Major and trace element chemistry of separated fragments from a hibonite-bearing Allende inclusion

ANDREW M. DAVIS, LAWRENCE GROSSMAN* and JOHN M. ALLEN†

Department of the Geophysical Sciences, University of Chicago
5734 S. Ellis Ave., Chicago, Illinois 60637

Abstract—Detailed mineralogical and textural study by Allen *et al.* (1978) of an unusual, hibonite-rich, coarse-grained inclusion from Allende, CG-11, reveals that it formed in a complex series of events involving at least two periods of condensation. Four hand-picked fragments, one hibonite-rich and three hibonite-poor, and a bulk sample were analyzed for major and trace elements by INAA. The mineralogy of the separated fragments was estimated from major element abundances. Two REE-bearing components are required to explain the REE patterns of the fragments. One, enriched in Eu and Lu relative to the other measured REE, is probably hibonite. The other, depleted in Eu and Lu, seems to be associated with the secondary alteration phases, grossular, anorthite and nepheline. Although melting of the primary phases, melilite and hibonite, prior to alteration cannot be excluded, condensation processes are required to explain the present REE distribution among the fragments. The enrichment of Lu over other measured REE in hibonite can be explained by present REE condensation models, but the enrichment of Eu which correlates with that of Lu cannot, perhaps because of a lack of thermodynamic data for relevant REE compounds. Variations in Sc/Hf ratios among the fragments require at least two carriers for Sc and Hf, probably hibonite and perovskite. The volatiles Na, Mn, Fe and Zn seem to have entered CG-11 with secondary alteration phases, but Co and Au did not.

INTRODUCTION

Microscopic examination of a slab surface of the Allende meteorite revealed a coarse-grained, irregularly-shaped white inclusion, CG-11, unusually rich in hibonite. A detailed mineralogical and textural study by Allen *et al.* (1978) revealed that CG-11 was formed by a complex history of mineral-forming events with at least two periods of crystal growth from a vapor. The bulk mineralogy of CG-11, a Type A inclusion, is dominated by two primary phases, melilite and hibonite, and three secondary phases, grossular, anorthite and nepheline, which formed by vapor phase alteration of the primary minerals.

Sample handling and analytical techniques developed in this laboratory now make it possible to analyze hand-picked samples weighing only a few tens of μg. Although there are strong indications from the rare earth element (REE) distribution between pyroxene and melilite that Type B coarse-grained, Ca-, Al-rich inclusions were at least partially molten at some stage of their history

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*Also Enrico Fermi Institute
†Present address: Department of Geology, University of Toronto, Toronto, Ontario, Canada M5S 1A1.

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Table 1. Major and trace elements of separated fragments and a bulk sample from CG-11 (values are in ppm unless otherwise indicated).

Sample	wt (µg)	Na (%)	MgO (%)	Al₂O₃ (%)	SiO₂ (%)	CaO (%)	Sc	TiO₂ (%)	V	Cr	Mn	Fe (%)	Co	Ni	Zn
3	12.56	0.600 ±.031	4.6 ±1.7	69.45 ±.55	3.5 ±2.1	17.2 ±1.1	605.2 ±.4	4.06 ±.19	3012 ±89	210.2 ±3.5	10.9 ±3.6	0.763 ±.019	2.71 ±.10	75 ±36	181 ±11
5	59.16	0.941 ±.021	2.08 ±.51	33.91 ±.20	33.11 ±.88	28.76 ±.66	92.06 ±.06	0.879 ±.054	98.8 ±5.7	27.02 ±0.45	107.8 ±3.5	1.540 ±.004	3.464 ±.026	41.8 ±6.0	278.8 ±3.3
6	32.40	0.877 ±.022	2.58 ±.66	33.41 ±.24	28.1 ±1.2	34.90 ±.95	139.40 ±.09	0.654 ±.068	278 ±11	16.0 ±2.0	80.8 ±2.9	1.188 ±.009	9.139 ±.054	178 ±14	186.0 ±4.8
7	15.41	0.629 ±.025	2.23 ±.91	34.52 ±.33	29.6 ±1.6	33.2 ±1.3	104.28 ±.08	0.89 ±.10	177 ±12	14.4 ±1.4	77.7 ±3.5	0.810 ±.011	2.235 ±.050	80 ±16	243.8 ±5.5
Bulk	9314	0.6142 ±.0009	4.3 ±1.6	37.59 ±.35	25.1 ±2.4	29.4 ±1.7	150.8 ±.4	1.03 ±.21	623 ±22	105.6 ±4.7	107.8 ±2.2	1.315 ±.054	10.32 ±0.71	240 ±84	
Standard[2]		SP	J-M[3] MgO	J-M[3] Al₂O₃	by diff.	J-M[3] CaCO₃	SP	J-M[3] TiO₂	BCR-1[4]	SP	SP	SP	SP	SP	SP
Isotope		²⁴Na	²⁷Mg	²⁸Al		⁴⁹Ca	⁴⁶Sc	⁵¹Ti	⁵²V	⁵¹Cr	⁵⁶Mn	⁵⁹Fe	⁶⁰Co	⁵⁸Co	⁶⁵Zn
Energy (keV)[6]		1368.5	1014.4	1778.9		3084.4	889.3	319.8	1433.9	320.0	846.6	1099.2	1332.5	810.8	1115.5
Half-life[7]		15.020H	9.462M	2.259M		8.68M	83.8D	5.808M	3.746M	27.72D	2.582H	45.1D	5.26Y	70.76D	244.1D

1. Eu in bulk determined with ¹⁵²ᴹ¹Eu (Energy = 121.8 keV; half-life = 9.3H).
2. Concentrations in SP from Perlman and Asaro (1971).
3. Johnson-Matthey Specpure compound.
4. Concentration of V in BCR-1 from Flanagan (1973).
5. Concentration of Tb in BCR-1 from Conard (1976.)
6. Bowman and McMurdo (1974).
7. Half-lives are taken from the most recent entry for each nuclide in *Nuclear Data Sheets*.

