

Chemical compositions of refractory inclusions from the Vigarano and Leoville carbonaceous chondrites

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Abstract—Major and trace elements were determined by INAA in two hibonite-rich refractory inclusions and a dark clast from Vigarano, three refractory inclusions from Leoville, and a hibonite-rich and a melilite-rich fraction from a composite refractory inclusion from Allende. The refractory inclusions from Vigarano and Leoville are all similar to their counterparts in Allende in that they have groups I, II, and III refractory element fractionation patterns, but a large proportion of these Vigarano and Leoville inclusions also contain refractory element features that are very infrequently encountered in Allende inclusions. For example, Vigarano 1623-2 is a group I inclusion with a large Ce anomaly ($\text{La/Ce} = 2.34 \pm 0.32$ relative to C1); Vigarano 1623-3 is a group III in which Os is strongly fractionated relative to other refractory siderophiles ($\text{Os/Re} = 2.13 \pm 0.08$ relative to C1); and Leoville 3537-1 is a modified group II in which removal of refractory REEs and condensation of the remaining REEs both occurred at unusually low temperatures. All samples from Vigarano and Leoville, including a fine-grained inclusion, have Na, Au, and other volatile element concentrations at or below the low end of the concentration ranges for these elements in Allende coarse-grained inclusions. This is consistent with the much lower amounts of Na-rich, secondary alteration products in the Vigarano and Leoville inclusions than in the ones from Allende. Even the Vigarano dark clast has a lower Na content than Allende dark clasts. Secondary alteration of refractory inclusions in the reduced subgroup of C3V meteorites occurred in a part of the solar nebula where grain-gas separation processes removed the inclusions from chemical communication with the gas at a higher temperature or after a shorter time than in the case of Allende inclusions. The hibonite- and melilite-rich parts of the Allende inclusion could have formed in separate parts of the same chemical reservoir by separation of early condensing hibonite from melilite. The relatively hibonite-rich Vigarano inclusions may have accumulated originally from condensates preferentially enriched in hibonite by gravitational settling of grains of this early condensate or by their transport in convection cells.

INTRODUCTION

STUDIES OF REFRACTORY, Ca-, Al-rich inclusions from the Allende meteorite have yielded considerable information about the physical conditions and degree of heterogeneity in the solar nebula and about chemical fractionations accompanying condensation therein. Inclusions from Allende have been studied much more thoroughly than those from other C3 chondrites largely because there is so much more material available for study from Allende than from the others. The danger in basing so many of our conclusions about the origin of the solar system on Allende inclusions, however, is that the latter may be only a sample of those nebular materials that happened to be available at a particular time in the immediate vicinity of a single accreting body and may not be representative of what was generally present in the solar nebula, or even in the region where C3V chondrites accreted. In fact, observations by MACPHERSON (1985) and DAVIS et al. (1987) suggest that refractory inclusions in the C3V chondrite Vigarano underwent much less secondary alteration to Na-rich feldspathoids than their counterparts in Allende. Furthermore, LIU and SCHMITT (1988) found that the relative

frequency with which groups I, II, and III REE patterns are encountered is quite different among refractory inclusions in each of the C3V chondrites Kaba, Mokoia, and Allende. For this reason, we initiated combined petrographic, chemical, and isotopic studies on a suite of inclusions collected from samples of the Vigarano and Leoville C3 chondrites. The results of a brief petrographic and ion microprobe study of one of the Vigarano inclusions was reported by DAVIS et al. (1987), and O and Si isotopic data on all of the Vigarano inclusions studied herein were presented by CLAYTON et al. (1987). Here we report the results of INAA on three inclusions each from Vigarano and Leoville. The complete results of ongoing mineralogical, petrographic, and ion microprobe studies on all of the inclusions studied herein will be the subject of a separate paper.

Although inclusions which are hibonite-rich, melilite-bearing, and poor in Na-rich secondary alteration products are apparently common in Vigarano (MACPHERSON, 1985; DAVIS et al., 1987), they are rare in Allende. An example of such an object in Allende is the hibonite-rich part of inclusion USNM 3529-42, described originally by MASON and TAYLOR (1982). MACPHERSON et al. (1986) reported that this inclusion is composite, containing a little-altered, hibonite-, spinel-rich portion which they interpreted as having crystallized from a melt and a highly altered, melilite-rich part which appears to have undergone solid-state recrystallization. Although the chemical composition of the bulk inclusion is known, we

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decided to determine the major and trace element contents of each portion in order to elucidate the genetic relations between the two parts and between Vigarano and Allende inclusions.

EXPERIMENTAL

Sampling

All samples were obtained from the collections of the Smithsonian Institution. Pieces of the Vigarano and Leoville chondrites were sliced into thin slabs in which were found a number of relatively large, whitish inclusions. In some cases, the plane of the saw-cut passed through an inclusion in such a way that large parts of the inclusion were exposed on each of the facing slabs. In these cases, a polished thin section was made of one piece of each inclusion, and material for trace element and isotopic analysis was scraped from the other piece with stainless steel dental tools in a clean room. In the case of Vigarano, development of orange stains and globules on and near refractory inclusions was observed on freshly exposed slab surfaces, presumably due to reactions of meteorite components with atmospheric water and mobilization of iron as FeCl_2 . Particular difficulty was encountered with the Leoville inclusions, as their physical toughness caused resistance to digging and scraping, and omnipresent, Fe_2O_3 -filled cracks made clean samples hard to find. Fractions rich in either orange or white material were separated from a previously crushed sample of Allende inclusion 3529-42 by hand-picking under a binocular microscope in a clean room.

Sample Descriptions

Vigarano 1623-2

On slab surface, this is a white, 4×2 mm, crudely elliptical inclusion whose margin is marked by numerous rounded irregularities. It consists predominantly of melilite (Ak 7–16), spinel, and hibonite (8–9% TiO_2 , $\sim 0.2\%$ SiO_2), with accessory perovskite and Ni-Fe beads, some containing Os, Ir, and Ru. The core of the inclusion contains dense hibonite-spinel (up to 1.2% FeO , 0.7% V_2O_3) intergrowths that enclose melilite islands. Outside of this is a polygonal-granular-textured mantle consisting mostly of melilite crystals having the same composition range as those in the core. Many of the mantle melilite crystals are reversely zoned. The entire inclusion is rimmed by thin layers of spinel, aluminous diopside, and olivine. It is brecciated in places but little altered, the only secondary phases being calcite (which occurs in fractures) and rare nepheline grains.

Vigarano 1623-3

This light-colored inclusion measures $\sim 4 \times 2$ mm on slab surface and has a butterfly shape (two outstretched "wings" extending from a narrow "body"). It has a dense core, consisting mostly of a polygonal-granular mosaic of melilite crystals (Ak 0–17), which encloses clusters of intergrown hibonite (4–5% TiO_2 , $\sim 0.5\%$ SiO_2) + spinel ($< 0.5\%$ FeO) + perovskite, and occasional Ni-Fe metal beads. At least one of the latter contains Ir and Ru peaks visible in an energy dispersive detector on the SEM. Minor CaAl_4O_7 (0.09% TiO_2 , 0.03% V_2O_3) is also present. Overlying this is a porous, melilite-free mantle of hibonite, spinel, and perovskite and then a compact mantle of melilite (Ak ~ 0), spinel, perovskite, and hibonite. The only secondary phase is calcite, found as wormy patches. DAVIS et al. (1987) reported a brief petrographic description and the oxygen isotopic composition of this inclusion, and ion microprobe measurements of REE concentrations and Mg isotopic compositions in phases within it. Those workers suggested that this inclusion may be an unaltered precursor to Allende fine-grained inclusions but the latter are so heavily altered to feldspathoids and grossular that it is difficult to imagine what their precursors may have resembled.

Vigarano 1623-S4-12

This is an irregularly shaped, ~ 4 mm, very fine-grained, black clast containing light-colored inclusions visible to the naked eye. Un-

like dark clasts in Allende, the matrix is not resolvable with a scanning electron microscope. The larger grains and aggregates are mainly olivine. Other phases identified by X-ray diffraction are troilite, pyroxene, and perhaps a trace of phyllosilicate.

