the inclusions form at low temperatures by the simultaneous condensation of volatiles and residual refractories.

Refractory element enrichment factors

GROSSMAN (1973) estimated that the Type A coarse-grained inclusions (GROSSMAN, 1975) represent about 4.46 wt % of the total condensable matter of the solar system. The presence in the Type B inclusions of large amounts of a Ti–Al-rich pyroxene, a mineral which does not appear in the equilibrium condensation sequence, introduces some uncertainty into the calculation when the two inclusion types are considered as a single population. The mean bulk chemical com-

position of ten Type B inclusions, the 'group I chondrules' of Martin and Mason (1974), suggests that they stopped equilibrating with the nebula after accreting between 4.5 and 6.3 wt % of the total condensable matter. If the entire solar complement of any particular refractory trace element were concentrated into this early, high-temperature condensate fraction, it would be enriched in it by a factor between 22.2 and 15.9 relative to C1 chondrites. Grossman and Ganapathy (1976) found that the mean enrichment factor for 15 refractories in a suite of ten Type A and Type B coarse-grained inclusions is 18.6 relative to C1's. If it is assumed that all of these elements were scavenged from the vapor by the inclusions with 100% efficiency, this enrichment factor implies that the coarse-grained inclusions represent 5.4 wt % of the total condensable matter, a value within the range estimated above from independent data. If, however, the refractories were incorporated by the inclusions with slightly less efficiency, as suggested above, the mean enrichment factor leads to a different estimate. For example, if the mean condensation efficiency for these elements were only 90%, the mean enrichment factor of 18.6 would imply that the coarse-grained inclusions accreted only 4.9% of the total condensable matter, a value which is also within the 4.5–6.3% range. In reality, probably each refractory element had its own particular accretion efficiency and this may be the ultimate cause of the fractionated refractory element enrichment pattern in the fine-grained inclusions.

If, as suggested above, the refractory elements in the fine-grained inclusions represent that fraction of the refractories that failed to condense into the coarse-grained ones, then the fine-grained inclusions should be most enriched in the refractory elements least enriched in the coarse-grained inclusions and vice versa. Thus, Fig. 2 suggests that Ta and Ce should be less enriched in the coarse-grained inclusions than Sc and Yb if this model is correct. Examination of Fig. 1 in Grossman and Ganapathy (1976), however, reveals that the opposite appears to be the case. Two important considerations must be taken into account, though, when comparing mean enrichment factors for different refractories in the coarse-grained inclusions. First, the concentration of any particular element is so variable from inclusion to inclusion that its mean enrichment factor usually has a standard deviation of 40–60% about itself. Add to this the different uncertainties for the concentrations of different refractories in C1 chondrites which are used for normalization and it is clear that little significance can be attached to the relatively small differences (44% maximum) between mean enrichment factors for different elements in the coarse-grained inclusions. Although the fine-grained inclusions are also highly variable in composition and the same C1 chondrite data are used for their normalization, mean enrichment factors for different refractory elements in them are so different from one another that their rela-

tive enrichments can be assigned with certainty in many cases.

Slight differences in the accretion efficiencies of different refractory elements in the coarse-grained inclusions can lead to markedly different enrichment factors in the fine-grained inclusions if the latter represent only a small fraction of the total condensable matter. If about 15% of the abundant refractories were left in the vapor after the condensation of the coarse-grained inclusions, the fine-grained ones would represent about 15% of 5% of the total condensable matter, or 0.75% plus whatever Na, Cl, FeO and other volatiles were incorporated. Assuming that the fine-grained inclusions represent 1% of the total condensable matter, total concentration of a trace refractory element in them would lead to an enrichment factor of 100 for it relative to C1 chondrites. If 95% of the Sc and only 70% of the Ta condensed into the coarse-grained inclusions, their enrichment factors in the fine-grained ones would be 5 and 30, respectively, as observed. Thus, differences in accretion efficiency which may not be detectable in the enrichment factors in coarse-grained inclusions can produce dramatic fractionations in the fine-grained inclusions.

An important feature of the model is that the fine-grained inclusions cannot contain much more than about 20% of the abundant refractory elements. Otherwise, the strikingly different enrichment factors for different trace refractories in the fine-grained inclusions would require such severe fractionations of refractory elements from one another during high-temperature condensation that they would begin to produce detectable and significant differences among the enrichment factors in the coarse-grained inclusions. Furthermore, if massive fractions of selected refractory major elements failed to condense into the coarse-grained inclusions, the equilibrium condensation model (Grossman, 1972) using a gas of solar composition would be unable to predict their mineralogy so well.

