Chemical compositions of refractory inclusions in the Murchison C2 chondrite

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Abstract—Samples from ten refractory inclusions in Murchison, some of which are splits of inclusions whose mineralogical and petrographic characteristics are known, have been analysed for thirty-six elements by neutron activation. Six inclusions have group II or group III patterns or variants of such patterns. Two inclusions, BB-5 and MUCH-1, have large negative Yb anomalies unaccompanied by correspondingly large negative Eu anomalies. It is possible that the latter condensed originally with group III patterns and preferentially took up Eu in later exchange processes under reducing conditions. One inclusion, SH-2, has heavy REE enrichment factors that increase with the refractoriness of the REE, indicating the presence of an extremely high-temperature, or ultrarefractory, REE condensate, but it also has a heavy REE/light REE ratio that indicates mixing of that component with a lower-temperature REE condensate. The frequency of highly fractionated REE patterns and absence of group I patterns suggest that refractory inclusions in Murchison stopped equilibrating with the nebular gas at higher temperatures than most Allende coarse-grained inclusions. The lower Ir/Os and Ru/Re ratios of some Murchison inclusions compared to those of Allende coarse-grained inclusions indicate that condensate alloys that contributed noble metals to the former also stopped equilibrating with the nebular gas at higher temperatures than those that contributed noble metals to the latter. Murchison inclusions tend to be lower in non-refractory elements than Allende coarse-grained inclusions, suggesting that, on average, the former underwent less severe secondary alteration than the latter.

INTRODUCTION

REFRACTORY INCLUSIONS in the Allende C3 chondrite have provided a wealth of information about processes and conditions in the early solar nebula. Trace element analyses of these objects have been used to establish that these objects formed in high-temperature, vapor-condensed phase fractionation processes and to determine what fraction of condensable solar system matter is represented by them, the chemical characteristics of the different reservoirs in which they formed and the degree of secondary alteration that has affected them. For a review, see GROSSMAN (1980).

Much less attention has been paid to refractory inclusions in C2 chondrites such as Murchison. From the petrographic and mineralogical work that has appeared (MACDOUGALL, 1979, 1981; ARMSTRONG *et al.*, 1982; BAR-MATTHEWS *et al.*, 1982; MACPHERSON *et al.*, 1983), it is clear that refractory inclusions in Murchison differ mineralogically from those in Allende in being more hibonite- and corundum-rich, suggesting that the former have higher solar nebular equilibration temperatures. Until now, trace element data have been published for only one refractory inclusion from Murchison (BOYNTON *et al.*, 1980) and they indeed show that object has a very high condensation temperature. The purpose of this study is to explore the range of

trace element patterns present in a large number of refractory objects from Murchison, to determine the physico-chemical similarities and differences between the formation sites of refractory inclusions in C2 and C3 chondrites, to ascertain if any relationship exists between chemical and mineralogical compositions of Murchison inclusions and to see how common it is for these objects to have higher equilibration temperatures than Allende coarse-grained inclusions.

TECHNIQUE

Sampling

Five of the samples discussed in this paper were found on surfaces of rough samples of the Murchison meteorite. Material for trace element analysis was removed from these inclusions by excavation with stainless steel dental tools and tweezers and/or tungsten needles while each inclusion was viewed with a binocular microscope in a clean room. In the case of MUCH-1 and SH-4, material remaining in the matrix was made into polished thin sections whose mineralogical and textural descriptions are given in MACPHERSON *et al.* (1983). The sample of MUCH-1 taken for trace element analysis is expected to be 100 per cent hibonite, far richer in this phase than the thin section, because blue material was easily excavated from the inclusion as relatively coarse crystals while remaining whitish material was very fine-grained and crumbled readily at each attempt to sample it. BB-6 is a blue spherule that was dug from the matrix in its entirety and then split into pieces. One of these was studied by SEM and found to contain major spinel and hibonite and minor perovskite and melilite. Texturally and mineralogically, it is very similar to BB-1 described by MACPHERSON *et al.* (1983). Very fine-grained blue and white material was sampled from SH-2, an irregular sugary-textured inclusion, for trace element analysis but the sample remaining in matrix and intended for mineralogical study was lost in the polishing step of section preparation. Several years before analysis of 1-10 μgm samples became routine in this laboratory, samples from two irregularly-shaped blue

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and white inclusions were scraped thoroughly from their matrix. Afraid that each of these samples would be too small to analyse for trace elements, we saved no material for mineralogical studies, mixed the two samples together prior to analysis and labeled the combined sample M-11.

The other five inclusions were hand-picked from the ρ > 3.50 fraction following freeze-thaw disaggregation of the bulk meteorite and heavy liquid separation as described by MACPHERSON *et al.* (1980). BB-5 was split into fragments, one of which was made into a polished thin section described by BAR-MATTHEWS *et al.* (1982). MUM-3 was split into fragments, one of which was made into a polished section that was found to be so similar in mineralogy and texture to MUM-1, described by MACPHERSON *et al.* (1983), that it may be a piece of the same inclusion.

DJ-2 was also split but the fragment taken for mineralogical study was lost during sectioning. Because of its similarity in appearance to other members of the DJ series of samples, DJ-2 is assumed to be identical to the latter, found by MAC-PHERSON *et al.* (1983) to be chips of blue hibonite crystals. SP-2, a pale blue octahedron, was analysed without taking a sample for mineralogical study. It is assumed to be identical to SP-1, another pale blue octahedron found by MACPHERSON *et al.* (1983) to be a spinel crystal. BB-3, a blue spherule, was also analysed in its entirety. It is assumed to be identical in mineralogy and texture to other blue spherules described by MACPHERSON *et al.* (1983).

Analytical

Eight of these samples were analysed together in the same series of short and long irradiations, but the remaining two, BB-3 and M-11, were each analysed in separate series of irradiations.

The procedure for the first eight samples was patterned after that described by DAVIS *et al.* (1978) for fragments from the inclusion CG-11. The first irradiation was designed to determine Mg, Al, Ca, Ti, Mn, V and Dy. The samples, Johnson-Matthey Specpure MgO, Al_2O_3, $CaCO_3$ and TiO_2, Standard Pottery SP (PERLMAN and ASARO, 1969), BCR-1 and Suprasil SiO_2 were each weighed at least ten times with a Perkin-Elmer AD-2Z electronic microbalance. They were then sealed into pouches weighing 1.9–4.6 mg which were made from HNO_3-washed, 38 μm thick, Dow 530 polyethylene film. They and some empty pouches for blank corrections were individually irradiated in the first row of the graphite reflector of the University of Missouri Research Reactor (MURR) for 5 min. at a flux of 1.0×10^{14} n-cm^{-2}-sec^{-1} using a pneumatic transfer system. After the irradiations, samples were mounted in their pouches on aluminum counting cards. After a 10 min. cooling interval, each was counted for 500 sec. for ^{27}Mg, ^{28}Al, ^{49}Ca, ^{51}Ti and ^{52}V using a Ge(Li) detector. After 1.8–7.8 hr., they were counted again for 10^3 sec. for ^{56}Mn and ^{165}Dy. Neutron flux variations were monitored by periodically irradiating Au- or Co-doped aluminum wires and counting ^{198}Au or ^{60}Co several days later at the University of Chicago. No significant variations were found throughout the runs. The counting data for Specpure Al_2O_3 and Suprasil SiO_2 were used to correct for the following interfering fast neutron reactions: ^{27}Al(n,p)^{27}Mg, and ^{28}Si(n,p)^{28}Al.