Leoville 3536-1

This is a fine-grained, greyish inclusion measuring 12×5 mm in its longest dimensions. It consists of two elongated arms protruding from one side of a torus. The direction of elongation is parallel to the foliation that characterizes Leoville as a whole (CAIN and MCSWEEEN, 1984). The inclusion is bleached along cracks that traverse both it and the surrounding matrix, and the cracks contain reddish-brown hematite. As Leoville is a find, the latter features may be terrestrial in origin. In thin section, the inclusion is very fine-grained and concentrically zoned. The interior consists mostly of spinel ($< 0.05\%$ FeO , $< 0.05\%$ V_2O_3), with rims of anorthite ($< 0.1\%$ Na_2O , $\sim 0.3\%$ MgO) and aluminous diopside that grades into titanian fassaite ($\text{TiO}_2 \sim 3.5\%$, $\text{Al}_2\text{O}_3 \sim 15\%$). The outer mantle consists of melilite (Ak 4–13) within which are spinel crystals, each of which is rimmed by thin rinds of diopside ($\sim 1\%$ Al_2O_3) and anorthite. This inclusion is very similar to Allende fine-grained, spinel-rich inclusions, but differs in being devoid of feldspathoids and in having abundant melilite in the mantle.

Leoville 3536-2

This is an irregularly shaped, greyish inclusion measuring $\sim 14 \times 6$ mm in its longest dimensions. Like 3536-1, its direction of elongation is parallel to the foliation of Leoville and it is criss-crossed by veins of red iron oxide of probable terrestrial origin. It contains $\sim 90\%$ melilite (Ak 15–52) with minor fassaite and anorthite (0.05–0.15% Na_2O) and very minor spinel and perovskite, reminiscent of Allende compact Type A inclusions. Most of the inclusion is very fine-grained (30–50 μm) and many of the crystals show evidence of intense strain. Also present are rare, large (up to 500 μm) grains of severely strained melilite and large (up to 400 μm), pale green fassaite (7–8% TiO_2) grains which are rimmed by more intensely colored fassaite (11–12% TiO_2). No Na-rich feldspathoids are present.

Leoville 3537-1

This cigar-shaped, white inclusion measuring 30×4 mm is criss-crossed by numerous veins of red iron oxide, like the other Leoville inclusions. In thin section, the inclusion is fine-grained and contains fassaite ($\sim 5\%$ TiO_2 , 18% Al_2O_3), anorthite ($< 0.06\%$ Na_2O , $\leq 0.2\%$ MgO), melilite (Ak 21–64), and very abundant, tiny crystals of spinel ($\text{FeO} < 1\%$). No Na-rich feldspathoids are present, the only secondary phase being calcite. Most of the inclusion consists of fine-grained, irregularly shaped and very spongy pyroxene crystals enclosing smaller spinel and melilite grains. Within this material are irregular, coarser-grained regions in which prismatic melilite and equant anorthite crystals are partially enclosed by large pyroxene crystals, and all phases enclose spinel, as in typical Type B inclusions from Allende.

Allende 3529-42

MASON and TAYLOR (1982) reported petrographic, mineralogical, and trace element data for this inclusion, and MACPHERSON et al. (1986) presented further petrographic and ion microprobe results. The inclusion is composite, one region consisting mostly of spinel, hibonite, and melilite with minor fassaite and secondary anorthite that replaces melilite. This part of the inclusion is little altered. The other region is rich in melilite which is highly altered and replaced by fine-grained secondary alteration products, mostly anorthite. Minor perovskite is present as a primary phase.

Rabbit Irradiation

Sample weighing and packaging, standards used, the irradiation position employed, and irradiation, decay, and counting times used were all exactly the same as in the short INAA irradiation of DAVIS et al. (1982), except that the neutron flux was $8 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$

in the present work. Co-doped Al wires irradiated at the beginning, middle, and end of the sequence of samples and standards indicated a 3.15% variation in neutron flux over the duration of the entire experiment. Accordingly, a flux correction was applied to each sample and standard, by assuming that the flux varied linearly with time. The only elements determined in this irradiation and which were also present in the empty polyethylene pouches are Al and V. Blank corrections were made for both elements in all samples. These corrections were always <3%, except for 1623-S4-12, in which they reached 15–20% of the amounts present. Counting data for spurious standards were used to correct for the interfering fast neutron reactions, $^{27}\text{Al}(n, p)^{27}\text{Mg}$ and $^{28}\text{Si}(n, p)^{28}\text{Al}$. Estimating the SiO_2 content of each sample by difference, corrections for the latter interference were always found to be smaller than the uncertainty in Al_2O_3 concentration due to counting statistics and were ignored. Nuclides used and concentrations of elements determined in the rabbit irradiation are shown in Table 1.

Long Irradiation

The samples were removed from their polyethylene pouches, reweighed, and sealed into 20–40 mg supersilica vials which had been washed in aqua regia. Substantial sample loss is possible at this stage due to adhesion of sample powders to the walls of the polyethylene pouches. A new aliquot of sample 3536-2 was weighed and wrapped in Al foil. New aliquots of SP and BCR-1 were weighed into supersilica vials, as were solutions of four group chemical standards. One of the latter contained La, Pr, Eu, Gd, Tb, Ho, and Yb, and another contained Ce, Nd, Sm, Dy, Er, Tm, and Lu, as in EKAMBARAM *et al.* (1984). The third contained Ni, Pd, Pt, Se, and Zn, as in DAVIS *et al.* (1982), and the fourth, containing Au, Ir, Re, Os, and Ru, was a combination of two separate standard solutions used in that work. Four empty vials were used for blanks. The collection of blank, sample, and standard vials was divided into seven sets of 3–5 vials, each of which was sealed into a larger supersilica tube, along with an additional small vial containing a Co-doped Al wire for monitoring the spatial variation of the neutron flux within the irradiation canister. The Al foil-wrapped sample of 3536-2 was also sealed into one of the larger supersilica tubes. All of the vial sets were irradiated simultaneously at a flux of $3.3 \times 10^{14} \text{ n cm}^{-2} \text{ sec}^{-1}$ for 285 h in the flux trap of the University of Missouri Research Reactor. After irradiation, the individual vials were washed in warm aqua regia and rinsed with distilled water. The Al foil was removed from sample 3536-2 which was then placed inside an inactive supersilica tube for counting. The samples were then counted at least three times at the University of Chicago on either a 7.5% efficiency Ge(Li) or a 37.9% efficiency intrinsic Ge detector: (1) for 1.2 to 12.5 h each, 2.5 to 4 days after irradiation; (2) for 6.4 to 52.5 h each, 10.5 to 28.5 days after irradiation; (3) for 0.9 to 7 days each, 38 to 147 days after irradiation.

Data reduction

Examination of the flux monitors indicated a maximum flux variation of 2.9%. Accordingly, flux corrections were applied to all activities, based on the deviation from the average of the ^{60}Co activity in the Co-doped Al wire in each tube. Lanthanum interference on cerium due to production of ^{141}Ce by double neutron capture on ^{139}La was corrected by counting ^{141}Ce in the Ce-free REE standard. These corrections amounted to 0.8 to 5.7% in all samples. Corrections for Eu interference on ^{153}Sm by double neutron capture on ^{151}Eu were made in a similar fashion and amounted to 2.4 to 16%. Corrections for Yb interference on ^{177}Lu by decay of reactor-produced ^{177}Yb were made as in GROSSMAN *et al.* (1977), amounting to 3 to 37%. Interferences caused by overlap of the photopeak of one nuclide on that of another were corrected for by multiplying the ratio of the integral of the interfering peak to that of a second peak of the same nuclide in the standard by the integral of the second peak in the sample, and subtracting the result from the total counts in the peak of interest in the sample. These corrections amounted to 0 to 14% for ^{182}Ta (84.7 keV) on ^{170}Tm (84.3 keV), 7 to 53% for ^{199}Au (208.2 keV) on ^{177}Lu (208.4 keV), and 0 to 4% for ^{156}Eu (811.6 keV) on ^{58}Co (810.8 keV). Because of large neutron fluences and high cross-

sections for production of ^{152}Eu from ^{151}Eu and of ^{153}Eu from ^{152}Eu , higher neutron fluence led to lower specific activity of ^{152}Eu , the nuclide used for determination of Eu. Thus, for Eu, corrections for neutron flux variations were made using half-lives and cross-sections from WALKER *et al.* (1977). It was found that the specific activity of ^{152}Eu in the samples varied from 7.4% less to 5.5% more than that of the REE standard.