This model does not rule out the possibility that other refractory-containing condensate components may have also formed. Small amounts of some residual refractories could have partially condensed from the gas after the high-temperature condensates formed but before the fine-grained inclusions appeared. Indeed, this is probably the cause of the much greater depletion of Ir relative to the lithophiles in the fine-grained inclusions compared to the coarse-grained ones (see Fig. 3) as Ir could have condensed in solid solution in nickel–iron. Other residual gaseous refractories may have only partially condensed into the fine-grained inclusions, leaving their remnants to condense at even lower temperatures.

An attempt to test the model

A crucial test of the incomplete condensation model can be made by estimating the relative proportions of coarse- and fine-grained inclusions in Allende.

If the model is correct, the mass ratio of coarse- to fine-grained inclusions should be no less than 3.2. Estimating the modal proportions of the two is difficult because the coarse-grained inclusions are much larger and more heterogeneously distributed than the fine-grained ones. In order to sample as large a volume of the meteorite as possible, slab surfaces were used rather than thin sections. Considerable uncertainty was encountered in attempting to measure the total volumes of fine- and coarse-grained inclusions on slab surfaces. The depth of each inclusion had to be estimated by averaging its length and width. It was often difficult to tell whether small inclusions were fine- or coarse-grained. A large fraction of the material of interest is <1 mm in maximum dimension and had to be ignored simply because there were too many inclusions of this size to complete the task in a reasonable length of time. The average aggregate density of 3 fine-grained inclusions was found to be 2.1 g $cm^{-3} \pm 10\%$ by weighing the material excavated from regularly-shaped holes whose dimensions were measured. This low value reflects the high porosity of the fine-grained inclusions as observed by GROSSMAN et al. (1975). A density of 3.0 g cm^{-3} was assigned to the coarse-grained inclusions by taking the weighted average of the densities of the major phases in their mean modal proportions. Using these densities and the total estimated volumes of fine- and coarse-grained inclusions, coarse/fine mass ratios of 2.4 and 3.0 were found in two slabs from different stones. This suggests that the fine-grained inclusions account for about 25% of the cosmic complement of the major refractories, an estimate close to the upper limit proposed above. This is not only a highly uncertain result for the reasons cited previously, but also because the measurement ignores all the refractory elements which now reside in other petrographic components, such as chondrules (OSBORN et al., 1974) and amoeboid olivine aggregates (GROSSMAN and STEELE, 1976). These may have been derived via secondary processes from the original primary condensates, the coarse- and fine-grained inclusions. It is not known whether either type of inclusion was sampled preferentially during the formation of these secondary components. Thus, it is clear that testing the model by the method attempted here is an over-simplification and not very accurate.

Rare earth elements

Our explanation for the highly fractionated REE patterns in the fine-grained inclusions is similar to that of BOYNTON (1975): these inclusions condensed from a vapor containing fractionated abundances of refractory elements due to prior condensation of the coarse-grained inclusions. Here the similarity ends, however, as severe pitfalls beset the assumptions in Boynton's model, rendering the applicability of his fractionation mechanism questionable. BOYNTON (1975) assumed that the REE pattern found in a sin-

gle, fine-grained, pink inclusion by TANAKA and MASUDA (1973) was almost the same as that of the nebular gas after removal of a single phase, perovskite, into which REE had condensed in solid solution under equilibrium conditions. BOYNTON (1975) had to arbitrarily assign activity coefficients for the REE in perovskite in order to make the discrepancies between his simple model and the observed pattern disappear.

As shown here, the REE patterns are highly variable from one fine-grained inclusion to the next. Thus, there can be no justification for singling out a particular inclusion as being representative of the composition of the gas phase, as Boynton did. The fractionated gas probably had a REE pattern much closer to the mean of the fine-grained inclusions studied here, as shown in Fig. 2. As demonstrated in MARTIN and MASON (1974) and in this paper, there is little mineralogical or textural difference between the Tanaka–Masuda and Martin–Mason types of fine-grained inclusions, indicating that they all belong to the same class of aggregates with similar condensation temperatures. While the Tanaka–Masuda inclusion has a normalized Sm/Dy ratio of 5, MARTIN and MASON (1974) reported two 'Group III' inclusions with a mean ratio of 0.5 and our inclusion 13 has a ratio of 1.4. The different patterns seen in individual inclusions may be the result of their incorporating different proportions of several phases, each of which preferentially accepted different REE into its structure during condensation. This provides further justification for averaging the compositions of many inclusions and suggests that the Tanaka–Masuda inclusion may be much more strongly depleted in heavy REE compared to the light ones than was the solar nebular vapor. In using only a single inclusion, BOYNTON (1975) ignored the mineralogical similarities between the two types of inclusions and may have unduly biased the gas phase composition.