The second irradiation was designed to determine elements with longer-lived activation products than the above. Samples were removed from their polyethylene pouches and, together with new samples of SP and BCR-1, were weighed and sealed into Suprasil vials weighing 10–25 mg, much smaller than those used previously. A standard solution of each REE was prepared as outlined by DAVIS *et al.* (1982) but these were then combined into two separate group standard solutions, one containing La, Pr, Eu, Tb, Ho, Tm and Yb and the other Ce, Nd, Sm, Gd, Dy, Er and Lu. This separation makes it possible to evaluate experimentally, rather than theoretically as in DAVIS *et al.* (1982), the magnitudes of interferences of neighboring REE on one another due to double neutron cap-

ture. Three other group standard solutions, Os-Ru, Au-Ir-Re and Ag-Ni-Pd-Pt-Se-Zn, were made exactly as in DAVIS *et al.* (1982). A small amount of each of these solutions was weighed into its own 17–57 mg Suprasil vial. The vials containing samples or standards, together with some empty blank vials, were divided into groups of five or six, each of which was sealed into a Suprasil vial equal in size to individual sample vials used previously. Included in each group was a small vial containing a piece of Co-doped aluminum wire for monitoring spatial variations in neutron flux. Samples, standards, empty vials and flux monitors were irradiated in the flux trap of the MURR at a flux of 6.0×10^{14} n-cm^{-2}-sec^{-1} for 93.2 hr. The largest deviation of the thermal neutron flux from the mean was found to be 3.7%. Corrections based on these variations were applied to all nuclides utilized in this study, including ^{58}Co which is produced by fast neutrons *via* ^{58}Ni(n,p)^{58}Co. Because of the large neutron fluences and high cross-sections for production of ^{152}Eu and ^{166}Dy, flux corrections for Eu and Dy were applied in the way described by DAVIS *et al.* (1982). After cooling for two days, the small vials were washed successively in aqua regia, nitric acid, distilled water, double distilled water, acetone and ethanol. They were then taped on aluminum cards, in such a way that the samples were centered, and counted with Ge(Li) detectors at Chicago. Each sample was counted three times: (1) for 1.0 to 10.5 hr. each, 2 to 4 days after irradiation; (2) for 4.6 to 25.3 hr. each, 4 to 9 days after irradiation; (3) for 1.8 to 8.1 days each, 9 to 54 days after irradiation.

The short irradiation of BB-3 was identical to the above short irradiation. The long irradiation of BB-3 was similar to the long irradiation described above, except that all REE were present in a single group chemical standard, spatial variations in neutron flux were monitored in the same way as in the RNAA irradiation of DAVIS *et al.* (1982), the irradiation time was 116.6 hr., the maximum flux variation was 9.6%, the second count lasted 42.1 hr. and a fourth count was performed for 7.3 days, 4.5 mo. after irradiation.

M-11 was run with SP, BCR-1 and chemical standards for Os, Ru, Pt, Au and Ag which were prepared as described in GROSSMAN and GANAPATHY (1976a). Samples and rock standards were weighed with a Mettler H-51 balance and sealed into large Suprasil vials. Chemical standards were micro-pipetted into similar vials. All sample and standard vials and an empty blank vial were irradiated for 1 hr. at a flux of 5 $\times 10^{12}$ n-cm^{-2}-sec^{-1} in the isotope tray of the CP-5 reactor at Argonne National Laboratory. All sample vials were counted for 15–30 min. each for ^{56}Mn and then 50–100 min. each for ^{24}Na at the University of Chicago. Spatial variations in neutron flux, determined by measuring activities of impurities in household aluminum foils, were found to be negligible. The vials were again irradiated for 75 hr. at a flux of 5 $\times 10^{14}$ n-cm^{-2}-sec^{-1} in the flux trap of the MURR. After two days of cooling, the vials were washed in aqua regia and the sample and rock standards were transferred into new vials for counting. Each was counted three times: (1) for 2–10 hr.; (2) for 5–49 hr.; (3) for 30–165 hr. Spatial variation of the neutron flux was monitored and corrected for in the same way as described by GROSSMAN *et al.* (1981) for the long irradiation of the bulk sample of ALHA 76005. Differences in flux of up to 17% were found. M-11 underwent a third irradiation for RNAA along with several samples of the inclusion HAL. The standards used and procedures followed were thus precisely those described by DAVIS *et al.* (1982) for the RNAA irradiation of HAL.

Data reduction

Calculated corrections for ^{24}Na produced by fast neutron reactions on ^{27}Al and ^{24}Mg total less than 1% of the total ^{24}Na counts for all samples except M-11 where they approach 2%. Fast neutron reactions with ^{27}Al produce ^{27}Mg and with ^{28}Si produce ^{28}Al which interfere with Mg and Al determinations, respectively. Corrections for these interferences, made

by counting pure Al_2O_3 and SiO_2, amounted to 2–59% of the total ^{27}Mg counts and a negligible fraction of the ^{28}Si counts, respectively, for all samples. Production of ^{95}Zr by neutron-induced fission of ^{238}U interferes with determination of Zr, as does a ^{154}Eu peak at almost the same energy as ^{95}Zr. Corrections for these effects, amounting to <1–9% and 1–16%, respectively, of the total counts at 756.7 keV, were made as in GROSSMAN et al. (1977) and DAVIS et al. (1982), respectively. Interference of ^{141}Ce produced by double neutron capture on ^{139}La with determination of Ce via ^{141}Ce was evaluated as in DAVIS et al. (1982) for M-11 and BB-3 but by counting ^{141}Ce in the Ce-free La standard for the other eight samples. This effect was found to be negligible for all samples, as were interference with determination of Ce by overlap of a ^{175}Yb peak and interference with determination of Sm via ^{153}Sm by overlap of X-rays from ^{239}Pu. The latter were evaluated as in DAVIS et al. (1982) and GROSSMAN et al. (1979), respectively. Determination of Sm via ^{153}Sm can also be complicated by production of this nuclide by double neutron capture on ^{151}Eu. Corrections for this effect amounting to <1–4% of the total ^{153}Sm counts were made to the first eight samples by determining the number of ^{153}Sm counts in the Sm-free Eu standard. The corrections to M-11 and BB-3, 0.7% and 1.7% of the total ^{153}Sm counts, respectively, were made as in DAVIS et al. (1982). Using the ratio of ^{182}Ta counts at 84.7 keV to those at 1221.4 keV in a sample of pure Ta and the counts at 1221.4 keV in the samples, we were able to correct the 84.3 keV peaks of ^{170}Tm in our samples for interference from ^{182}Ta. This correction amounted to 1–21% of the total counts at 84.3 keV. Corrections of <1–3% of the total counts at 208.4 keV were made for the interference of 208.2 keV ^{199}Au from double neutron capture on ^{197}Au and from decay following neutron capture on ^{198}Pt with the 208.2 keV peak of ^{177}Lu as in GROSSMAN et al. (1977). As in DAVIS et al. (1982), corrections were also made to the Lu data for interference of ^{177}Lu produced from Yb, <1–17% of the total counts at 208.4 keV, and of Compton backscattered γ-rays from ^{46}Sc, 1–20%.

Because of large neutron fluences and high cross-sections for production of ^{152}Eu and ^{166}Dy, corrections for neutron flux variations were applied in the special way described by DAVIS et al. (1982). In the irradiation of the first eight samples, the sample with the largest difference in neutron fluence from the REE standards experienced a 6.2% higher fluence than the standard. In it, the specific activities of ^{152}Eu and ^{166}Dy were 7.2% lower and 10.8% higher, respectively, than in the standard. The specific activities of ^{152}Eu and ^{166}Dy were calculated to be 21.7% lower and 25.1% higher, respectively, in BB-3 than its REE standard, though the latter experienced a 14.9% lower flux than BB-3. Because M-11 experienced a higher flux than its REE standard by 10.6%, the specific activity of ^{166}Dy was 16.7% higher in M-11 than in the standard but the specific activity of ^{152}Eu was also higher by 50.9% in M-11. The reason why the ^{152}Eu specific activity was not lower in M-11 than in its standard is that M-11 was irradiated for a shorter period of time than its REE standard.

RESULTS

INAA data for all samples are given in Table 1, along with the isotope and standard used for each element and the irradiation in which each element was determined. Table 2 shows RNAA data for REE, Sr and Ba in M-11. The RNAA data are in excellent agreement with values obtained by INAA, except for those for Ce and Eu which are lower than their INAA values by 14% and 12%, respectively. We have adopted the RNAA data in this paper.

Sample weights

M-11 was weighed with a chemical balance. Since major elements were not determined in it via a rabbit irradiation, there was no transfer of sample from a polyethylene pouch

to a silica vial prior to a longer irradiation. Sample loss during transfer from an irradiation vial to an unirradiated counting vial following the long irradiation was assumed to be negligible because Sc contents determined after short and long irradiations were within error of one another. This was also assumed to be the case during removal of the sample from this vial following the RNAA irradiation, as ^{46}Sc activity remaining in the vial was a negligible fraction of its pre-removal value. Each of the other samples was weighed with a microbalance and underwent a rabbit irradiation in a polyethylene pouch to determine major elements, followed by transfer to a silica vial for a long irradiation. The weights of seven of these samples are uncertain for two reasons. The first is the possibility of loss of sample during transfer from pouch to vial. Visual inspection revealed this to be the case for two samples which were re-weighed prior to the long irradiation. The remaining five were not re-weighed but comparisons of concentrations of elements determined in both the short and long irradiations revealed no compelling evidence for sample loss in each of these samples. The second source of uncertainty in the weights is the erratic behavior of the microbalance which was found much later to have been yielding erroneous results due to a malfunctioning torque motor. The weight of each of these samples was derived as follows.