Since all samples except 3536-2 were counted in the same supersilica vials in which they were irradiated, blank corrections were made for the amount of each element of interest present in the supersilica vials themselves. This was done by counting four empty supersilica vials irradiated along with the samples of this study, as well as six other empty vials irradiated in a later experiment. All vials were cut, sealed, and washed in an identical fashion to those used for the samples in this study. The mean and standard deviation of the amount of each element of interest was calculated for the ten empty vials. Blank corrections were in excess of 10% of the amount present for Na in one sample (37%), Hf in one sample (20%), Cs in two samples (maximum 26%), Ce in two samples (maximum 19%), Co in four samples (maximum 61%), and La in four samples (maximum 16%). Blank corrections were applied to all of the data in Table 1, except those for sample 3536-2 for which the blanks are all zero. In Table 1, the uncertainty quoted for each concentration is based only on propagation of 1σ counting statistics errors on all peaks used in the analysis and the standard deviations of the blank corrections.

RESULTS AND DISCUSSION

Major Elements

Because mineralogical and mineral-chemical studies have been conducted on polished thin sections of splits of six of the seven inclusions studied herein, the major element data of this study can be used to determine the relative mineralogical abundances in seven of the samples in Table 1. This is done by solving a system of mass-balance equations for each sample. For each oxide, an equation is written in which the sum of the products of the abundance of each mineral and the concentration of that oxide in it, determined by electron microprobe analysis, is equated to the bulk concentration of that oxide, determined by INAA. Silica is the only major constituent of Ca-, Al-rich inclusions not determined in this work, so computation of SiO_2 by difference is a very good approximation for these eight samples.

For 1623-2, this procedure yields 63% melilite (Ak 12), 19% spinel, 16% hibonite, and 0.84% perovskite, in excellent agreement with petrographic observations. Inclusion 1623-3 contains 3.3% Fe. As no Fe-bearing phases are present in thin section, the Fe may be due to deposition in the inclusion of FeCl_2 formed by reaction of meteorite constituents with atmospheric water. Excluding this Fe, 38% hibonite, 35% melilite (Ak 13), 21% spinel, and 1% perovskite is obtained for 1623-3. Although this sample is somewhat more hibonite-rich than inspection of the whole inclusion would suggest, the thin section shows that this inclusion is extremely heterogeneous and that pockets exist which are much more hibonite-rich than the bulk inclusion. For 3536-1, we obtain 51% pyroxene (CaO—24.5; Al_2O_3 —14.9; TiO_2 —3.4), 35% spinel, 11% melilite, and 2.5% anorthite, which is in good agreement with petrographic observations. In the case of 3536-2, 80% melilite (Ak 43), 9.1% anorthite, 7.3% pyroxene (CaO—24.3; Al_2O_3 —17.3; TiO_2 —7.2), 2.0% spinel, and 1.7% perovskite was obtained, which is in excellent agreement with petrographic observations. For 3537-1, we obtain 40% melilite (Ak 43), 31% spinel, and 27% pyroxene (CaO—24.7; Al_2O_3 —

Table 1. Chemical Compositions of Vigarano, Leoville and Allende Inclusions
(ppm, unless otherwise indicated)

Sample	Description	Mass (μ g)	Mass (μ g)	Na ₂ O	MgO (%)	Al ₂ O ₃ (%)	CaO (%)	Sc	TiO ₂ (%)	V
VIG 1623-2	hib-sp-mel	131.1 ± 0.1	50.9 ± 0.2	418 ± 24	6.64 ± 0.63	46.8 ± 0.3	27.5 ± 0.9	284.4 ± 0.3	1.94 ± 0.07	1100 ± 20
VIG 1623-3	sp-hib-mel	44.9 ± 0.2	43.3 ± 0.1	300 ± 15	6.4 ± 1.2	57.9 ± 0.5	16.8 ± 1.2	109.2 ± 0.2	2.36 ± 0.12	331 ± 14
VIG 1623-S4-12	black clast	20.2 ± 0.2	10.2 ± 0.2	122 ± 50	19.3 ± 1.3	2.31 ± 0.15	<0.98	6.54 ± 0.40	<0.24	68.7 ± 9.4
LEO 3536-1	fine-grained	236.7 ± 0.1	232.4 ± 0.1	250 ± 6	15.7 ± 0.5	37.7 ± 0.2	17.8 ± 0.6	25.80 ± 0.04	1.27 ± 0.04	379 ± 7
LEO 3536-2	compact Type A	13.9 ± 0.2	59.4 ± 0.2	1100 ± 30	5.4 ± 1.1	23.1 ± 0.5	37.9 ± 3.1	158.1 ± 0.2	1.55 ± 0.18	424 ± 24
LEO 3537-1	Type B2	652.1 ± 0.4	478.7 ± 0.2	530 ± 22	13.7 ± 0.3	34.9 ± 0.2	23.4 ± 0.5	13.07 ± 0.02	1.53 ± 0.04	1390 ± 20
ALL 3529-42-W	Type A anorthite-rich	148.3 ± 0.3	90.3 ± 0.2	12400 ± 300	3.96 ± 0.48	38.9 ± 0.3	20.8 ± 0.7	52.75 ± 0.09	0.857 ± 0.053	157 ± 8
ALL 3529-42-O	Type A hibonite-rich	196.1 ± 0.1	194.3 ± 0.1	643 ± 32	10.3 ± 0.7	66.6 ± 0.4	15.2 ± 0.6	46.62 ± 0.05	0.925 ± 0.063	2510 ± 30
Irradiation [†]		1	2	2	1	1	1	2	1	1
Nuclide				²⁴ Na	²⁷ Mg	²⁸ Al	⁴⁹ Ca	⁴⁶ Sc	⁵¹ Ti	⁵² V
Standard				SP	C*	C	C	SP	C	BCR-1
C1 Chondrites (A.M. Davis, pers. comm.)				6626	15.80	1.58	1.26	5.902	.0711	55.65

Sample	Cr	Mn	Fe (%)	Co	Ni	Zn	As	Se	Sr	Zr	Ru
VIG 1623-2	179 ± 7	55.9 ± 4.4	0.650 ± 0.023	<23	<86	<1.9	<0.18	<0.32	98 ± 18	181 ± 24	6.71 ± 0.24
VIG 1623-3	142 ± 8	174 ± 11	3.33 ± 0.03	<17	<46	2760 ± 10	<0.12	<0.086	<20	62 ± 11	7.55 ± 0.25
VIG 1623-S4-12	2580 ± 50	2680 ± 50	23.8 ± 0.2	750 ± 74	16600 ± 300	3480 ± 40	1.42 ± 0.08	10.1 ± 0.2	<24	<32	<0.34
LEO 3536-1	1530 ± 20	31.3 ± 1.9	0.245 ± 0.005	3.6 ± 1.5	127 ± 12	<0.30	0.114 ± 0.030	<0.030	121 ± 3	<6.0	0.097 ± 0.031
LEO 3536-2	69.6 ± 2.2	145 ± 14	0.418 ± 0.003	14.20 ± 0.02	341 ± 5	<0.93	<0.28	25.1 ± 0.1	295 ± 14	<27	2.08 ± 0.19
LEO 3537-1	436 ± 7	5.61 ± 0.50	0.348 ± 0.003	34.4 ± 2.9	727 ± 6	<0.19	<0.031	<0.022	145 ± 3	16.5 ± 1.6	0.699 ± 0.014
ALL 3529-42-W	185 ± 4	175 ± 7	1.60 ± 0.02	9.9 ± 4.1	<62	330 ± 5	<0.30	<0.072	144 ± 6	<12	<0.18
ALL 3529-42-O	286 ± 5	27.2 ± 2.0	0.339 ± 0.006	8.8 ± 2.0	138 ± 15	561 ± 2	<0.099	0.098 ± 0.034	88.7 ± 4.1	<8.2	29.0 ± 0.1
Irradiation	2	1	2	2	2	2	2	2	2	2	2
Nuclide	⁵¹ Cr	⁵⁵ Mn	⁵⁹ Fe	⁶⁰ Co	⁵⁸ Co	⁶⁵ Zn	⁷⁶ As	⁷⁵ Se	⁸⁶ Sr	⁹⁵ Zr	¹⁰³ Ru
Standard	SP	SP	SP	SP	C	C	SP	C	SP	SP	C
C1 Chondrites	2606	1887	18.32	505.2	10830	311.8	1.858	19.71	7.715	3.184	.7131

18.2; TiO₂—5.3). This is a surprising result, as the thin section contains more than 10% anorthite. For this sample, the selected pyroxene composition is based on a limited number of analyses and may not be representative of the average composition of this phase. This may account for the discrepancy.