(Mason and Martin, 1974; Nagasawa *et al.*, 1977), no such inference has yet been drawn for Type A inclusions, which contain so little pyroxene that a mineral separate of it cannot be obtained. Several grains were hand-picked from CG-11 with the intention of analyzing separated hibonite and other phases to see if the REE distribution implies melting. If the inclusion had not been melted, the trace element abundances in hibonite, probably the earliest condensate of any of the major elements (Grossman, 1972), would provide new information about the condensation behavior of refractory elements.

EXPERIMENTAL

The bulk sample of CG-11 was analyzed with several other coarse-grained inclusions whose results will be reported elsewhere. These samples were sealed in 0.5 ml, low-density polyethylene vials and individually irradiated in the Oregon State University TRIGA Reactor via a pneumatic rabbit system for 4 minutes at a flux of 1.4×10^{12} neutrons cm⁻² sec⁻¹. After a 10 minute decay, the samples were counted for 400 seconds each for ²⁷Mg, ²⁸Al, ⁴⁹Ca, ⁵¹Ti and ⁵²V with a Ge-Li detector. After about 8 hours, the samples were counted again for 1000 seconds each for ²⁴Na, ⁵⁶Mn and ¹⁶⁵Dy. Variations in neutron flux throughout the run were monitored by irradiating Cu discs with several samples and counting ⁶⁴Cu several hours later. No significant variations in neutron flux were found. The standards, gamma-ray energies and half-lives used are given in Table 1. Johnson-Matthey Specpure MgO, Al₂O₃ and SiO₂ were irradiated inside Cd foil to allow correction for the following interfering fast neutron reactions: ²⁴Mg(n,p)²⁴Na; ²⁷Al(n,α)²⁴Na; ²⁷Al(n,p)²⁷Mg; and ²⁸Si(n,p)²⁸Al. SiO₂ was

Table 1. (*Continued*).

Sr	Ru	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu	Hf	Ta	Os	Ir	Au
<369	<2.7	2.479 ±.089	6.4 ±1.4	<55	1.955 ±.028	1.430 ±.072	0.35 ±.12	<2.8	1.90 ±.19	0.490 ±.050	1.488 ±.074	0.190 ±.083	1.28 ±.49	1.05 ±.11	0.492 ±.050
324 ±33	5.77 ±.19	4.410 ±.081	12.56 ±.23	11.9 ±4.6	3.449 ±.020	1.884 ±.019	1.063 ±.025	2.88 ±.57	3.80 ±.11	0.463 ±.011	1.198 ±.030	0.206 ±.016	3.65 ±.38	3.49 ±.35	0.097 ±.010
234 ±74	37.92 ±.60	2.84 ±.11	7.72 ±.95	<16	2.251 ±.041	1.294 ±.028	0.690 ±.051	2.81 ±.49	2.23 ±.15	0.245 ±.031	0.54 ±.15	0.085 ±.033	27.4 ±2.7	25.0 ±2.5	0.258 ±.026
222 ±84	<1.0	3.55 ±.13	10.39 ±.51	<15	2.566 ±.033	1.655 ±.044	0.617 ±.074	3.03 ±.76	2.70 ±.15	0.483 ±.021	0.835 ±.087	0.185 ±.048	0.33 ±.13	0.210 ±.021	0.400 ±.041
	6.5 ±2.1	3.145 ±.081	9.6 ±1.0		2.151 ±.010	1.211[1] ±.016	<0.71	3.39 ±.34	2.11 ±.10	0.235 ±.016	0.78 ±.16		3.64 ±.22	3.663 ±.022	0.0781 ±.0024
SP	chem.	SP	SP	SP	SP	SP	BCR-1[5]	SP	SP	SP	SP	SP	chem.	chem.	chem.
^{85}Sr	^{103}Ru	^{140}La	^{141}Ce	^{147}Nd	^{153}Sm	^{152}Eu	^{160}Tb	^{165}Dy	^{175}Yb	^{177}Lu	^{181}Hf	^{182}Ta	^{191}Os	^{192}Ir	^{198}Au
514.0	497.0	1596.4	145.5	531.4	103.2	1408.0	1177.9	94.7	396.3	208.4	133.0	1221.4	129.4	468.1	411.8
65.19D	39.35D	40.22H	32.50D	11.06D	46.7H	13.2Y	72.3D	2.334H	4.19D	6.71D	42.4D	115.0D	15.4D	74.02D	2.696D