SP-2 was found to weigh 2.24 ± 0.41 μgm by microbalance. An independent estimate was obtained from the Al_2O_3 content determined by INAA, 1.97 ± 0.10 μgm, by assuming that SP-2 has the same composition as SP-1, another blue spinel octahedron, whose electron probe analysis yielded 71.69% Al_2O_3 (MACPHERSON et al., 1983). The computed mass which we adopt herein is 2.75 ± 0.14 μgm. The resulting MgO concentration, <23.3%, is in fair agreement with that of SP-1, 27.6%.

DJ-2 was found to have a mass of 5.12 ± 0.67 μgm by microbalance. The Al_2O_3 concentration of other DJ hibonite samples is remarkably constant, the average of 14 electron probe analyses from this laboratory being 89.12 ± 0.84%. Using this value and the Al_2O_3 content of 4.80 ± 0.16 μgm in DJ-2 obtained by INAA, we calculate the adopted mass, 5.39 ± 0.23 μgm. The resulting CaO, TiO_2 and MgO concentrations, 10.5 ± 1.3%, <2.6% and <10.5%, respectively, are consistent with electron probe analyses of DJ hibonite, 8.4 ± 0.3%, 1.7 ± 0.3% and 0.89 ± 0.15%, respectively.

MUCH-1 was found to weigh 6.65 ± 0.38 μgm by microbalance. The only major oxides detectable by INAA are Al_2O_3 and CaO, consistent with our earlier assumption that hibonite is the only phase present. The sum of the masses of these oxides is 3.13 ± 0.13 μgm and, considering upper limits to the masses of MgO and TiO_2, MUCH-1 must weigh <3.88 ± 0.13 μgm. Electron probe analyses by MACPHERSON et al. (1983) of hibonite in a split of this inclusion yield Al_2O_3—88.35 ± 0.57, CaO—8.87 ± 0.14, TiO_2—1.82 ± 0.33 and MgO—0.91 ± 0.20%. Using the Al_2O_3 content obtained by INAA, 2.91 ± 0.13 μgm, and the mean Al_2O_3 concentration in MUCH-1 hibonite found by electron probe, we calculate the adopted sample weight of 3.30 ± 0.16 μgm. The resulting CaO concentration, 6.4 ± 1.1%, is in fair agreement with the average hibonite analysis and the upper limits for TiO_2 and MgO, <4.2 and <18.3%, respectively, are also consistent with hibonite.

Although the weight of BB-5 obtained by microbalance is 3.92 ± 0.49 μgm, INAA showed that this sample contains 7.89 ± 0.03 μgm Al_2O_3 alone. From the modal mineralogy and electron probe analyses of the constituents of a chip of this inclusion, BAR-MATTHEWS et al. (1982) calculated its bulk composition to be 91.5% Al_2O_3, 6.4% CaO, 1.6% TiO_2 and 0.5% MgO. Assuming the chip analysed herein has the same Al_2O_3 concentration, we calculate the adopted mass of 8.62 ± 0.03 μgm from the mass of Al_2O_3 found by INAA. The resulting CaO concentration, 6.1 ± 0.9%, is in excellent agreement with the above estimate.

Using the mass obtained by microbalance, 63.08 ± 0.25 μgm, the sum of the concentrations of all oxides determined

Table 1. Elemental Abundances[1] in Murchison Inclusions

Sample	Description	Wt. μg	Wt. μg	Na₂O %	MgO %	Al₂O₃ %	CaO %	Sc	TiO₂ %	V
MUCH-1	Hibonite from irregular inclusion	3.30 ±.16		0.0260 ±.0013	<18	88.4 ±3.8	6.48 ±.79	353.12 ±.34	<4.3	<610
SH-4	Spinel-hibonite-feldspathoid inclusion	18.02 ±.60	7.42 ±.43	1.6995 ±.0052	8.6 ±3.6	38.3 ±1.1	27.49 ±.98	115.36 ±.23	2.94 ±.59	1040 ±87
BB-6	Blue hibonite-spinel spherule	0.58 ±.37		<0.01	n.d.	n.d.	<0.26	13.078 ±.061	n.d.	<5200
SH-2	Bluish, sugary-textured inclusion	0.90 ±.31		0.1720 ±.0059	<59	<18	13.5 ±4.6	1511.4 ±2.3	<15	<630
BB-5	Blue corundum-hibonite spherule	8.62 ±.03		0.02572 ±.00031	<7.3	≅91.50 ±.30	6.18 ±.88	367.96 ±.21	<1.9	<170
MUM-3	Melilite-spinel-hibonite inclusion	63.08 ±.25		0.02232 ±.00021	12.3 ±1.9	55.71 ±.72	23.03 ±.72	171.82 ±.16	1.78 ±.25	816 ±50
DJ-2	Chip of blue hibonite crystal	5.39 ±.23		0.02891 ±.00056	<11	≡89.12 ±2.89	10.5 ±1.3	421.76 ±.50	<2.6	<210
SP-2	Pale blue spinel octahedron	2.75 ±.14		0.0402 ±.0079	<23	72.8 ±3.8	0.82 ±.27	6.470 ±.019	<5.2	3000 ±330
BB-3	Dark blue spherule	10.4 ±.4	9.62 ±.26	<0.03	17.1 ±2.7	75.07 ±.78	4.76 ±.49	161.87 ±.20	2.46 ±.15	1965 ±66
M-11	Mixture of two blue and white inclusions	106 ±5		0.0735 ±.0017	n.d.	n.d.	15.33 ±.33	112.20 ±.04	1.97 ±.23	<5200
Irradiation[2], standard[3]		1	2	2,S	1,C	1,C	2,B	2,S	1,C	1,S
Isotope				²⁴Na	²⁷Mg	²⁸Al	⁴⁷Ca	⁴⁶Sc	⁵¹Ti	⁵²V
Cl Chondrites				0.6627	15.80	1.581	1.259	5.695	0.0711	55.65

by INAA to be >0.1% (Al_2O_3, CaO, MgO, TiO_2 and FeO) in MUM-3 is 93.1%. From the mineralogy of a split of this inclusion, SiO_2 is the only major oxide present which was not determined by INAA. If the sample mass is correct, the SiO_2 content obtained by difference should be in the range 0–14%, considering maximum uncertainties. Using electron probe analyses of the phases in MUM-3 and the bulk composition based on the above mass, calculated mineral assemblages are in good agreement with the one in thin section. We thus adopted the mass obtained by microbalance.

Using the microbalance, SH-4 was found to weigh 18.02 ± 0.60 μgm prior to the short irradiation but only 7.42 ± 0.43 μgm after partial removal from its polyethylene pouch. Concentration data for CaO, Na_2O, Sm, Eu, Dy and Sc from the short irradiation are in excellent agreement with those from the long one when these weights are used. Further evidence that these weights are correct is the consistency of the bulk composition determined by INAA with the mineral assemblage in a split of this inclusion (MACPHERSON et al., 1983).