Sample 3529-42 is an Allende Type A inclusion containing primary spinel, melilite, hibonite, and perovskite and secondary anorthite. By hand-picking an orange (O) and a white (W) fraction from previously crushed material, we hoped to obtain a hibonite-rich and a melilite-rich sample, respectively. Using an average melilite composition of Ak 5 and an average hibonite composition containing 2.9% MgO and 5.5% TiO₂,

we obtained 42% hibonite, 31% spinel, 27% melilite, and 0.22% anorthite for sample O, as expected. Sample W, however, contains 56% anorthite, 22% melilite (Ak 15), 12% spinel, 5.7% nepheline, 1.4% perovskite, and 0.84% hibonite, indicating that it is dominated by secondary alteration products, rather than melilite.

Trace Elements

Vigarano inclusions

REE patterns for both refractory inclusions from Vigarano are shown in Fig. 1. Sample 1623-3 has a group III REE pattern, with most REEs enriched by factors of 21–25 and

Table 1. (Continued)

Sample	Cs	Ba	La	Ce	Sm	Eu	Tb	Dy	Tm	Yb	Lu
VIG 1623-2	<0.014	<63	6.63 ±0.81	7.28 ±0.44	3.99 ±0.13	1.20 ±0.04	0.608 ±0.017	6.19 ±0.37	0.455 ±0.025	3.31 ±0.11	0.489 ±0.027
VIG 1623-3	<0.017	78 ±25	5.26 ±0.90	13.0 ±0.3	3.61 ±0.06	0.930 ±0.019	0.832 ±0.018	5.95 ±0.61	0.511 ±0.015	2.36 ±0.04	0.527 ±0.016
VIG 1623-S4-12	<0.045	7530 ±140	n.d. [†]	n.d.	<0.36	0.120 ±0.047	<0.050	<1.5	<0.061	0.305 ±0.019	0.0748 ±0.0057
LEO 3536-1	0.0303 ±0.0019	24.1 ±6.6	8.08 ±0.18	21.3 ±0.1	4.59 ±0.01	0.972 ±0.006	0.660 ±0.006	3.46 ±0.15	0.757 ±0.004	1.56 ±0.02	0.0224 ±0.0041
LEO 3536-2	<0.016	<43	3.18 ±0.03	6.02 ±0.15	2.317 ±0.009	1.87 ±0.02	0.835 ±0.014	n.d.	0.383 ±0.013	2.89 ±0.05	0.218 ±0.014
LEO 3537-1	0.0243 ±0.0017	39.4 ±2.0	0.534 ±0.086	4.07 ±0.03	0.760 ±0.007	0.980 ±0.006	0.0890 ±0.0017	0.744 ±0.040	0.351 ±0.003	2.94 ±0.01	0.168 ±0.003
ALL 3529-42-W	0.0318 ±0.0043	<27	6.57 ±0.46	15.7 ±0.2	4.49 ±0.03	0.785 ±0.009	1.10 ±0.01	8.43 ±0.37	0.704 ±0.008	2.45 ±0.03	0.706 ±0.013
ALL 3529-42-O	0.0120 ±0.0037	129 ±12	2.30 ±0.22	5.44 ±0.19	1.69 ±0.05	0.487 ±0.009	0.384 ±0.006	2.76 ±0.14	0.267 ±0.009	1.25 ±0.04	0.0673 ±0.0098
Irradiation	2	2	2	2	2	2	2	1	2	2	2
Nuclide	¹³⁴ Cs	¹³¹ Ba	¹⁴⁰ La	¹⁴¹ Ce	¹⁵³ Sm	¹⁵² Eu	¹⁶⁰ Tb	¹⁶⁵ Dy	¹⁷⁰ Tm	¹⁷⁵ Yb	¹⁷⁷ Lu
Standard	SP	SP	C	C	C	C	C	SP	C	C	C
C1 Chondrites	.1836	2.299	.2349	.6035	.1472	.05603	.03539	.2428	.02484	.1626	.02433

Sample	Hf	Ta	Re	Os	Ir	Au (ppb)	Th
VIG 1623-2	4.84 ±0.09	<0.090	0.301 ±0.022	4.60 ±0.15	4.561 ±0.003	<5.4	<0.15
VIG 1623-3	2.16 ±0.07	0.213 ±0.014	0.461 ±0.017	13.4 ±0.2	4.664 ±0.003	<8.0	<0.14
VIG 1623-S4-12	<0.15	0.208 ±0.040	<0.016	0.512 ±0.033	0.399 ±0.001	151 ±10	0.228 ±0.021
LEO 3536-1	0.037 ±0.012	0.443 ±0.006	0.0063 ±0.0027	0.119 ±0.019	0.0761 ±0.0002	<1.3	0.605 ±0.025
LEO 3536-2	2.01 ±0.05	0.062 ±0.015	0.109 ±0.009	1.85 ±0.11	0.982 ±0.001	35.2 ±2.7	<0.22
LEO 3537-1	0.432 ±0.007	0.408 ±0.005	0.0338 ±0.0023	0.221 ±0.005	0.2573 ±0.0002	<0.70	0.0469 ±0.0027
ALL 3529-42-W	0.560 ±0.033	0.168 ±0.010	0.0369 ±0.0098	0.220 ±0.032	0.0655 ±0.0005	<4.4	0.196 ±0.046
ALL 3529-42-O	0.975 ±0.020	0.119 ±0.008	1.42 ±0.05	19.4 ±0.5	17.02 ±0.01	8.2 ±1.1	<0.046
Irradiation	2	2	2	2	2	2	2
Nuclide	¹⁸¹ Hf	¹⁸² Ta	¹⁸⁶ Re	¹⁹¹ Os	¹⁹² Ir	¹⁹⁸ Au	²³³ Pa
Standard	SP	SP	C	C	C	C	SP
C1 Chondrites	.1023	.01380	.03680	.5017	.4675	.1484	.02930

† Elements determined in the rabbit irradiation are designated by 1; in the long irradiation by 2.

* C denotes use of a chemical standard.

[†] n.d. — not determined

Eu and Yb enriched by factors of only 17 and 15, respectively, relative to C1 chondrites. This is in apparent conflict with the suggestion of DAVIS et al. (1987) that this inclusion has a group I REE pattern. That assessment, however, was based on only three ion microprobe analyses of perovskite, all of which have large negative Eu anomalies and small kinks at

Yb, and one of hibonite, which has a large negative Eu anomaly and very large errors for the heavy REEs. A group III REE pattern for the bulk inclusion is not necessarily inconsistent with these data, particularly considering the complexity of this inclusion, the small number of ion probe analyses of perovskite and hibonite, and the absence of such anal-

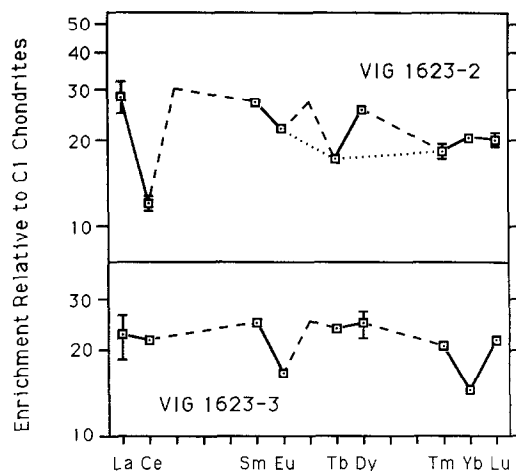


FIG. 1. REE patterns for two hibonite-, melilite-rich refractory inclusions from Vigarano. Error bars (1σ) are shown when they are larger than the data points. See text for different possibilities for the REE pattern of 1623-2.

yses for other potential REE host phases such as melilite and CaAl_2O_7 . Because Eu and Yb are the two most volatile REEs, group III patterns are thought to be due either to total condensation of most REEs at a high enough temperature that Eu and Yb were only partially condensed or to selective volatilization of Eu and Yb from a precursor with uniform enrichments of all REEs. Enrichment factors relative to C1 chondrites for Hf, Zr, Sc, and Ta, refractory lithophile elements with comparable volatilities to those of the REEs, lie between those of Yb and the other REEs, while those of slightly less refractory V and Sr are 6.0 and <2.6 , respectively, less than those of Eu and Yb. Relative abundances of refractory lithophile elements in 1623-3 are very similar to those seen in Allende group III inclusions (CONARD, 1976; MASON and TAYLOR, 1982).