determined by difference, using Na_2O, MgO, Al_2O_3, CaO, TiO_2 and V_2O_3 from this irradiation and FeO from the following irradiation. The bulk sample of CG-11, the other coarse-grained inclusions and the standards, "Standard Pottery" (Perlman and Asaro, 1969), USGS standard rocks BCR-1 and PCC-1 and several chemical standards described by Grossman and Ganapathy (1976a), were then irradiated in the rotating rack of the OSU Reactor for 3 hours at a flux of 5.6×10^{12} neutrons $cm^{-2}sec^{-1}$. After 24 hours of cooling, they were counted on high resolution Ge-Li detectors at the University of Chicago for the remaining elements reported in bulk CG-11. Details of the data reduction procedure are given by Grossman and Ganapathy (1976a; 1976b) and Grossman *et al.* (1977; Grossman, pers. comm., 1978).

Four fragments, one hibonite-rich and three hibonite-poor, were handpicked from the remaining powder of CG-11 on the basis of color and accurately weighed with a Perkin-Elmer AM-2 electronic microbalance. The samples weighed 12 to 60 μg each. Since the smallest available polyethylene vials, which weigh about 150 mg each, have unacceptably high blank levels of some elements for INAA of small samples, the fragments were sealed in tiny pouches fabricated from HNO_3-washed, 38 μm thick, Dow 530 polyethylene film. These containers weighed about 3 mg each. The samples, standards and three empty pouches were individually irradiated in the first row of graphite reflector of the University of Missouri Research Reactor (MURR) via a pneumatic rabbit for 10 minutes at a flux of 1.0×10^{14} neutrons $cm^{-2}sec^{-1}$. After the irradiations, the samples were removed from the rabbits and mounted in their polyethylene pouches on aluminum counting cards. After a decay of 5 minutes, each was counted for 100 seconds for ^{28}Al and, after 10 minutes of decay, for 500 seconds for ^{27}Mg, ^{49}Ca, ^{51}Ti and ^{52}V using a Ge-Li detector. After 3½ to 8 hours, the samples were counted for 1000 seconds each for ^{24}Na, ^{56}Mn and ^{165}Dy. Variations in neutron flux throughout the run were monitored by periodically irradiating aluminum wires doped with gold and counting ^{198}Au several days later. No significant flux variations were found. Fast neutron interferences were corrected for by the same technique used in the OSU irradiation. The samples were removed from the polyethylene bags, sealed in Suprasil quartz vials and irradiated with standards in the flux trap of the MURR for 89.5 hours at a flux of 5×10^{14} neutrons $cm^{-2}sec^{-1}$. After two days of cooling, the Suprasil quartz irradiation vials were washed in aqua regia and the samples and rock standards were transferred from them into new vials and counted on high resolution Ge-Li detectors at the University of Chicago. Each sample was counted three times: 1) for 21 to 46 hours each; 2) until the highest peak had reached a height of 10^6

counts, 30 to 107 hours; and 3) until the highest part of the background reached 5×10^5 counts, 9 to 14 days each. By allowing the dominant peaks to overflow several times in the final count, substantial improvements in counting statistics were achieved for several elements with long-lived activation products. Due to improper cooling of the samples during the irradiation, all chemical standards except the Ru standard were destroyed. The specific activities of ^{191}Os, ^{192}Ir and ^{198}Au at the end of the irradiation were calculated from their values in a previous irradiation at the same flux in the same reactor by correcting for differences in neutron fluence using ^{103}Ru in the Ru standard. Os, Ir and Au concentrations listed for the four fragments have been assigned an error of $\pm 10\%$, in addition to counting statistics, to reflect the uncertainty in calculations of specific activities of ^{198}Au, ^{191}Os and ^{192}Ir from the previous irradiation.

^{199}Au can be produced by successive neutron capture on ^{198}Au and ^{197}Au and by decay of ^{199}Pt produced by neutron capture on stable ^{198}Pt. ^{199}Au has a 208.2 keV peak which can interfere with the 208.4 keV peak of ^{177}Lu, which is used to determine Lu. This effect can become significant in samples with high Au/Lu ratios, especially when high neutron fluences are used. Since this is the case for the separated fragments from CG-11, it was necessary to correct the ^{177}Lu peak for this interference by the method outlined by Grossman *et al.* (1977). The ratio of ^{199}Au counts at 208.2 keV to those at 158.4 keV was measured in a Au standard from another irradiation and found to be 0.162 for the detector and position in which the samples were counted. In all four fragments, the 158.4 keV peak of ^{199}Au appears as a large bump on the side of the 159.4 keV peak of ^{47}Sc, which is produced by the decay of reactor-produced ^{47}Ca. The excellent resolution of the detector (0.9 keV FWHM at 159.4 keV) allowed graphical integration of the 158.4 keV ^{199}Au peaks. Although counting statistics give an uncertainty of about 3% in the area of this peak, we have assigned a liberal uncertainty of 20% to this peak area to reflect the uncertainty in the shape of the background under the peak. Using these data, the area of the 208.4 keV peak was corrected for ^{199}Au interference in each sample. Although the Lu data were taken from counts made 10 to 15 days after irradiation to minimize ^{199}Au interference, the corrections were substantial for some samples. The corrections applied to fragments 3, 5, 6 and 7 were 19, 4, 32 and 17% of the total peak area, respectively. No correction was necessary for the Lu standard, SP, because it contains undetectable Au and Pt. The Lu results were also corrected for ^{177}Lu produced by decay of reactor-produced ^{177}Yb following the method of Grossman *et al.* (1977).