Table 1. (Continued)

Sample	Nd	Sm	Eu	Tb	Dy	Ho	Tm	Yb	Lu	Hf	Re
MUCH-1	<32	6.222 ±.022	1.79 ±.17	1.181 ±.083	8.48 ±.83	1.64 ±.47	0.425 ±.077	<0.30	0.390 ±.045	4.356 ±.079	<0.14
SH-4	<14	4.436 ±.018	2.195 ±.063	0.489 ±.032	3.96 ±.29	0.51 ±.21	0.530 ±.030	4.881 ±.097	0.330 ±.051	1.761 ±.039	1.469 ±.041
BB-6	<39	4.63 ±.13	0.80 ±.33	<0.47	2.00 ±.96	<0.77	<0.46	1.88 ±.37	<0.18	<0.70	<0.56
SH-2	<280	11.99 ±.16	<1.3	5.95 ±.55	53.9 ±3.6	16.1 ±2.3	5.02 ±.72	1.94 ±.68	25.29 ±.40	186.3 ±1.5	139.0 ±1.1
BB-5	30.3 ±9.5	5.003 ±.010	1.557 ±.090	1.542 ±.054	9.95 ±.17	2.79 ±.11	0.868 ±.045	0.179 ±.055	0.834 ±.024	5.659 ±.072	<0.15
MUM-3	19.84 ±.64	6.7251 ±.0075	1.709 ±.045	1.356 ±.033	10.190 ±.089	2.174 ±.064	1.220 ±.027	5.141 ±.052	1.223 ±.012	4.859 ±.059	1.553 ±.024
DJ-2	<44	11.454 ±.061	2.55 ±.13	2.08 ±.10	12.81 ±.84	2.14 ±.34	0.56 ±.12	<0.56	<0.13	5.38 ±.19	11.02 ±.18
SP-2	<7.0	<0.021	<0.16	<0.090	<0.27	<0.15	<0.090	<0.12	<0.022	<0.12	0.183 ±.035
BB-3	n.d.	5.692 ±.027	1.057 ±.037	1.352 ±.089	8.51 ±.18	n.d.	0.850 ±.099	3.70 ±.12	0.847 ±.020	3.71 ±.13	1.671 ±.034
M-11	28.6 ±3.9	7.090 ±.063	0.6089 ±.0091	1.168 ±.026	n.d.	n.d.	n.d.	3.118 ±.064	0.2236 ±.0090	0.832 ±.063	0.484 ±.061
Irr.[2], Std.[3]	2,C	2,C	2,C	2,C	2,C	2,C	2,C	2,C	2,C	2,S	2,C
Isotope	¹⁴⁷Nd	¹⁵³Sm	¹⁵²Eu	¹⁶⁰Tb	¹⁶⁶Dy	¹⁶⁶Ho	¹⁷⁰Tm	¹⁷⁵Yb	¹⁷⁷Lu	¹⁸¹Hf	¹⁸⁶Re
Cl Chon.	0.4488	0.1461	0.05504	0.03606	0.2397	0.05542	0.02395	0.1587	0.02391	0.1265	0.0368

Table 1. (Continued)

Cr	Mn	Fe %	Co	Ni	Zn	Br	Sr	Zr	Ru	Cs	La	Ce
362.7 ±1.4	59 ±10	0.185 ±.011	1.76 ±.18	<47	<30	<0.29	234 ±87	<190	<1.7	<0.49	10.22 ±.15	23.02 ±.56
476.0 ±1.0	59.1 ±3.1	0.4881 ±.0046	7.941 ±.075	503 ±10	<9.5	2.07 ±.56	80 ±34	44 ±20	21.74 ±.36	<0.17	4.80 ±.11	15.86 ±.32
1108.2 ±5.5	<50	0.470 ±.025	3.32 ±.49	181 ±32	<27	<2.3	<250	<220	3.3 ±1.5	<0.45	7.91 ±.83	26.7 ±2.6
373 ±20	<23	<0.05	4.00 ±.76	<330	<380	<1.2	<1700	4860 ±760	115.0 ±9.3	<2.4	28.71 ±.97	63 ±14
26.27 ±.79	40.2 ±2.7	0.5003 ±.0081	1.01 ±.10	38 ±18	<8.1	<0.59	<120	165 ±62	<1.3	<0.29	7.767 ±.017	17.66 ±.37
314.3 ±1.1	14.20 ±.91	0.2670 ±.0057	2.757 ±.047	145 ±10	<7.8	<0.23	148 ±35	214 ±37	14.66 ±.47	<0.13	11.493 ±.060	26.07 ±.42
53.3 ±3.1	23.5 ±4.9	<0.03	1.21 ±.15	<63	<26	<0.94	300 ±110	<240	156.4 ±1.6	<0.44	28.21 ±.34	61.9 ±1.9
911.4 ±2.4	<15	0.1026 ±.0044	2.706 ±.098	84.1 ±7.5	<19	<0.66	<70	<57	1.61 ±.30	<0.13	<0.15	0.92 ±.43
517.3 ±6.6	47.9 ±2.4	0.286 ±.014	19.81 ±.42	41 ±16	n.d.	<0.61	n.d.	<120	21.1 ±1.3	<0.13	9.70 ±.21	27.5 ±1.4
612.3 ±4.1	153.8 ±9.6	1.2442 ±.0067	16.880 ±.048	415.2 ±7.2	<120	4.72 ±.29	<66	<170	7.36 ±.70	<0.087	11.928 ±.077	27.28 ±.68
2,S	1,S	2,S	2,S	2,S	2,S	2,S	2,S	2,S	2,C	2,S	2,C	2,C
^{51}Cr	^{56}Mn	^{59}Fe	^{60}Co	^{58}Co	^{65}Zn	^{82}Br	^{85}Sr	^{95}Zr	^{103}Ru	^{134}Cs	^{140}La	^{141}Ce
2606	1887	18.32	505.2	10830	311.8	3.285	7.776	3.807	0.7131	0.1832	0.2347	0.6096

BB-3 was found to weigh 9.08 ± 0.81 μgm by microbalance, but the sum of the masses of its constituent Al₂O₃, MgO, CaO, TiO₂, V₂O₃ and FeO was determined to be 10.4 ± 0.4 μgm by INAA. Assuming that BB-3, like other BB's, has a negligible SiO₂ content, we adopted the latter as the weight for the short irradiation. After partial transfer, the sample was re-weighed prior to the long irradiation. The resulting

mass, 9.62 ± 0.26 μgm, was used for the long irradiation since this resulted in Sc, Sm, Eu and Dy concentrations which are in excellent agreement with those found from the short irradiation.

Long after irradiation, SH-2 and BB-6 were weighed with the microbalance after it was repaired. These weights, 0.90 ± 0.31 and 0.58 ± 0.37 μgm, respectively, were adopted for

Table 1. (Continued)

Os	Ir	Au	Th	U
<1.0	0.345 ±.010	<0.12	<1.1	<2.0
14.82 ±.28	13.94 ±.21	<0.046	<0.18	<0.79
<2.7	0.065 ±.013	<0.11	<0.80	<3.6
1506.8 ±8.0	815.7 ±1.7	<0.37	<5.3	<7.6
<0.59	<0.028	<0.027	<0.31	<0.44
16.89 ±.19	13.51 ±.20	<0.012	1.212 ±.059	0.40 ±.10
151.0 ±1.1	125.4 ±1.9	<0.11	<0.50	<2.0
1.21 ±.19	0.977 ±.010	0.0264 ±.0073	<0.17	<0.26
27.66 ±.35	15.001 ±.020	0.016	1.90 ±.30	0.94 ±.26
4.54 ±.13	3.952 ±.034	0.0220 ±.0010	1.16 ±.11	0.156 ±.014
2,C	2,C	2,C	2,S	2,S
^{191}Os	^{192}Ir	^{198}Au	^{233}Pa	^{239}Np
0.5017	0.4675	0.1484	0.0293	0.008119

[1]All data in ppm unless otherwise indicated; errors given are 1σ uncertainties based on counting statistics alone for samples, standards and all other counting data used in making corrections for interferences and blanks; upper limits are based on 2σ counting statistics.

[2]1 indicates data determined *via* the short INAA irradiation; 2, the long INAA irradiation.

[3]B indicates use of USGS standard rock BCR-1; S, use of the Standard Pottery, SP (Perlman and Asaro, 1969); and C, use of a chemical standard except for REE in M-11 for which either SP or BCR-1 was used.

*Ti was determined in M-11 *via* ^{48}Sc, using BCR-1 as a standard.

Table 2. Radiochemical neutron activation analyses of M-11 (concentrations in ppm)

La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Tm	Yb	Lu	Sr	Ba
11.39	23.37	24.9	7.147	0.533	<6.4	1.111	5.986	0.8087	3.106	0.2270	36.8	15.9
±0.05*	±0.06	±1.2	±0.064	±0.011		±0.006	±0.096	±0.0071	±0.017	±0.0025	±4.4	±1.5

*Uncertainties quoted are based on 1σ counting statistics alone. Additional error due to uncertainty in chemical yield determinations is 4-9% for most elements but 25% for Ce.

both irradiations as there is no compelling evidence for sample loss during transfer. Because the weight of BB-6 is smaller than its 2σ error, the reader should be particularly wary of the concentrations reported for this sample. It should be noted, however, that uncertainty in the weight of a sample produces uncertainty in the absolute concentrations of elements in it but not in the fractionation patterns within it because the latter depend only on abundances of elements relative to one another.