Among refractory siderophiles, Ru, Re, and Ir are relatively unfractionated from one another, with enrichment factors of 10 to 12.5 relative to C1 chondrites, but Os has a much higher enrichment factor than these, 26.7 ± 0.4 . In thermodynamic calculations of the condensation of refractory siderophiles from the solar nebula into a common alloy (SYLVESTER et al., 1989), Re is slightly more refractory than Os, and both of these are much more refractory than Ir and Ru. Thus, at the temperature of initial condensation of the alloy, ~ 2050 K at 10^{-3} atm total pressure, the C1 chondrite-normalized Os/Re, Ir/Re, and Ru/Re ratios are 0.64, 8.7×10^{-4} , and 2.0×10^{-4} , respectively. As the alloy equilibrates its composition with the gas as the temperature falls, all three ratios gradually approach 1, with Os/Re reaching this value first, Ir/Re second, and Ru/Re last. The problem with 1623-3 is the Os abundance. The relatively unfractionated proportions of Ru, Re, and Ir in 1623-3 imply total condensation of all three elements. This occurs at a temperature at which Os is also totally condensed, which should result in, for example, an Os/Re ratio of 1 relative to C1 chondrites, rather than the observed value of 2.13 ± 0.08 . The siderophile element abundances in 1623-3 can be considered a mixture of a component in which all refractory siderophiles condensed totally and a component consisting of pure Os, although how the latter

component could have formed in the absence of Re, an element with very similar volatility, is not known. FEGLEY and PALME (1985) have explained depletions in W and Mo relative to other refractory siderophiles in some inclusions relative to C1 chondrites by condensation under oxidizing conditions, a process which makes W and Mo more volatile than the others. Although it might be tempting to explain the high Os/Re ratio in 1623-3 in terms of a similar Re depletion due to its enhanced volatility under even more oxidizing conditions, it is uncertain which of Re or Os would be made more volatile, and the similarity of enrichment factors between Re on the one hand and Ru and Ir on the other would have to be regarded as coincidence.

Although Os/Re fractionations comparable to those seen in 1623-3 have been reported from individual metal nuggets in Allende inclusions by WARK (1986) and PAQUE (1989), Re, Ir, and Ru in these nuggets are not all in chondritic proportion to one another, as they are in 1623-3. Furthermore, except for the FUN inclusion TE where the Os/Re ratio is 1.6 (FEGLEY and PALME, 1985), ratios comparable to that in 1623-3 have not been found in the bulk composition of any other coarse-grained inclusion from Allende. For example, in the suite of inclusions studied by GROSSMAN and GANAPATHY (1976a,b) and GROSSMAN et al. (1977), the entire range of C1 chondrite-normalized Os/Re ratios is only 0.91–1.10. Despite the unusual oxygen isotopic composition of this spinel-rich inclusion compared to spinel-rich samples from Allende refractory inclusions (CLAYTON et al., 1987), 1623-3 has no other refractory element differences from the latter.

Only two volatile elements, Fe and Zn, are present in 1623-3 at levels in excess of 10% of their C1 chondrite concentrations. As mentioned above, there is evidence for mobilization of Fe and deposition of FeCl_2 in refractory inclusions due to interaction of atmospheric water vapor with Vigarano in the laboratory. The enhanced level of Fe, and possibly also Zn, in 1623-3 may be due to this effect. All other non-refractory elements, including Na, have concentrations at the low ends of their concentration ranges in Allende coarse-grained inclusions (EKAMBARAM et al., 1984). BISCHOFF et al. (1987) noted that coarse-grained inclusions which they studied from Leoville, Arch, and Efremovka, members of the reduced subgroup of C3V chondrites, are lower in both Na and Au than those from Allende and Grosnaja, members of the oxidized subgroup. Their data are shown in Fig. 2, in which we have also plotted data from this laboratory. Our values include both published and unpublished data from Allende coarse-grained inclusions, the former taken from GROSSMAN and GANAPATHY (1975, 1976a), DAVIS et al. (1978), and CLAYTON et al. (1984), as well as data from the Vigarano and Leoville inclusions studied herein. On this figure, 1623-3 plots among the most volatile-poor, coarse-grained inclusions in C3V meteorites, those from other members of the reduced subgroup, Leoville, Efremovka, and Arch. Like Vigarano inclusion VI-1 (WARK et al., 1988), 1623-3 has suffered less volatile element contamination due to secondary alteration than most Allende coarse-grained inclusions, but it is not free of such effects.

In 1623-2, most LREEs are enriched by factors of 28–30 and HREEs by 18–20 relative to C1 chondrites. This sample has a large negative Ce anomaly ($\text{La/Ce} = 2.34 \pm 0.32$ relative

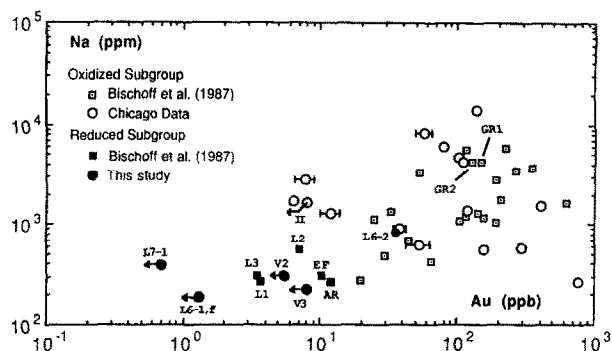


FIG. 2. Sodium and gold concentrations are higher in coarse-grained inclusions from the oxidized subgroup of C3V chondrites than from the reduced subgroup. All inclusions in the oxidized subgroup are from Allende, except two which are from Grosnaja and labelled GR. In the reduced subgroup, inclusions are from Arch (AR), Efremovka (EF), Leoville (L), and Vigarano (V). Inclusions from the present study are: Vigarano 1623-2—V2; 1623-3—V3; Leoville 3536-1—L6-1; 3536-2—L6-2; 3537-1—L7-1. f indicates fine-grained inclusion.

to C1 chondrites) but no Yb anomaly ($\text{Yb/Lu} = 1.01 \pm 0.07$ relative to C1 chondrites). Dy is the only REE determined along with the major elements in the rabbit irradiation. Over 60% of the sample of 1623-2 analyzed in that irradiation was lost during transfer to a silica tube prior to the long irradiation in which all other REEs were determined. The unusual enrichment of Dy over Tb and other HREEs in the pattern in Fig. 1 could have resulted from preferential loss between irradiations of phases enriched in Dy relative to the remaining material. If so, the enrichment factor for Dy might be as low as those of the other HREEs in the sample whose REEs were measured in the long irradiation, and the drop from Sm to Eu might simply be part of a gradual decline in enrichment factor from light to heavy REE, rather than a negative Eu anomaly. This possibility is indicated by the dotted curve in Fig. 1. If the lost phases were HREE-enriched relative to the remainder, the bulk inclusion may be less HREE-depleted than the sample analyzed here. Except for the large Ce anomaly, the bulk REE pattern of 1623-2 is probably a flat or gently sloping group I pattern. Group I REE patterns signify condensation at a low enough temperature that each REE was totally condensed. Enrichment factors for Sc, Zr, and Hf are ~ 50 , for V ~ 20 , and for Sr ~ 13 in 1623-2 relative to C1 chondrites. Refractory siderophiles are unfractionated relative to one another, with C1 chondrite-normalized enrichment factors for Ru, Re, Os, and Ir being 9.41 ± 0.34 , 8.18 ± 0.60 , 9.17 ± 0.30 , and 9.76 ± 0.01 , respectively.