Results and Discussion

Blank corrections due to polyethylene irradiation containers were made for all short-lived nuclides and were always less than one percent. Data for all samples are shown in Table 1. The abundances of major and trace elements in the bulk sample are within the ranges observed in other coarse-grained inclusions (Grossman and Ganapathy, 1975, 1976a; Grossman *et al.*, 1977; and Davis *et al.*, 1978).

Although the Au contents of the four fragments are higher than that of the bulk sample, we have no other reason to suspect Au contamination. Plastic gloves and stainless steel tweezers were used during sample handling which was all done in a clean room. Although the Au standard vial burst during the irradiation, no Au was detected in an empty quartz vial included in the irradiation, indicating that any Au which may have been mobilized during the irradiation was removed by our washing procedure. Furthermore, no Au was detected in SP and BCR-1, which were transferred from their irradiation vials into inactive counting vials in the same manner as the samples, so that contamination during transfer also seems unlikely.
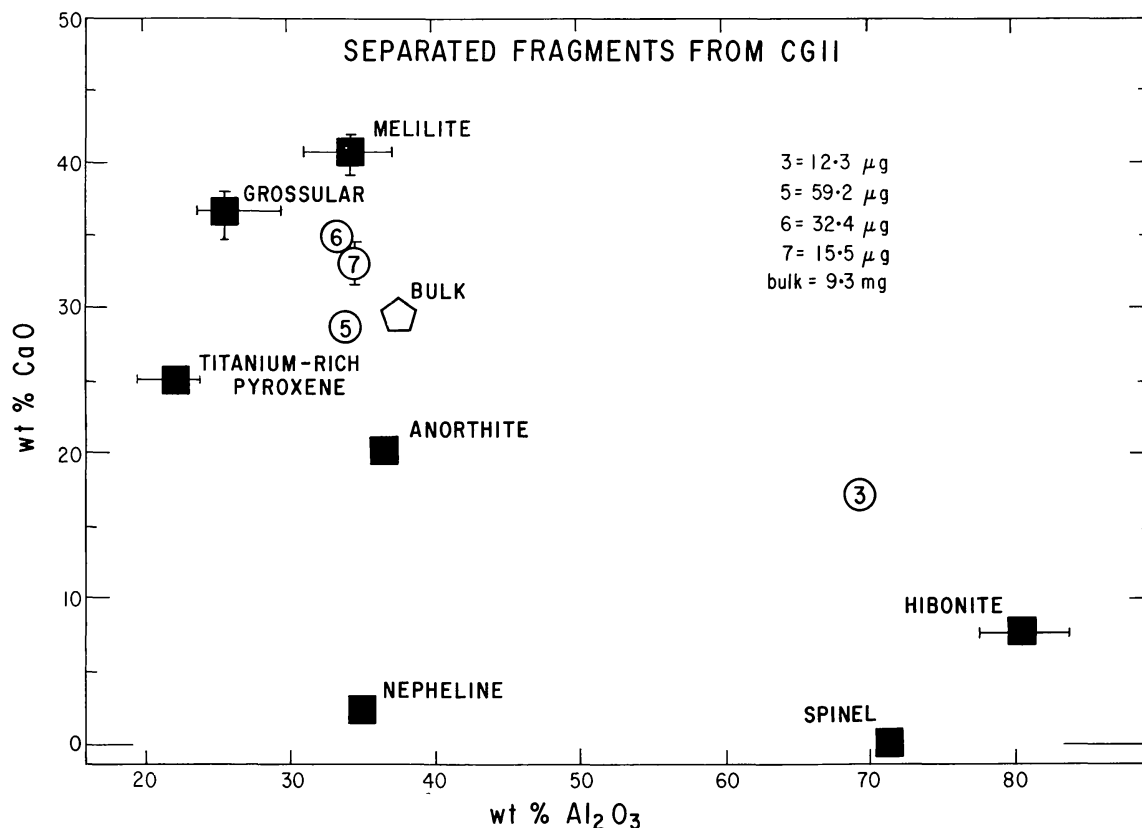
Fig. 1. The mineralogical compositions of fragments 5, 6 and 7 are dominated by melilite, grossular and anorthite. Fragment 3 consists almost entirely of the primary minerals of CG-11, hibonite and melilite.

Major elements

The exact mineralogy of the bulk sample and separated fragments cannot be unambiguously determined from major element abundances because of the large number of phases possibly present and variations in their composition (Fig. 1). Petrographic analysis of CG-11 (Allen *et al.*, 1978), however, shows that the mineralogy is dominated by two primary phases, melilite and hibonite, and three secondary phases, grossular, anorthite and nepheline. Since the dark-colored material was avoided during sampling of the fragments and the bulk sample, a minimum of material from the rim or regions outside it is believed to have been sampled. Since nepheline is the dominant Na-bearing mineral in CG-11, its concentration in the fragments and the bulk sample can be calculated from their bulk Na contents and microprobe data for nepheline (Allen *et al.*, 1978). From the range of V concentrations measured in hibonite with the electron microprobe (Allen *et al.*, 1978), upper limits of 4, 12, 8 and 28% were established for the hibonite contents of fragments 5, 6 and 7 and the bulk sample, respectively. Actually, these samples may contain no hibonite, since minor phases such as perovskite and spinel also contain V (Allen *et al.*, 1978). If the Al_2O_3, SiO_2 and CaO contents of fragments 5, 6 and 7 and the bulk are corrected for nepheline

Table 2. Estimated major mineralogical composition of separated fragments and a bulk sample from CG-11 (in wt.%).