Another difficulty for Boynton's model is its requirement that removal of a *single*, high-temperature condensate phase, perovskite, was responsible for the fractionated REE pattern of the vapor. GROSSMAN and GANAPATHY (1976) showed that REE patterns of bulk coarse-grained inclusions are independent of the major mineral phases in them, indicating that those phases were not solvents for the condensing REE. From the highly irregular and variable REE patterns in the coarse-grained inclusions, GROSSMAN and GANAPATHY (1976) concluded that REE must have condensed in the form of several trace, REE-rich phases. The presence of at least three such phases in these inclusions has now been confirmed by LOVERING et al. (1976), although insufficient thermodynamic data are available to calculate whether they could all be primary condensates. It is extremely unlikely that each of these phases has the same relative REE activity coefficients as those calculated by BOYNTON (1975). According to the model proposed in this paper, these phases or the interiors of their grains were isolated from continued reaction with the solar

nebular gas after most of the REE had condensed, leaving behind in the vapor a slightly larger fraction of the light REE than the heavy ones, as reflected in the pattern in Fig. 2.

Coarse-grained inclusion 5

Among the coarse-grained inclusions analysed by GROSSMAN and GANAPATHY (1976), sample 5 has a REE pattern which appears to belong to the same family of patterns observed in fine-grained inclusions in this work and in the studies of TANAKA and MASUDA (1973) and MARTIN and MASON (1974). According to the model proposed above, however, high-temperature condensate inclusions should not contain such a REE pattern because it represents the composition of the gas phase after their removal. The physical appearance of inclusion 5 is exactly like that of many other coarse-grained inclusions except for its faint, but distinct, pink hue. Its X-ray powder pattern contains many strong lines of melilite, spinel, pyroxene and plagioclase, phases characteristic of coarse-grained inclusions. Weak lines of grossular are also present but nepheline and sodalite, minerals typical of the fine-grained inclusions, are absent. The REE are not the only refractories whose levels in inclusion 5 are like those in fine-grained and unlike those in coarse-grained inclusions. Its Ca content, 8.6%, is the lowest of all the coarse-grained inclusions studied in GROSSMAN and GANAPATHY (1976) and within the range of Ca contents reported here for fine-grained inclusions. Its Ir content, 162 ppb, is depleted by a factor of 46 relative to the average coarse-grained inclusion in that study but is again within the range for fine-grained inclusions. Its Sc and Ta contents are not unreasonable for fine-grained inclusions. It may be that not all coarse-grained inclusions have a simple origin as high-temperature condensates. Inclusion 5 may have originally condensed as a fine-grained inclusion which was subsequently melted and partially volatilized in the nebula, accounting for its lower volatile element content than that of the average fine-grained inclusion. Crystallization of this small melt droplet could have produced the coarse grain size. When corrected for loss of volatiles, the average bulk chemical composition of the fine-grained inclusions (MARTIN and MASON, 1974) is similar to that for the coarse-grained ones, except for a lower Ca/Al ratio. A melt of this composition would probably crystallize into a mixture of the same phases as in the coarse-grained inclusions. Thus, melting and evaporation could have converted the texture and mineralogy of a fine-grained inclusion into those of a coarse-grained inclusion while preserving its original refractory element enrichment pattern. When inclusion 5 is removed from consideration, the recomputed mean enrichment factors for all refractory elements in the remaining nine coarse-grained inclusions in GROSSMAN and GANAPATHY (1976) are brought into significantly closer agreement with one another.

CONCLUSION

The fine-grained, Ca-rich inclusions in the Allende meteorite contain a highly fractionated refractory element enrichment pattern. Textural, mineralogical and chemical data suggest that they formed in the solar nebula by the simultaneous condensation of volatiles with refractory lithophile elements which failed to condense into the coarse-grained, high-temperature condensate inclusions in this meteorite. The marked fractionations among the refractories, including the REE, in the fine-grained inclusions are caused by relatively small differences in their efficiencies of incorporation into the coarse-grained ones. The trace element data suggest that the refractories in the fine- and coarse-grained inclusions can only be the cosmic complements of one another if the fine-grained inclusions represent no more than $\sim 20\%$ of the most abundant refractory elements. One coarse-grained inclusion has refractory element concentrations which indicate that it may have formed by the melting and partial volatilization of a fine-grained inclusion.

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