Holmium

This is the first time that we have reported INAA data for Ho. The major complication is that Ho is determined *via* ^{166}Ho which is also produced both during and after high fluence irradiation from ^{164}Dy through the reaction chains listed by DAVIS *et al.* (1982) and also through ^{164}Dy-$(n,\gamma)^{165m}$Dy$(\beta^-)^{165}$Ho$(n,\gamma)^{166}$Ho. This interference could be corrected for in the case of the first eight samples because Ho and Dy were present in separate REE standards during the irradiation of those samples. The Dy standard was used to determine Dy in the samples *via* ^{166}Dy and to obtain the number of counts of ^{166}Ho produced per μgm of Dy. The latter was feasible because the number of ^{166}Ho counts due to impurity Ho in the REE standard containing Dy was calculated to be <10^{-3} of the Dy-produced ^{166}Ho counts. The Dy-produced ^{166}Ho counts were then deducted from the total ^{166}Ho counts in the samples and Ho was determined from the remaining counts by comparison with the Ho peak in the Ho standard. Despite the fact that from 58-75% of the total ^{166}Ho counts in the samples were due to Dy, data for some samples have relatively small errors because of good counting statistics in both standards and those samples. Ho data obtained in this way for BCR-1, 1.22 ± 0.08 ppm, are in excellent agreement with literature values obtained after low-fluence irradiations, 1.2 ppm (LAUL and SCHMITT, 1975) and 1.26 ppm (CONARD, 1976). Similarly, our result for SP is 0.98 ± 0.04 ppm which compares favorably to 1.07 ± 0.07 ppm, a value determined by interpolation between the Cl-normalized Dy and Yb data of PERLMAN and ASARO (1971).

REFRACTORY LITHOPHILES

Existing models

MARTIN and MASON (1974) classified refractory inclusions in the Allende C3 chondrite according to their REE patterns. The first type, which they called group I, have flat patterns in which all REE are enriched by a factor of 15 to 20 relative to Cl chondrites. Group II inclusions are uniformly enriched in light REE and Tm by a factor of 20 to 60 relative to Cl chondrites, are strongly depleted in Eu and Yb relative to light REE and otherwise show progressively greater depletions with increasing atomic number from Gd to Lu relative to light REE. Group III inclusions are uniformly enriched in REE by a factor of 15 to 50 relative to Cl chondrites except for negative Eu and Yb anomalies.

All of these REE patterns have been interpreted in terms of condensation models. Group I REE patterns are a common feature of coarse-grained, Ca-rich inclusions in Allende, as defined by GROSSMAN and GANAPATHY (1975). As shown by GROSSMAN (1973), GROSSMAN and GANAPATHY (1976a) and GROSSMAN *et al.* (1977), group I REE patterns are only a part of a broader chemical pattern in which the average concentration of *every* refractory element in a group of such inclusions, including siderophiles and lithophiles other than REE, divided by the abundance of that element in Cl chondrites yields the same enrichment factor, 17.5 ± 1.8. That coarse-grained inclusions did not fractionate refractories from one another relative to Cl chondrites was interpreted by GROSSMAN *et al.* (1977) to imply total condensation of each element from a gas of solar composition and incorporation of all condensate components, regardless of chemical differences, into coarse-grained inclusions. As argued by GROSSMAN *et al.* (1977), the enrichment factor of 17.5 implies that coarse-grained inclusions represent the first $100/17.5 = 5.7$ wt.% of the total condensable matter of the solar system to condense from the cooling solar nebula, a value in excellent agreement with independent estimates from condensation calculations of the fraction of matter that should have condensed above the accretion temperature of the inclusions, $\sim 1440°$K at a total nebular pressure of 10^{-3} atm. (GROSSMAN, 1980). An alternative, that coarse-grained inclusions are refractory residues (KURAT, 1970) remaining after volatilization of 94.3% of the matter from Cl chondrites, cannot be dismissed.

Group II patterns are a common feature of fine-grained inclusions (TANAKA and MASUDA, 1973; CONARD, 1976; GROSSMAN and GANAPATHY, 1976b), as defined by GROSSMAN and GANAPATHY (1975). BOYNTON (1975) showed that a REE pattern with these general characteristics would result if these inclusions condensed with the REE remaining in the gas after prior removal of the most refractory REE in an earlier, very high-temperature condensate, as Tm and the light REE are more volatile than the heavy REE whose depletions in these inclusions increase in the order of their refractoriness. The Eu and Yb depletions in these inclusions were caused by accretion at a nebular temperature high enough that these two elements, the most volatile REE, had not yet fully condensed. DAVIS and GROSSMAN (1979) showed that a more realistic way of matching calculated and actual REE patterns in a wide variety of group II inclusions could be achieved if these inclusions were considered mixtures of two REE-bearing components, one which formed in this way and the other with a flat REE pattern. The idea that a component with a flat REE pattern is present in these inclusions was originally proposed by TANAKA and MASUDA (1973).

Group III patterns are usually found in GROSSMAN and GANAPATHY's (1975) coarse-grained inclusion category and are thought to have formed in the same way as group I patterns but at a slightly higher nebular equilibration temperature such that Eu and Yb, the two most volatile REE, were excluded when most other refractory elements were fully condensed.

These considerations alone lead to the conclusion that refractory inclusions in Allende did not all form in a single nebular reservoir but, instead, represent a variety of nebular locales which had little or no contact with one another at the time of REE condensation (BOYNTON, 1978). For example, inclusions with group II, highly fractionated REE patterns formed from a gas of solar composition after removal of a very high-temperature condensate with a complementary pattern. Assuming that these inclusions represent a significant fraction of the total rare earths in the nebular site where this fractionation occurred, it is impossible to form in that same reservoir inclusions with group I patterns, representing total condensation of all REE without fractionation from one another, or with group III patterns, representing total condensation of all REE except Eu and Yb. Furthermore, groups I and III patterns could not have originated in the same reservoir. This is because inclusions with group III patterns formed at a higher temperature than those with group I patterns and, had they come from the same reservoir, the latter would not be flat but, instead, would contain excess Eu and Yb which were excluded from the former. Finally, REE components from separate nebular reservoirs may be present within individual inclusions as well as within the Allende meteorite as a whole. If DAVIS and GROSSMAN (1979) are correct, fine-grained inclusions contain a component that formed after condensation of the most refractory REE and a component with a flat REE pattern which, as we have already seen, could not have originated in the same reservoir.

C1 chondrite-normalized REE patterns for all inclusions studied herein except SP-2 are shown in Fig. 1. First, we note that, despite their high frequency of occurrence in refractory inclusions in Allende, group I REE patterns have not been observed in any of these refractory inclusions in Murchison.

M-11 and BB-6

These samples have group II patterns. This is certain for M-11 but, because of poor counting statistics due to the small sample size of BB-6, is only inferred for the latter from the depletion of Tb, Dy and Ho as well as Eu and Yb relative to light REE and from the depletion of Lu relative to Yb compared to C1 chondrites. Recall that M-11 is a mixture of two, irregularly-shaped inclusions for which the only mineralogical information, provided by their deep blue color, is that they contain hibonite. BB-6, on the other hand, is a typical blue spherule (MACDOUGALL, 1981; MACPHERSON et al., 1983), containing major amounts of spinel and hibonite with minor perovskite and melilite. The REE patterns of these inclusions must have formed in the same way as group II patterns in Allende inclusions, although that for M-11 is slightly unusual in that the C1 chondrite-normalized Yb/Sm ratio, 0.40 ± 0.01, is much larger than that for Eu/Sm, 0.20 ± 0.01. It is normal in group II patterns for these ratios to be similar (DAVIS and GROSSMAN, 1979), although at least one in an Allende fine-grained inclusion, sample 15 of NAGASAWA et al. (1977), also has a substantially larger C1 chondrite-normalized Yb/Sm ratio, 0.21, than its Eu/Sm ratio, 0.14. The ratios of Sc, Th, U,
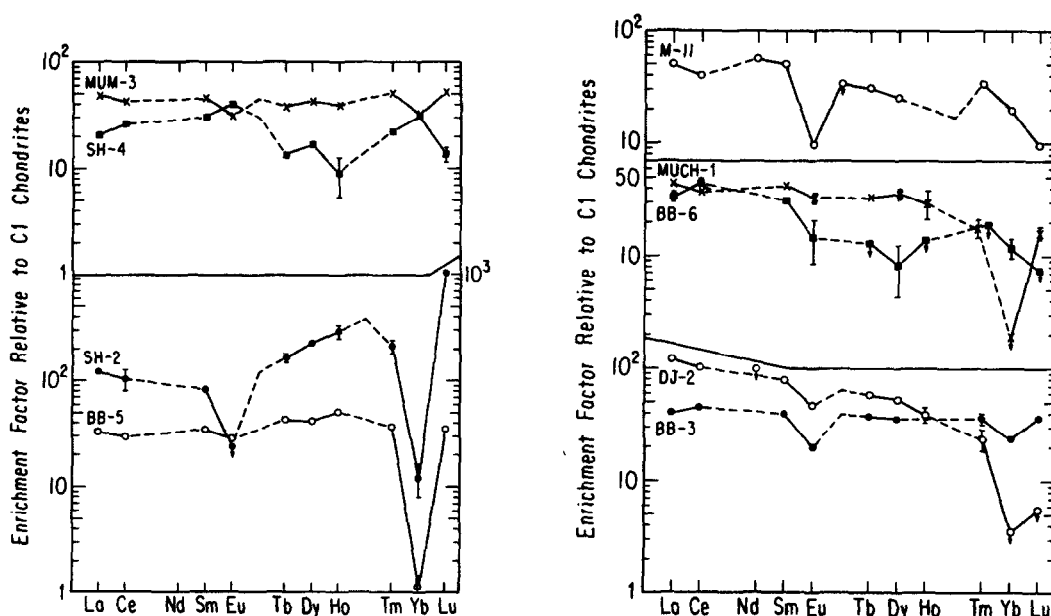