Sample	Hibonite	Melilite	Grossular	Anorthite	Nepheline
3	70	26	<3	<1	5
5	0–4	29–44	7–29	28–39	8
6	0–5	55–72	8–33	0–11	7
7	0–8	39–67	1–41	7–26	5
Bulk	10–19	28–59	0–44	0–21	5

and hibonite, the proportions of melilite, grossular and anorthite in the remainder can be calculated through solution of simultaneous equations. The results of these calculations are shown in Table 2 for the range of hibonite contents allowed by the range of V concentrations in hibonite. Assuming that the dominant minerals in CG-11 are as given by Allen *et al.* (1978), fragment 6 must contain less than 5% hibonite, since modal compositions with more than 5% hibonite require negative anorthite contents. The Al_2O_3 and CaO contents of fragment 3 were also corrected for nepheline using Na. The corrected composition lies above the join between mean hibonite and mean melilite on the CaO vs. Al_2O_3 plot (Fig. 1), but on the join between the most Al_2O_3-rich melilites and hibonites measured with the electron microprobe (Allen *et al.*, 1978). The range of CaO concentrations in fragment 3 allowed by 1σ counting statistics indicates that it contains less than 3% grossular and less than 1% anorthite, thus constraining its hibonite and melilite contents. The MgO, SiO_2 and TiO_2 concentrations in fragment 3 are consistent with the mineralogical composition given in Table 2.

Rare earth elements

The Cl chondrite-normalized REE patterns of the bulk inclusion and separated fragments, shown in Fig. 2, are characterized by positive Eu anomalies and variable Lu/Yb ratios. Shown in Table 3 are ratios of several REE normalized to Cl chondritic ratios. There is no evidence that La, Ce, Sm, Tb, Dy and Yb are significantly fractionated from one another among the separated fragments and the bulk inclusion, since the 2σ error limits of all possible ratios of these elements to one another overlap for all five samples. In contrast, the abundances of Eu and Lu vary significantly relative to the other measured REE. Further, the Eu/Sm and Lu/Yb ratios are positively correlated with one another (Fig. 3). Although variable Eu anomalies can be produced by partitioning of REE during an igneous event, large variations in Lu/Yb ratios with no significant variations in Yb/La, Yb/Ce and Yb/Sm ratios cannot, since igneous partitioning yields smooth fractionations as a function of ionic radius for all trivalent REE. Therefore, the REE distribution among these samples of CG-11 was not established during a melting event. The high degree of correlation between Eu/Sm ratios and Lu/Yb ratios indicates that the REE patterns of these samples are controlled by two
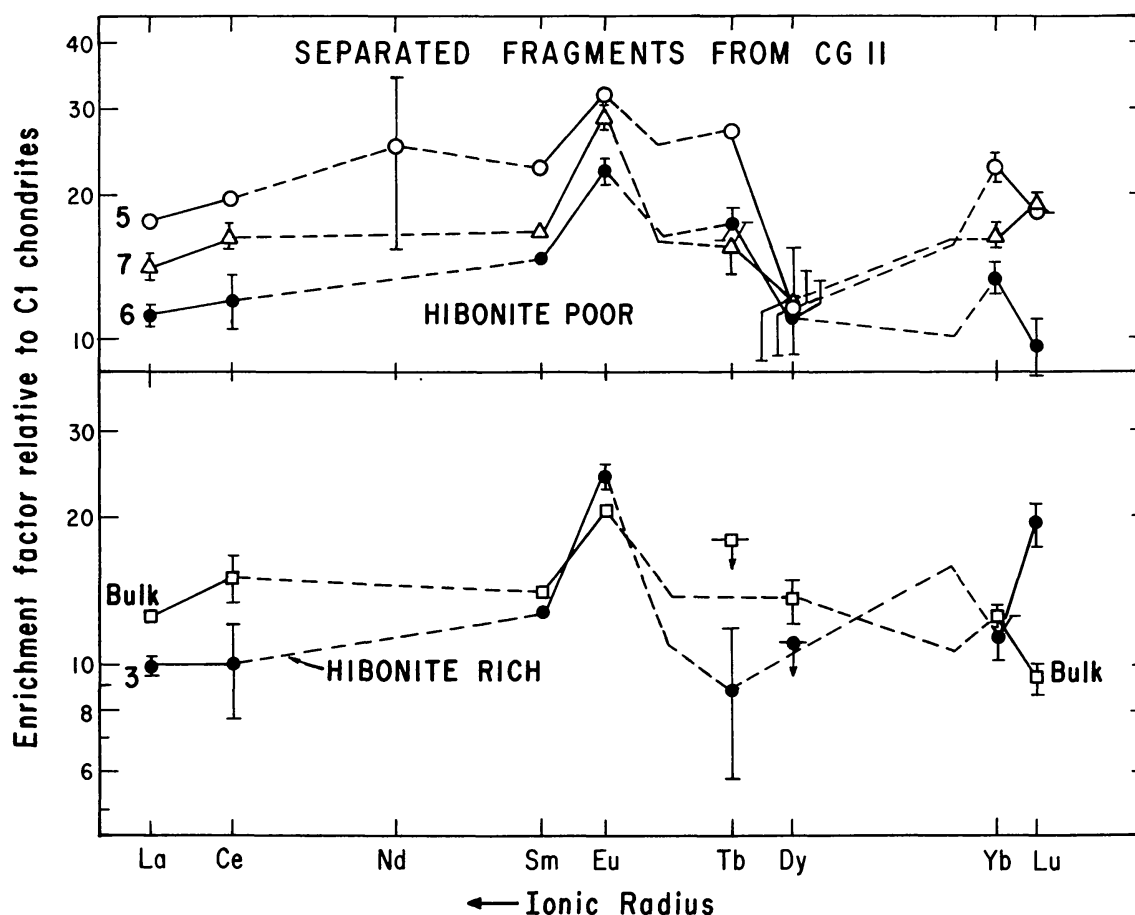
Fig. 2. The Cl chondrite-normalized REE patterns of separated fragments are characterized by variable Lu/Yb ratios and variable Eu anomalies. The Cl chondrite abundances are from Nakamura (1974) except for Tb, which was derived by Davis and Grossman (pers. comm., 1978) from literature data.