Ce anomalies of the size seen here may be caused by the volatility of Ce^{3+} relative to most of the other trivalent REEs under normal solar nebular reducing conditions (HINTON et al., 1988) or by the volatility of Ce^{4+} relative to trivalent REEs under much more oxidizing conditions (BOYNTON and CUNNINGHAM, 1981; DAVIS et al., 1982). Clues to whether the Ce anomaly in 1623-2 is due to formation from a reducing or oxidizing gas are provided by the abundances of V, Ir, and Ru. Thermodynamic calculations (BOYNTON and CUNNINGHAM, 1981; DAVIS et al., 1982) show that V is more volatile than Ce in a solar gas and becomes even more volatile than Ce in an oxidizing gas. Ir and Ru are comparable in volatility to Ce in a solar gas and become slightly less volatile

than Ce relative to La in an oxidizing gas (DAVIS et al., 1982). Hibonite grains in Allende inclusion HAL and in a refractory inclusion in Dhajala have such large Ce anomalies that they must have formed under oxidizing conditions. HINTON et al. (1988) showed that the La/Ce ratios of HAL and Dhajala hibonite are 543 ± 122 and 1770 ± 770 , respectively, relative to C1 chondrites, and that V is more depleted than Ce in each, the C1 chondrite-normalized La/V ratios being $>7 \times 10^3$ and $>5 \times 10^4$, respectively, as expected from thermodynamic calculations. DAVIS et al. (1982) showed that, like Ce, Ir is depleted in HAL hibonite crystal fragments, the lowest La/Ir ratio being 9.2 relative to C1 chondrites, also as expected from thermodynamic calculations. Because each of V, Ir, and Ru is often depleted relative to La in normal Allende coarse-grained inclusions without Ce anomalies, however, these depletions are necessary, but not sufficient, conditions for formation under oxidizing conditions. In 1623-2, the C1 chondrite-normalized ratios of La/V and La/Ir are 1.43 ± 0.18 and 2.89 ± 0.35 , respectively. Because the La/V ratio is smaller than the La/Ce ratio and because Ir is not strongly depleted, there is no compelling reason to attribute the relatively small Ce anomaly in 1623-2 to formation under oxidizing conditions. Rather, it may be due to condensation under normal solar nebular reducing conditions at a high enough temperature that Ce had not fully condensed because of its greater volatility than other trivalent REEs. As Eu and Yb are more volatile than Ce under these conditions (BOYNTON, 1975; DAVIS et al., 1982), however, 1623-2 would be expected to exhibit negative Eu and Yb anomalies that are even larger than the Ce anomaly. This is certainly not the case. A possible solution to this dilemma is suggested by the evidence for nonrepresentative sampling alluded to above. Because of the latter, we cannot exclude the possibility that, as in the case of Allende inclusion C1 (HUTCHEON et al., 1989), internal redistribution of Ce occurred under oxidizing conditions after formation in a solar gas and that we have preferentially sampled those phases depleted in Ce. Inclusion C1 is the only Allende inclusion known to show this feature. Regardless of their origin, Ce anomalies of this size are very rare in Allende coarse-grained inclusions. There is a hint of a negative Ce anomaly in another group I Vigarano inclusion, VI-1 (WARK et al., 1988). The oxygen isotopic composition of 1623-2 is similar to those of refractory inclusions from Allende (CLAYTON et al., 1987).

The concentrations of the more volatile elements such as Na, Fe, Mn, and Cr in 1623-2 are all at the low ends of their concentration ranges in Allende coarse-grained inclusions (EKAMBARAM et al., 1984). As is the case for 1623-3, this inclusion also plots with the very volatile-poor, coarse-grained inclusions from the reduced subgroup of C3V chondrites on Fig. 2.

The dark clast 1623-S4-12 has a similar chemical composition to dark clasts from Allende that have been analyzed by CLARKE et al. (1970), GROSSMAN et al. (1976a,b), and BISCHOFF et al. (1988). Among refractory lithophiles, the concentrations of Al, Sc, and V in the Vigarano dark clast are within their ranges in Allende dark clasts, but Ca is substantially lower and Eu, Yb, and Lu 10 to 50% higher in the former than in the latter. Barium is so much more enhanced than other refractory lithophiles in 1623-S4-12 compared to Allende dark clasts that it is probably due to laboratory con-

tamination. Among non-refractory lithophiles, Mg and Cr contents are similar to values seen in Allende dark clasts, but Mn is 15% higher than the highest value seen in Allende, Fe is 7% lower than the lowest in Allende, and, most notably, Na is a factor of 5 lower than the lowest value seen in any dark clast from Allende. Most siderophile and chalcophile element contents are within the ranges seen in Allende dark clasts, although Zn is so much higher in the Vigarano clast that it is also thought to be due to contamination.

The Vigarano dark clast has a different oxygen isotopic composition from similar clasts in Allende (CLAYTON et al., 1987), suggesting that the dark clast in Vigarano had a different nebular formation site from those in Allende. Both refractory inclusions and the dark clast in Vigarano are poorer in Na than their counterparts in Allende. Refractory inclusions in Allende obtained their high Na concentrations in relatively low temperature, secondary alteration reactions with the solar nebular gas (ALLEN et al., 1978). The relatively low Na concentrations in refractory inclusions in Vigarano reflect their secondary alteration under different physico-chemical conditions from those in Allende, suggesting that the refractory inclusions accreted by Vigarano were altered in a different nebular region from those accreted by Allende. BISCHOFF et al. (1988) reported the presence of refractory inclusions in Allende dark clasts. If refractory inclusions are significant contributors to the Na contents of dark clasts in C3V chondrites, the refractory inclusions accreted by dark clasts in Vigarano are lower in Na than those accreted by dark clasts in Allende. It thus appears that dark clasts in Vigarano sampled similarly altered refractory inclusions as Vigarano itself and that these were less extremely altered than those sampled by both Allende and its dark clasts. The dark clasts within a meteorite probably accreted in the same nebular region as their host.

Leoville inclusions

REE patterns for all three Leoville inclusions are shown in Fig. 3. Sample 3536-1, a fine-grained inclusion, has the typical group II REE pattern found in many Allende inclusions. After removal of the most refractory REEs (the heavy ones except Tm and Yb) in an early, high-temperature condensate or residue, such REE patterns form by condensation of the remaining REEs at a high enough temperature that Eu and Yb, the two most volatile REEs, fail to condense fully (BOYNTON, 1975). The abundances of all refractory lithophile elements in 3536-1 are typical of Allende inclusions with such REE patterns; i.e., Ta is enriched to the level of the LREEs, Th is enriched to ~ 0.6 times the level of the LREEs, Sr is enriched by a similar factor to Eu, Ba is slightly less enriched than Sr and Eu, Sc has enrichment factors between 2 and 9, and Zr and Hf have enrichment factors of ~ 1 relative to C1 chondrites (CONARD, 1976; GROSSMAN and GANAPATHY, 1976b; MASON and TAYLOR, 1982; and unpubl. data from this laboratory). Similarly, as is typical of most group II inclusions from Allende, 3536-1 is depleted in all refractory siderophiles relative to C1 chondrites. Data have been reported for only one other group II inclusion from Leoville, Leo-3 (PALME et al., 1987). It differs from 3536-1 in being coarse-grained and in having refractory siderophile enrichment factors of ~ 6 .

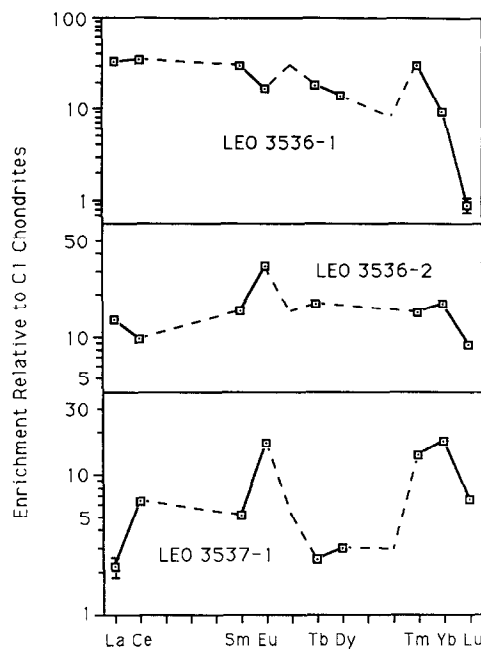


FIG. 3. REE patterns for three refractory inclusions from Leoville: 3536-1 is fine-grained; 3536-2 is a compact Type A; and 3537-1 is a Type B2. Error bars as in Fig. 1.