FIG. 1. a and b. Rare earth patterns in refractory inclusions from Murchison.

Sr and Ba to La in M-11 are 0.41, 0.78, 0.38, 0.098 and 0.14, respectively, relative to C1 chondrites, very similar to those found in Allende group II inclusions (GROSSMAN and GANAPATHY, 1976b; MASON and TAYLOR, 1982; unpublished data from this laboratory), but its C1 chondrite-normalized Hf/La ratio, 0.13, is an order of magnitude greater than in those inclusions (unpublished RNAA data from this laboratory). The C1 chondrite-normalized Sc/La ratio of BB-6, 0.068, is similar to that of many Allende group II inclusions (GROSSMAN and GANAPATHY, 1976b).

SH-4

From the fact that its light REE and Tm are twice as enriched as Tb, Dy, Ho and Lu, a third inclusion from Murchison, SH-4, has a REE pattern with strong affinities to group II's. It is not identical to the latter, however, since it has positive, instead of negative, Eu and Yb anomalies. It is very similar to patterns reported from Allende inclusions A-2 (CONARD, 1976) and A-19 (PALME, pers. commun., reproduced in DAVIS and GROSSMAN, 1979). No mineralogical or textural information is available for A-19 but A-2 appears to be a normal Type B coarse-grained inclusion, based on its description by GRAY *et al.* (1973). Although MAC-PHERSON *et al.* (1983) show that SH-4 is highly altered, they point out that this inclusion contains primary fassaite and hibonite, suggesting that it has little relationship to Type B inclusions like A-2 which contain no primary hibonite. Formation of such REE patterns must involve removal of the most refractory REE in an earlier condensate just as in the case of group II's but, unlike the latter, must also involve mixing of the residual REE with a component, either gaseous or condensed, having higher-than-chondritic Eu/Sm and Yb/Sm ratios. Such a component could form by fractionation of Eu and Yb, the two most volatile REE, from their cosmic complement of all other REE which had largely condensed elsewhere. There is evidence that this component may have contained other lithophiles in non-chondritic proportion to one another. The Sc/La ratio of SH-4 is 1.0 relative to C1 chondrites, instead of two to five times less than this as in Allende group II inclusions, and Zr/La and Hf/La ratios are ~0.6, rather than ~0.01. Sr and V, whose volatilities are similar to those of Eu and Yb (DAVIS *et al.*, 1982), might be expected to be enriched in SH-4 relative to light REE compared to C1 chondrites but they are depleted instead.

MUM-3 and BB-3

Figure 1 shows that these two inclusions have normal group III REE patterns which presumably formed in the same way as those in Allende inclusions. MAC-PHERSON *et al.* (1983) showed that MUM-3 is similar in mineralogy and texture to Allende coarse-grained Type A inclusions, which do not normally have group III patterns (GROSSMAN and GANAPATHY, 1976a), but quite different from blue spherules like BB-3 which

has a group III pattern. As expected for an inclusion with a group III pattern, enrichments of Zr, Hf, Th and U in MUM-3 are like those of most of the REE, ~40–50, while those of more volatile V and Sr, like those of Eu and Yb, are lower, ~15–19, relative to C1 chondrites. The enrichment factor for Sc, 30.2, is unusually low compared to those of other highly refractory elements. In BB-3, enrichment factors for Sc, V and Hf are nearly uniform, 28.4, 35.3 and 29.3, respectively, though slightly lower than those of REE. Th and U appear to have greater enrichments than all of these but this may not be real because of their very large error bounds.

DJ-2

This hibonite crystal fragment has a negative Eu anomaly and, although we only have upper limits to the enrichments for Yb and Lu, the data also allow a negative Yb anomaly. The remainder of the REE in this sample show progressively decreasing enrichment factors with increasing atomic number, rather than the flat pattern typical of group III's. Such a steady decline in enrichment factor was observed in hibonite from the isotopically-unusual inclusion HAL, although the La/Tm ratio in it is ~27 relative to C1 chondrites (DAVIS *et al.*, 1982), rather than the ratio of ~5 seen in DJ-2. DAVIS *et al.* (1982) interpreted the HAL hibonite pattern to mean that that phase coexisted in the gas cloud with other phases having a crystal chemical affinity for heavy relative to light REE which condensed preferentially into hibonite while heavy REE condensed preferentially into the other phases. The same thing could have happened to DJ-2, in which case some complementary material preferentially enriched in heavy REE must exist which we have not sampled. A similar crystal chemical affinity of hibonite for Sc, which has been invoked to account for the unusually high Sc contents in HAL and in a hibonite-rich sample from Allende (DAVIS *et al.*, 1978), may account for the Sc enrichment factor of ~74 in DJ-2 relative to C1 chondrites, a value much higher than that of Hf, ~42, whose volatility is similar to that of Sc (DAVIS *et al.*, 1982). Similarly, the relatively low enrichment factor, <17, for Th, whose volatility is like that of Lu (DAVIS *et al.*, 1982), may also be due to crystal chemical effects as the ionic radius of Th in the tetravalent state is like that of heavy REE. Negative anomalies in both Eu and Yb would indicate cessation of equilibrium between hibonite and the gas phase at a temperature high enough that these elements had not yet totally condensed. This interpretation is supported by the fact that V, whose volatility is like that of Eu and Yb, is only enriched by a factor of <3.8 relative to C1 chondrites, much less than most other refractory lithophiles.

BB-5

The results of mineralogical, textural and Mg isotopic studies of this unique, corundum-rich inclusion

were presented by BAR-MATTHEWS et al. (1982). Despite vastly different $^{27}Al/^{24}Mg$ ratios, corundum and hibonite have the same $^{26}Mg/^{24}Mg$ ratio, 7‰ higher than normal Mg. Figure 1 shows that this inclusion also has a very unusual REE pattern. Except for Yb, the pattern is nearly flat, with heavy REE enriched by factors of 35–50 and light REE by factors of 30–35 relative to C1 chondrites. It has a very large negative Yb anomaly, the Yb/Sm ratio being 0.033 ± 0.010 relative to C1 chondrites, but a much smaller negative Eu anomaly, the Eu/Sm ratio being 0.83 ± 0.05. We have seen how Eu and Yb are generally enriched or depleted together in refractory inclusions and that the sizes of C1 chondrite-normalized Eu/Sm and Yb/Sm ratios are always within a factor of two of one another in any given inclusion. To our knowledge, this is the first time that a REE pattern has been reported in which a large negative Yb anomaly is not accompanied by an Eu anomaly of comparable size. Condensation calculations show that, although the two elements have very similar volatilities, Yb begins to condense from a gas of solar composition at a slightly higher temperature than Eu (DAVIS and GROSSMAN, 1979). Thus, even if it were possible to separate Eu from Yb by their slight difference in volatility, negative Eu anomalies without Yb anomalies would be expected instead of the reverse which is observed. In a gas more reducing than one of solar composition, the difference in volatility between Yb and Eu narrows somewhat (DAVIS and GROSSMAN, 1979). In a gas more oxidizing than a solar gas, both Yb and Eu become more refractory, Yb more so than Eu (DAVIS et al., 1982). In all cases considered, Yb remains less volatile than Eu, providing no explanation for the REE pattern of BB-5. Perhaps BB-5 originally condensed with a group III pattern but later re-equilibrated with an Eu-bearing condensed phase under reducing conditions. If Eu^{2+} strongly favored a phase or phases in BB-5 over the unknown phase, the Eu anomaly in BB-5 would shrink while the anomaly in trivalent Yb would be largely unaffected. That this process would have been capable of adding just enough Eu to yield the near-chondritic Eu/Sm ratio seen in BB-5 seems highly improbable. Such a process would, however, support one possible interpretation of the Mg isotopic data advanced by BAR-MATTHEWS et al. (1982), that BB-5 originally condensed with live ^{26}Al which decayed to ^{26}Mg in situ but became homogeneous in Mg isotopic composition during exchange with an external reservoir containing normal Mg. This was considered unlikely by BAR-MATTHEWS et al. (1982) and is still considered unlikely by us because there is no petrographic evidence for such a two-stage model. Nevertheless, we have no other explanation for the REE pattern of BB-5. Zr and Hf have enrichment factors of ~44 relative to C1 chondrites, like the heavy REE, but that of Sc, 64.6, is higher than that of any REE, presumably because of the large amount of hibonite in BB-5. In addition to Yb, upper limit data show that V, Sr and Th are substantially less enriched than other refractories relative to C1