components: one Lu-, Eu-rich and the other Lu-, Eu-poor. Since the order of increasing amount of the Lu-, Eu-rich component, 5 and 6 to 7 to 3, is not the same as the order of La, Ce, Sm and Yb abundances, 3 to 6 to 7 to 5, a third REE-free component must be acting to dilute the two REE-bearing components. Hibonite may be or may carry the Lu-, Eu-rich component, since fragment 3 contains the largest proportion of this phase by far. The proportion of the Lu-, Eu-poor component increases in the same order as the amount of secondary minerals (Table 2), indicating that it may be associated with the alteration process. The fact that the distribution of REE between primary and secondary phases is controlled by condensation processes is in accord with petrographic evidence (Allen *et al.*, 1978) that the secondary alteration products formed in a later condensation event, after that which produced the original primary phases of the inclusion. Since we were unable to measure the REE distribution between melilite and hibonite, we cannot exclude the possibility that the primary condensate phases were melted and equilibrated prior to the alteration process.

Table 3. REE ratios in separated fragments and a bulk sample from CG-11, normalized to Cl chondrite ratios.

Sample	La/Sm	Ce/Sm	Eu/Sm	Tb/Sm	Dy/Sm	Yb/Sm	Lu/Sm	Lu/Yb
3	0.77	0.78	1.92	0.69	<0.88	0.89	1.53	1.71
	±.03	±.17	±.10	±.24		±.09	±.16	±.24
5	0.78	0.87	1.43	1.20	0.51	1.01	0.82	0.81
	±.02	±.02	±.02	±.03	±.10	±.03	±.02	±.03
6	0.77	0.82	1.51	1.19	0.76	0.91	0.66	0.73
	±.03	±.10	±.04	±.09	±.13	±.06	±.08	±.10
7	0.84	0.97	1.69	0.93	0.72	0.97	1.15	1.19
	±.03	±.05	±.05	±.11	±.18	±.06	±.05	±.08
Bulk	0.89	1.07	1.48	<1.28	0.96	0.90	0.67	0.74
	±.03	±.11	±.02		±.10	±.04	±.05	±.06

The significance of correlations between REE components and major minerals may be limited, however, since potential REE-bearing minerals such as perovskite and Ti-, Al-rich pyroxene occur as minor phases in these samples. Also, El Goresy *et al.* (1977; 1978) report that complex assemblages rich in refractory lithophile and siderophile trace elements, which they refer to as "Fremdlinge", occur in both Type A and Type B coarse-grained inclusions. Since the REE in separated fragments from CG-11 may be contained within such assemblages, correlations between REE concentrations and contents of major phases may be fortuitous. Calculations of the condensation behavior of the REE (Boynton, 1975; Grossman and Ganapathy, 1976a; Davis and Grossman, pers. comm., 1978) indicate that Lu, the most refractory REE, can be fractionated from the other REE measured in CG-11 during condensation. In order to produce the observed factor of two fractionation of the Lu/Yb and Lu/Sm ratios, separation of gas and dust must have occurred at very high temperatures. Assuming ideal solid solution of the REE sesquioxides in hibonite or perovskite, the fractionation must have taken place when 1% or less of the host phase had condensed. Otherwise, each of Tb, Dy and Lu would have been totally condensed and Tb and Dy would have fractionated to nearly the same extent as Lu relative to Yb and Sm. The coexistence of Eu/Sm and Lu/Yb enrichments in the same phase is not predicted by current REE condensation models, since they indicate that Eu is more volatile than all other REE. However, phases such as $EuO \cdot 6Al_2O_3$, for which no thermodynamic data exist, may be so refractory that Eu may have condensed as such at much higher temperatures than present calculations of solid solution of EuO or Eu_2O_3 in refractory minerals indicate.