The similarities in refractory elements serve to make the differences in volatile element contents between 3536-1 and Allende group II inclusions all the more striking. The Na_2O content of 3536-1 is 100 times smaller than that typical of Allende fine-grained group II inclusions (GROSSMAN and GANAPATHY, 1975) and 10 times smaller than in a coarse-grained group II inclusion, sample 5 of GROSSMAN and GANAPATHY (1975). Manganese is 10 times lower than in fine-grained group II inclusions and comparable in abundance to the coarse-grained group II (GROSSMAN and GANAPATHY, 1975). Iron is 20 times lower than in fine-grained group II inclusions (GROSSMAN and GANAPATHY, 1976b) and 5 times lower than in the coarse-grained group II (GROSSMAN and GANAPATHY, 1976a). In 3536-1, Zn is lower than in fine-grained group II inclusions by a factor $> \sim 3000$ (CONARD, 1976; GROSSMAN and GANAPATHY, 1976b) and lower than in the coarse-grained group II by a factor > 1000 (GROSSMAN et al., 1977). The low volatile element content of 3536-1 may be related to the low concentrations of volatiles in coarse-grained inclusions in Leoville, Vigarano, and other members of the reduced subgroup of C3V chondrites. In Fig. 2, the Na content of 3536-1 falls below every coarse-grained inclusion plotted, even though, as a fine-grained inclusion, it would be expected to be 10 times higher in Na than the average coarse-grained inclusion (GROSSMAN and GANAPATHY, 1975). Although fine-grained inclusions are more intensely altered than coarse-grained ones, both are thought to have obtained their volatiles in the same sort of relatively low temperature, secondary alteration reactions with the solar nebular gas (MCGUIRE and HASHIMOTO, 1989). Apparently, both coarse- and fine-grained inclusions sampled by the reduced subgroup of C3V chondrites were altered under conditions which introduced smaller amounts of volatile elements than in the case of their counterparts in Allende, a member of the

oxidized subgroup. This implies that Leoville, in particular, sampled refractory inclusions that were altered in a different part of the solar nebula from those in Allende, as suggested for coarse-grained inclusions by WLOTZKA and WARK (1982), and that the reduced subgroup, in general, sampled refractory inclusions that were altered in a different part of the solar nebula from those in the oxidized subgroup, as suggested for coarse-grained inclusions by PALME *et al.* (1987).

Sample 3536-2 has a group I REE pattern with enrichment factors relative to C1 chondrites which increase slightly from 10–13 for La and Ce to 16–18 for Sm and HREEs. There is a slight downturn to Lu, having an enrichment factor of only 9.0 ± 0.6 , and a positive Eu anomaly (C1 chondrite-normalized $\text{Eu/Sm} = 2.12 \pm 0.02$). Some of these deviations from a flat pattern may be due to a slight degree of nonrepresentative sampling of phases which have different REE patterns from one another due to igneous partitioning. Other refractory lithophiles exhibit a wide range of enrichment factors, from a high value of 38 ± 2 for Sr to a low one of 4.5 ± 1.1 for Ta. Refractory siderophile elements are less enriched than the lithophiles and are slightly fractionated from one another, enrichment factors relative to C1 chondrites being 2.10 ± 0.01 for Ir, 2.92 ± 0.27 for Ru, 2.96 ± 0.24 for Re, and 3.69 ± 0.22 for Os.

Among Vigarano and Leoville inclusions, 3536-2 has unusually high volatile element contents. For example, on Fig. 2, this inclusion plots far above the field populated by other refractory inclusions from the reduced subgroup and well within the field occupied by Allende coarse-grained inclusions. There may simply be an overlap between the ranges of volatile element concentrations in refractory inclusions from the two subgroups such that inclusions with the highest volatile contents in the reduced subgroup have the same concentrations as those with the lowest volatile contents in the oxidized subgroup. Alternatively, this particular inclusion may owe its enhanced volatile element content to terrestrial contamination which left its imprint in the form of hematite-filled cracks, although 3536-1 is similarly veined yet very low in volatiles.

Sample 3537-1 is very unusual. It appears to have a modified group II REE pattern. The group II character is indicated by the greater enrichment factors for the LREEs Ce, 6.7, and Sm, 5.2, than the HREEs Tb, 2.5, and Dy, 3.1, relative to C1 chondrites, and by the large positive anomaly for Tm, whose enrichment factor is 14.1. The REE pattern of 3537-1, however, is different from most group II patterns in Allende inclusions in three ways. First, it has large positive, rather than negative, Eu and Yb anomalies. Second, La is substantially depleted relative to Ce, the C1 chondrite-normalized La/Ce ratio being 0.34 ± 0.05 . Third, the LREE enrichment factors are 5–10 times smaller than usual. Some of the other trace element features of 3537-1 are characteristic of Allende inclusions with normal group II REE patterns. These include low enrichment factors (≤ 5) for Sc, Zr, Hf, and Th, a large enrichment factor for Ta (30), and enrichment factors for refractory siderophiles which are <1 . Compared to the only other group II inclusions known from Leoville, 3537-1 has refractory siderophile element concentrations intermediate between the low values found in 3536-1 and the high ones in Leo-3 (PALME *et al.*, 1987). This inclusion also has trace element features which are uncharacteristic of most Allende

group II inclusions. Three elements which, along with Eu and Yb, are among the most volatile of those commonly considered refractory lithophiles have enrichment factors comparable to those of Eu and Yb and are therefore more enriched than the LREEs. These are V, Sr, and Ba whose enrichment factors are 25.0, 18.8, and 17.1, respectively.

Only one Allende inclusion is known to have such a REE pattern, A-2 of CONARD (1976). In it, Ce is also enriched over La, but only by 30% relative to C1 chondrites, rather than the factor of three seen in 3537-1. As in 3537-1, Sc and Hf are depleted and Ta enriched in A-2 relative to LREEs compared to C1 chondrites. In inclusion A-2, Sr and Ba enrichment accompany the positive Eu and Yb anomalies as in 3537-1, but, unlike 3537-1, V is not enriched relative to LREEs. Similar REE patterns were obtained by ion microprobe for two hibonite-bearing microspherules in the unique chondrite ALH85085 (MACPHERSON *et al.*, 1989) and for one hibonite and three perovskite grains in Murchison (IRELAND *et al.*, 1988). In the latter, all of the hibonite and perovskite grains are depleted in La compared to Ce relative to C1 chondrites, have large positive Yb anomalies, and are less enriched in Sc, Zr, and Hf than the LREEs, as in 3537-1. The hibonite grain is enriched in Eu, Ba, Sr, and V relative to LREEs compared to C1 chondrites, also as in 3537-1, but the perovskite grains are not. Exact equivalence between the REE pattern in a whole inclusion such as 3537-1 and those in individual mineral grains is not expected, as the latter are parts of assemblages within which REE partitioning occurred between the different phases, while the former represents an entire assemblage. Nevertheless, the similarity in relative abundances is clear.

As outlined by MACPHERSON *et al.* (1989), these modified group II patterns form by removal of the early, refractory condensate or residue after it equilibrates with the nebular gas at a lower temperature than in the case of most Allende group II inclusions. At this temperature, not only are the extremely refractory HREEs such as Ho, Er, and Lu removed but so also are portions of the moderately refractory LREEs. Because La is more refractory than Ce under reducing conditions, more La than Ce is removed with the early condensate in this case, and the remaining REEs which condense to yield the group II pattern are depleted in La relative to Ce compared to C1 chondrites. The second difference between formation of the group II pattern of 3537-1 and most Allende group II patterns is that the final condensation stage also occurred at a lower temperature in the former than in the latter. At this temperature, the most volatile of the refractory lithophiles, Eu, Yb, Sr, Ba, and V, are nearly fully condensed and, because some of the LREEs were removed earlier, have greater enrichment factors than the LREEs. Because Sc, Zr, Hf, and Th are similar in volatility to the refractory HREEs (DAVIS *et al.*, 1982), larger fractions of them than of LREEs were removed in the early condensate, and they are thus less enriched than the LREEs. Because Ta is less refractory than LREEs, a smaller fraction of it is removed in the early condensate, and it is thus more enriched than the LREEs.

The concentrations of the volatiles, Na_2O , Mn, Cr, Fe, and Au in 3537-1 are at the low ends of the concentration ranges for these elements in Allende coarse-grained inclusions. In fact, the Mn content is the lowest ever measured by this laboratory in a coarse-grained inclusion. In Fig. 2, the Na content

of 3537-1 lies at the high end of the range of those for coarse-grained inclusions from the reduced subgroup of C3V chondrites and the low end of the range of those from Allende. The Au content, however, is the lowest of all of those on the diagram and in this study.