chondrites. The relative depletion of V and Sr lends support to the idea that the Yb anomaly is due to its greater volatility than most other REE.

MUCH-1

The REE pattern of MUCH-1 hibonite is very similar to that of BB-5 in that it has a very large negative Yb anomaly and a comparatively small Eu anomaly, the Yb/Sm and Eu/Sm ratios being <0.044 and 0.76 ± 0.07, respectively, relative to C1 chondrites. In this inclusion, however, light REE are enriched by a factor of ~40 and Tm and Lu only by a factor of ~17 relative to C1 chondrites, a fact which tends to make the Yb/Sm ratio an overestimate of the size of the anomaly of Yb relative to its immediate neighbors. Nevertheless, even comparing the C1 chondrite-normalized ratio of Yb/Tm, <0.11, to that of Eu/Sm reveals a very much larger Yb than Eu anomaly in this inclusion. MACPHERSON et al. (1983) showed that this inclusion consists of a radial aggregate of hibonite crystals rimmed by layers of alteration products including calcite, gypsum, iron-rich phyllosilicate and iron-free diopside. Thus, unlike BB-5, there is abundant petrographic evidence for a two-stage history for MUCH-1. In this case, an origin by condensation of a group III pattern into hibonite followed by partitioning of Eu into it by exchange with an external reservoir is more plausible than for BB-5, although it would have to be regarded again as highly coincidental for Eu addition to have resulted in an Eu/Sm ratio so close to the C1 value. Because Eu only behaves differently from other REE under reducing conditions, however, the reservoir was not the Murchison parent body which was rich in water and oxidized iron. Although it is conceivable that the iron-rich phyllosilicate in MUCH-1 formed by alteration in the parent body, the diopside, requiring less hydrous and more reducing conditions, did not. Perhaps Eu exchange, if it occurred at all, was associated with that stage of secondary alteration that produced diopside. Relative to C1 chondrites, Hf is enriched by the same factor as light REE but the enrichment factor for Sc is much greater, 62, presumably because of the hibonite effect. The enrichment factor for V, <11.0, is again less than that of most other refractory lithophiles, presumably because of its similar volatility to Yb.

SH-2

In this sample, light REE are enriched by factors of 80–120 relative to C1 chondrites and the negative Eu anomaly is not significantly smaller than that for Yb, the C1 chondrite-normalized Eu/Sm and Yb/Sm ratios being <0.29 and 0.15 ± 0.05, respectively. The remarkable feature of the REE pattern of SH-2 is the progressive enrichment of the refractory heavy REE relative to light REE with increasing atomic number. The C1 chondrite-normalized Tb/Sm, Dy/Sm, Ho/Sm and Lu/Sm ratios are 2.01 $\pm$ 0.21, 2.74 $\pm$ 0.22,

3.54 ± 0.55 and 12.89 ± 2.23, respectively. It might be possible to produce such a pattern by condensation of REE at a high enough temperature that Eu and Yb were excluded and into an assemblage of host phases, one or some of which, represented by SH-2, have a preference for heavy relative to light REE compared to other phases. Alternatively, perhaps SH-2 condensed with a group III pattern but preferentially lost light REE in a later exchange process. Both of these possibilities seem to be ruled out, however, by the fact that the C1 chondrite-normalized Tm/Sm ratio, 2.55 ± 0.40, falls off the smooth trend for the other heavy REE. Because Tm is slightly more volatile than Ho or Lu, the depletion of Tm relative to these suggests that the REE pattern is the result of a vapor-condensed phase fractionation process. In order to produce the observed large fractionations among the heavy REE during solar nebular condensation, extremely high temperatures are required, as we will now show.

LATTIMER and GROSSMAN (1978) presented results of full equilibrium, solar nebular condensation calculations for major elements. Using the same technique as in that paper and an updated set of thermodynamic data, it is found that corundum condenses first at 1743°K. It reacts with the gas to form hibonite at 1727°K and then perovskite condenses at 1676°K at a total pressure of 10^{-3} atm. (J. M. LATTIMER, pers. commun.). These results are in precise agreement with those of KORNACKI and FEGLEY (1984) but the latter workers also calculate that $CaAl_4O_7$ condenses next by reaction of the gas with hibonite at 1646°K. We have not included $CaAl_4O_7$ in our calculations because uncertainty in thermochemical data makes its stability questionable in a solar gas (MACPHERSON and GROSSMAN, 1984) and because it is absent from SH-5 and SH-6, direct vapor-solid condensate inclusions that clearly preserve a record of the lower-temperature reaction of hibonite with the gas to form spinel (MACPHERSON et al., 1984).

Using the above results and the calculation technique and thermodynamic data for REE species employed by DAVIS et al. (1982), we have calculated the REE pattern of the condensate under several conditions. All calculations assume ideal solid solution. Although absolute condensation temperatures are uncertain by at least ten degrees, it is known that the heavy REE fractionations appear and disappear within only a few one-hundredths of a degree of the condensation temperature of the first-appearing major REE host phase. Consequently, a larger number of significant figures are quoted here for absolute condensation temperatures than are justified by the sizes of uncertainties in thermochemical data. Hibonite is the first-appearing potential REE host phase. Its precise condensation temperature is calculated to be 1726.97°K. Figure 2a shows that, at this temperature, there are strong fractionations among the heavy REE in the condensate, the order of increasing enrichment being Dy, Ho ~ Tb, Er and Lu. Such material is also strongly depleted in light relative to heavy REE, predicted C1 chondrite-nor-
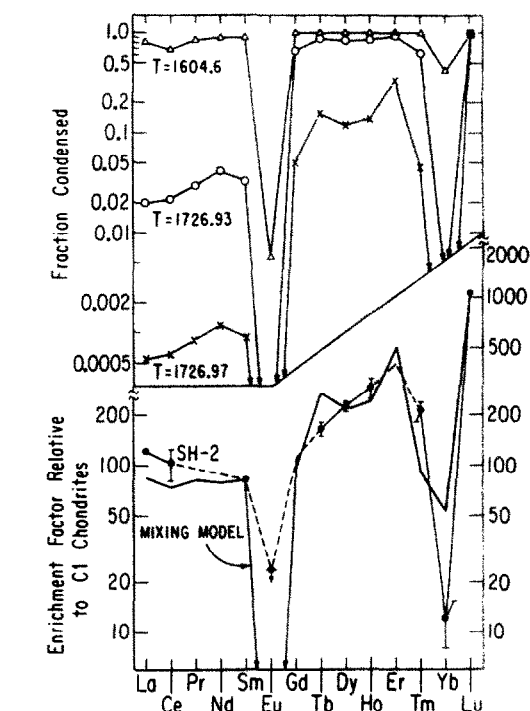

FIG. 2. a (upper). During solar nebular condensation, fractionations among heavy rare earths are only possible by isolation of condensates from further reaction with the gas at an extremely high temperature, just below their initial condensation temperature. Fractionation of heavy from light REE persists to lower temperatures. b (lower). The REE pattern of SH-2 can be approximated by mixing an ultrarefractory condensate with a relatively low-temperature condensate and losing an intermediate temperature condensate (see text).

malized Sm/Lu ratios being ~1 × 10^{-3}. The figure also shows, however, that all of the above heavy REE are so refractory that, when the temperature falls to only 0.04° below the condensation temperature of hibonite, each of them is nearly totally condensed and the fractionations among them disappear as a consequence. Note that fractionations among the heavy REE disappear at such a high temperature that they are not at all affected by the presence or absence of $CaAl_4O_7$ in the condensation sequence. Also seen in Fig. 2a is that the light REE only approach total condensation when the temperature falls another 125°, at which point the Eu and Yb anomalies are considerably smaller than at higher temperatures. We conclude that the heavy REE pattern of SH-2 indicates cessation of equilibrium with the nebular gas at a temperature above 1726.93°K.