Other refractory lithophile elements

Fragment 3 is richest in Sc, V and Ti, consistent with electron microprobe data
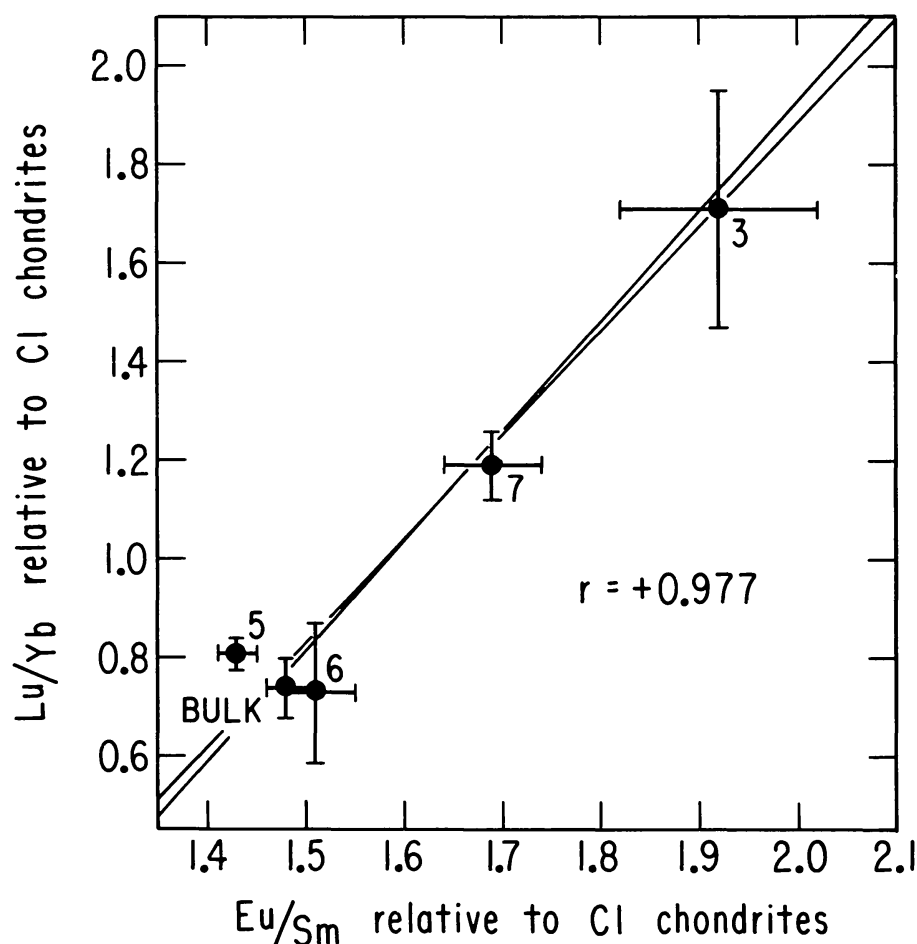
Fig. 3. Lu/Yb ratios are correlated with Eu/Sm ratios at a significance level of greater than 99%, indicating that the REE distribution within separated fragments of CG-11 is controlled by only two REE bearing components.

for these elements in hibonite (Allen *et al.*, 1978). Only one Sc-bearing condensate component is required by the data for most coarse-grained inclusions (Grossman *et al.*, 1977), but microprobe data (Allen *et al.*, 1978) show that there are at least two such components in CG-11, perovskite and hibonite. If perovskite and hibonite in CG-11 did not equilibrate their trace element contents with one another, we can conclude that either these phases entered coarse-grained inclusions in constant relative proportions or the condensation of hibonite, an uncommon mineral in these inclusions, was inhibited where most coarse-grained inclusions formed. In the latter case, gehlenite and spinel would have been the first major Al-bearing condensate phases.

If the Sc/Hf ratio of hibonite is given by that of fragment 3, 407 ± 20, then fragments 5, 6 and 7 must have at least one other Hf-bearing component with a lower Sc/Hf ratio, since their ratios are 77 ± 2, 258 ± 72 and 125 ± 13, respectively. Baddeleyite, ZrO_2, which occurs with other refractory lithophile trace element oxide minerals in some coarse-grained inclusions (El Goresy *et al.*,

1977; 1978), is a candidate for this component. If baddeleyite possesses the C1 chondritic Zr/Hf ratio (Ganapathy *et al.*, 1976), it contains 2.5% Hf and must, therefore, have a lower Sc/Hf ratio than 77. The range of Sc/Hf ratios in perovskite, calculated from the Cl chondritic Zr/Hf ratio and the range of Sc/Zr ratios measured in perovskite with the electron microprobe (Allen *et al.*, 1978), is 10 to 33. This corresponds to a range of Hf contents from 113 to 29 ppm. Thus, the variations in Sc/Hf ratios among the fragments can be explained by differing proportions of hibonite and perovskite or baddeleyite. A third component, containing little or no Sc and Hf, is required, since hibonite-poor fragments have lower Sc and Hf contents than mixtures of perovskite and hibonite or baddeleyite and hibonite.