Allende inclusion 3529-42

REE patterns for the two fractions collected from the powder of this inclusion are shown in Fig. 4. The white fraction, sample W, of this inclusion has a typical group III REE pattern, with most REEs enriched by a factor of 25–30 relative to C1 chondrites, while Eu and Yb are only enriched by factors of 14 and 15, respectively. Enrichment factors for V, Sr, and Ba are less than those of most REEs, as in other group III inclusions, but, unlike the latter, enrichment factors for Sc, Ta, Th, Zr, Hf, and refractory siderophiles in sample W are also lower than those of LREEs. These differences may be due in part to the secondary alteration process which gave rise to much of the material in this sample and which is also indicated by the relatively high concentrations of Fe, 1.6%, and Na₂O, 1.24%. The REE pattern of the orange fraction, sample O, is very similar to that of the bulk sample reported by MASON and TAYLOR (1982). It mimics that of sample W, except that the former is displaced to lower enrichment factors, 9–11, and Lu is substantially less enriched than Yb, rather than more. The latter feature reflects the crystal chemical preference of light over heavy REEs by the structure of hibonite, which is a major constituent of this sample. Enrichment factors for some of the other refractory lithophiles, Sc, Sr, Ta, and Hf, are comparable to those of the REEs, while those of Zr and Th are significantly lower and those of Ba and V are much higher, 56 and 45, respectively, relative to C1 chondrites. Refractory siderophiles are much higher in the hibonite-rich separate than in the anorthite-rich one, and they are unfractionated relative to one another, all having enrichment factors of 36–40 compared to C1 chondrites. The amount of secondary alteration products present in sample O is much less than in sample W, as can be seen from the much lower contents of Na₂O, 643 ppm, and Fe, 0.34%, in the former.

The two refractory inclusions from Vigarano studied in this work are rich in hibonite and melilite, and poor in Na-bearing secondary alteration products. Melilite-rich inclusions

so rich in hibonite and poor in alteration products are rare in Allende. One such object is the hibonite-rich part of Allende inclusion 3529-42. This inclusion was interpreted by MACPHERSON et al. (1986) as composite, the hibonite-rich part having crystallized from a melt and the melilite-rich part having undergone solid-state recrystallization. The hibonite-rich part is relatively little altered but the melilite-rich part is heavily altered. By analyzing the hibonite- and melilite-rich parts of 3529-42 separately, we hoped to constrain the genetic relationships between them and possibly between Vigarano and Allende inclusions. The high proportion of secondary phases in sample W and of hibonite in sample O indicate that W and O come from the melilite- and hibonite-rich parts of the inclusion, respectively. Here we assume that the REE pattern of alteration product-rich sample W represents that of the primary melilite which the alteration products have replaced, plus that of primary perovskite. The REE pattern of sample O is not simply a mixture of the REE patterns found by ion microprobe in individual hibonite grains in the hibonite-rich part of this inclusion (MACPHERSON et al., 1986), as sample O is more enriched in Tm than these. Rather, sample O must also contain a phase more enriched in heavy relative to light REE than the hibonite. This would also account for the fact that Lu is the only REE in sample O, other than Eu and Yb, whose enrichment factor is less than those of the LREEs, even though progressive decrease of REE enrichment factor with increasing atomic number in hibonite normally begins at Tb (HINTON et al., 1988). Both parts of 3529-42, represented by samples O and W, formed by nearly total condensation of all REEs except Eu and Yb from a chondritic reservoir into an assemblage of hibonite, melilite, spinel, perovskite, and an unknown, HREE-enriched, probably minor phase. Similar Mg isotopic fractionations (MACPHERSON et al., 1986) suggest that the two assemblages also formed from the same Mg isotopic reservoir. In one region of this nebular reservoir, the melilite-rich part of 3529-42 formed by accretion of these phases in the proportions in which they condensed. In another region, the hibonite-rich part formed by preferential sampling of hibonite relative to melilite, perovskite, and the HREE-enriched phase. After initial condensation and before consolidation into a single inclusion, the two assemblages underwent different thermal and secondary alteration histories, resulting in melting of the hibonite-rich one and recrystallization and more extensive alteration of the melilite-rich one, as discussed by MACPHERSON et al. (1986). In an analogous way, the refractory inclusions from Vigarano studied herein may have accumulated from condensates preferentially enriched in hibonite compared to the precursors of most refractory inclusions in Allende. As hibonite is the highest-temperature condensate phase in these inclusions, it could have concentrated in specific locations by various grain-gas fractionation processes, such as gravitational settling or transport in convection cells, before any of the other phases condensed.

CONCLUSION

Despite the fact that the two refractory inclusions from Vigarano are unusually hibonite-rich compared to their counterparts in Allende and that refractory inclusions from Leoville (CLAYTON et al., 1986) and those from Vigarano probably plot on separate oxygen isotope mixing lines from

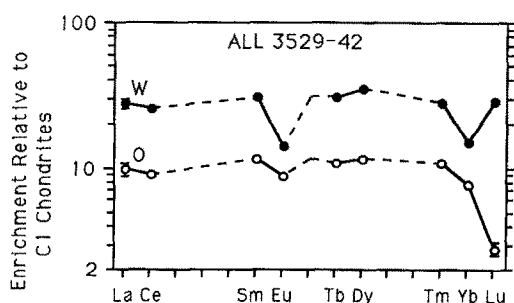


FIG. 4. REE patterns for two fractions removed from the powder of Allende Type A inclusion 3529-42. Sample O is an orange fraction from the hibonite-rich part of this inclusion; sample W is a white fraction rich in alteration products from the melilite-rich part. Error bars as in Figs. 1 and 2.

their counterparts in Allende, no refractory element fractionation patterns are present in these inclusions which are completely different from those seen previously in refractory inclusions in Allende. Nevertheless, Vigarano 1623-2 has a negative Ce anomaly, Vigarano 1623-3 is significantly enriched in Os relative to other refractory siderophiles compared to C1 chondrites, and Leoville 3537-1 has a modified group II REE pattern produced by prior removal of refractory REEs and subsequent condensation of remaining REEs at unusually low temperatures. Each of these trace element characteristics is rare in Allende inclusions, yet, in this small sampling, both refractory inclusions from Vigarano and two out of three of those from Leoville have some unusual trace element feature. On the basis of these primary refractory element characteristics, it thus appears that the population of refractory inclusions in Allende may not be particularly representative of all those that formed in the solar nebula or even those that accreted into C3V chondrites. In particular, refractory inclusions sampled by one C3V chondrite may have formed in a variety of nebular regions where physico-chemical conditions were slightly different from those in the regions where the refractory inclusions in another C3V chondrite formed. Just such a model has been proposed for the C3V chondrites Kaba, Mokoia, and Allende by LIU and SCHMITT (1988) on the basis of REE patterns in refractory inclusions from these meteorites. It is thus likely that searches for refractory inclusions that record previously undiscovered nebular fractionations will be more successful if conducted in Vigarano and Leoville than in Allende.

Two out of the three refractory inclusions from Leoville and both of those from Vigarano studied herein have lower Na and Au contents than coarse-grained inclusions from Allende, confirming the BISCHOFF et al. (1987) observation for Leoville and extending it to Vigarano, an additional member of the reduced subgroup of C3V meteorites. This is entirely consistent with the much lower amounts of secondary alteration products in general and Na-bearing ones in particular in refractory inclusions from Leoville and Vigarano than in those from Allende, as seen petrographically. Our work shows that the concentrations of all volatile elements in refractory inclusions in the former two meteorites tend to be either below or at the low end of their concentration ranges in Allende coarse-grained inclusions. Since most volatiles were introduced into refractory inclusions during secondary alteration, the lower concentrations of these elements in refractory inclusions in the reduced subgroup compared to those in Allende are probably due to the fact that the former were altered in parts of the solar nebula where grain-gas separation processes removed the inclusions from chemical communication with the gas at a higher temperature or after a shorter time than in the case of inclusions from Allende and other members of the oxidized subgroup.

The hibonite- and melilite-rich parts of Allende inclusion 3529-42 could have formed in separate parts of the same chemical and isotopic reservoir by fractionation of early condensing hibonite from lower temperature melilite. In an analogous way, the relatively hibonite-rich Vigarano inclusions studied herein may have accumulated originally from condensates preferentially enriched in hibonite via a grain-gas separation process such as gravitational settling or transport in a convection cell.

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