The abundances of Sr and Ta are not well determined in some fragments because of poor counting statistics. The enrichment factors of Sr relative to Cl chondrites (Gopalan and Wetherill, 1971) in fragments 5, 6 and 7 are 38 ± 4, 27 ± 9 and 26 ± 10, respectively. No measurable variation in Sr content exists among these three fragments.

Refractory siderophile elements

Three fragments contain comparatively low abundances of refractory siderophile elements, enriched by less than a factor of 8 over Cl chondrites; however, fragment 6 is enriched in Ru, Os and Ir by factors of 55 ± 1, 61 ± 6 and 49 ± 5 relative to the concentrations of these elements in Cl chondrites given by Crocket *et al.* (1967), Higuchi *et al.* (1977) and Krähenbühl *et al.* (1973), respectively. Although variation in refractory siderophile element abundances among fragments indicates a rather inhomogeneous distribution of the refractory noble metal-rich nuggets observed by Allen *et al.* (1978) in CG-11, there is no significant fractionation of Ru, Os and Ir from one another. There appears to be no relationship between the abundance of refractory noble metal-rich nuggets and major mineral abundances among the four fragments.

Volatile elements

Among the four separated fragments, Co is correlated with Os and Ir at significance levels greater than 99.9% and Ni, which has poorer counting statistics than the other three elements, is correlated with significance levels greater than 90%. Least squares linear regression of Co vs. Ir shows that the fragments of CG-11 contain two Co components of constant composition. One has an Ir/Co ratio of 3.7, 3400 times the Cl chondrite ratio. The other contains no Ir and 2.4 ppm Co, only 26% of the Co content of the most Ir-rich fragment. The bulk inclusion plots on the high-Co side of the Co-Ir correlation line defined by the fragments and so contains a third Co component, probably due to contamination by about one percent Allende matrix material. The special property of the separated fragments of CG-11 which allows us to see the

Ir-correlated Co component is their relatively low Co content due to the other two components.

Because of its enrichment in refractory siderophile Ir relative to more volatile Co, the high-Ir component is inferred to be the refractory metal-rich condensate nuggets which are preserved inside coarse-grained inclusions (Wark and Lovering, 1976) and have been observed in CG-11 by Allen *et al.* (1978). The Ir/Co ratio determined above is a factor of 2.8 lower than that found by Palme and Wlotzka (1976) in a single metal-bearing fragment in a coarse-grained inclusion, but large variations in nugget compositions were noted by Wark and Lovering (1976). Assuming that metal nuggets in coarse-grained inclusions have Cl chondritic Ni/Co ratios as given by Moore (1971) (Ni) and Grossman and Ganapathy (1976a) (Co), the mean Ir/Ni ratio of refractory noble metal-rich nuggets measured by Wark and Lovering (1978) corresponds to an Ir/Co ratio of 130, 35 times the ratio inferred for nuggets in CG-11. In calculating the mean Ir/Ni ratio, however, Wark and Lovering (1978) included only those nuggets whose bulk compositions were dominated by refractory noble metals and excluded the Fe-, Ni-, Co-rich grains usually associated with them. The strong correlations between Os, Ir and Co observed herein suggest that so many of these tiny particles exist in each inclusion that their compositional differences are averaged out in fragments as small as 80 to 130 μm across.

Au concentrations in the separated fragments are high. Au/Co ratios of the separated fragments are higher than those of all bulk coarse-grained inclusions, which are, in turn, all higher than the Cl chondritic Au/Co ratio. The abundances of Au do not appear to be related to the abundances of Co or secondary alteration phases.

Among the four separated fragments, the amount of secondary alteration phases increases in the order 3 to 6 to 5. Fragment 7 has a possible range of secondary mineral contents which overlaps those of both 5 and 6. The volatile elements Na, Mn and Fe increase in the order 3 to 7 to 6 to 5 and Zn increases from 3 to 6 to 7 to 5. This indicates that lithophile volatile elements were introduced into CG-11 at the same time as the secondary minerals associated with alteration of primary melilite and hibonite. The abundance of Cr increases in the order 7 to 6 to 5 among the three hibonite-poor fragments, but is highest in fragment 3. If Cr occurs in hibonite, it must be at the level of about 300 ppm, which is below the 500 ppm detection limit for Cr in hibonite by electron microprobe. Since fragments 5, 6 and 7 contain little hibonite (Table 2), the order of Cr abundances in the hibonite-poor fragments indicates that some Cr was introduced into CG-11 with the other lithophile volatile elements.

Conclusions

The REE patterns of separated fragments can be explained by two components, one of which is Lu-, Eu-poor and associated with secondary alteration phases and the other Lu-, Eu-rich and associated with hibonite. The REE distribution in CG-11 precludes melting events subsequent to the formation of

secondary alteration phases, but cannot preclude a melting event involving the primary minerals. Two Hf-bearing components, probably hibonite and perovskite, are required to explain variations in Sc/Hf ratios among fragments. The amount of refractory noble metal-rich nuggets varies from fragment to fragment but there seems to be little variation in the Ni, Co, Ru, Os and Ir contents of the nuggets. The lithophile volatile elements Na, Mn, Fe, Zn and probably Cr increase in the same order as the amount of secondary alteration minerals, but the volatile siderophile elements Co and Au do not. The separate behavior of Fe from Co and Au indicates that deposition of the secondary minerals took place under oxidizing conditions.

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