PALME et al. (1982) reported an inclusion from the C3 chondrite Ornans in which they found both the fractionation pattern among the heavy REE seen in SH-2 and the required several hundredfold depletion of light relative to heavy REE. As the authors claim, the REE pattern of that inclusion indicates cessation of equilibrium with the solar nebular gas at a much higher temperature than any other refractory inclusion

seen and has those characteristics required of the material that was originally postulated by BOYNTON (1975) to have been isolated from the gas prior to condensation of group II REE patterns. Earlier, BOYNTON et-al. (1980) had found a hibonite-bearing Murchison inclusion, MH-115, in which light REE are depleted relative to heavy REE by a factor of 3 compared to C1 chondrites, a fact which suggested to those workers that the REE pattern resulted from cessation of equilibrium with the gas at an extremely high temperature. It is clear, however, from the lack of significant fractionations among the heavy REE in MH-115 and the much smaller fractionation of light from heavy REE in MH-115 than in the inclusion of PALME et al. (1982) that the latter has a higher equilibration temperature than the former. The C1 chondrite-normalized Lu/Dy ratio of SH-2, 4.70 ± 0.39, is not quite as great as that for the inclusion of PALME et al. (1982), 6.4, indicating a slightly lower equilibration temperature for SH-2. On the other hand, the depletion of light relative to heavy REE in SH-2 as measured by the C1 chondrite-normalized Sm/Lu ratio, 7.7×10^{-2}, though much lower than that of MH-115, is much higher than predicted by condensation calculations for such a high equilibration temperature and much higher than that of the inclusion of PALME et al. (1982). Perhaps a second REE-bearing component brought light REE into SH-2 without significantly affecting the heavy REE pattern. This is illustrated in Fig. 2b in which we attempt to model the REE pattern of SH-2 by mixing two condensate components. The first is hibonite which stopped equilibrating with the solar nebular gas at 1726.97°K, just below the initial condensation temperature of hibonite where only ~0.9% of the hibonite which can ultimately condense has done so. This temperature dictates the slope of the REE pattern from Tb to Lu. The model requires the REE to continue to condense into hibonite until the temperature falls to 1686.8°K, at which point the next 80.6% of the hibonite is condensed. The second mixing component forms when this second batch of hibonite is separated from the system and the REE remaining in the gas continue to condense into hibonite and perovskite until the temperature reaches 1604.6°K, at which point 97.8% of the perovskite which can ultimately condense has done so, as well as virtually all of the remaining hibonite. Figure 2b shows the best fit to the data for SH-2 which is obtained by mixing 16.4% of component one with 56.5% of this perovskite-hibonite mixture and 27.1% of REE-free material. The mixing in of the relatively low-temperature, perovskite-bearing component is necessary in order to raise the light REE to their approximate level in SH-2. If the model is correct, the implication is that SH-2 formed in a region of the nebula in which grain transport mechanisms operated which were capable of moving condensates from their formation site and of reuniting them with later condensates from the same place.

As might be expected for a sample containing a component with such a high nebular equilibration temperature, SH-2 is also strikingly enriched in other very refractory elements. Zr and Hf, whose volatilities are comparable to that of Lu (DAVIS et al., 1982), are enriched in SH-2 by factors of 1277 ± 200 and 1473 ± 12 while Sc, which is not quite as refractory as these elements, is enriched by a factor of 265 and V, one of the most volatile of the elements normally considered refractory, is only enriched by a factor of <11.3.

SP-2

Most refractory lithophiles are below detection in SP-2, presumably because of the well-known intolerance of the spinel structure for most large ion lithophiles. Exceptional in this regard is the high V content of SP-2, 3000 ± 330 ppm, probably due to the crystal-chemical affinity of spinel for V^{3+}. This is about a factor of two higher than that found in a similar Murchison spinel crystal, SP-1 (MACPHERSON et al., 1983), spinel in the Murchison Blue Angel inclusion (ARMSTRONG et al., 1982) and spinel in an Allende Type B inclusion (MACPHERSON and GROSSMAN, 1981) but equal to or lower than that of other low-iron spinels in Allende (MEEKER et al., 1983; MACPHERSON and GROSSMAN, 1984).

Relationship between mineralogical and chemical composition

Mineralogical and petrographic characteristics give few clues as to the type of REE pattern to be expected in any particular kind of refractory inclusion in Murchison. For example, among inclusions with group II patterns are objects like BB-6 and SH-4 with little petrographic or mineralogical relationship to one another. Similarly, MUM-3 and BB-3 both have group III patterns but are quite distinct from one another petrographically. In fact, although we have not studied a thin section of BB-3, it is probably very similar in mineralogy and texture to BB-6, a typical blue spherule, which has a group II pattern.

These observations are at least partially understandable even though they demonstrate that these trace element patterns cannot be predicted from mineralogy. Inclusions with group III patterns record cessation of equilibrium with the gas above the temperature at which Yb is fully condensed, ~1575°K at 10^{-3} atm. total pressure. Those with group II patterns record loss of an ultrarefractory REE component which, according to Fig. 2a, condenses above 1725°K where only corundum and a small amount of hibonite have condensed. These inclusions also have negative Yb anomalies and thus stopped equilibrating with the gas above ~1575°K, like those with group III patterns. Inclusions with different mineralogical compositions from one another represent mixtures of condensates that equilibrated with the gas at different temperatures. BB-6, the only group II inclusion studied herein whose mineralogical composition is known, has a primary phase assemblage consisting of hibonite, spinel, perovskite

and a trace of melilite. This is quite compatible with the requirement that it formed after prior loss of an ultrarefractory component consisting only of corundum and a small amount of hibonite, as are phase assemblages in most refractory inclusions in Allende and Murchison. BB-3 and MUM-3 are the only group III inclusions studied herein whose mineralogical compositions are known or can be inferred with reasonable certainty. According to equilibrium condensation calculations, however, neither these two inclusions nor BB-6 have mineralogical compositions that are entirely compatible with cessation of equilibrium above 1575°K, as is indicated by their REE patterns. Recall that these calculations predict that corundum reacts completely to form hibonite at 1727° and perovskite condenses at 1676°K at 10^{-3} atm. total pressure. Melilite begins to condense by reaction of hibonite with the gas at 1606°K and the amount of melilite increases at the expense of hibonite with falling temperature until the remaining hibonite reacts totally to form spinel at 1511°K. Thus, although the presence of hibonite, perovskite and melilite in the three inclusions in question is compatible with equilibration above 1575°K, the presence of spinel suggests equilibration well below this temperature. Hibonite can coexist with spinel but only for a few degrees and only after abundant melilite has condensed. BAR-MATTHEWS et al. (1982), MACPHERSON et al. (1983) and MACPHERSON and GROSSMAN (1984) discussed the anomalous coexistence of hibonite and spinel, particularly in inclusions that lack melilite, and suggested that spinel somehow condensed before melilite, in conflict with the calculated condensation sequence. Negative Yb anomalies in groups II and III REE patterns of hibonite-, spinel-bearing Murchison inclusions suggest that these assemblages stopped equilibrating with the solar nebular gas at some temperature above a point just below the condensation temperature of melilite. The presence of spinel in these inclusions may imply that this phase condensed at a higher temperature than predicted by equilibrium calculations. This could have occurred, for example, if no Al-bearing condensate precursors of spinel, e.g. corundum and hibonite, nucleated, leaving relatively large amounts of Al in the vapor. If spinel indeed condensed at a higher temperature than melilite, then the mineralogical compositions of BB-6, MUM-3 and BB-3 are all compatible with their negative Yb anomalies, despite the different melilite contents of these inclusions.

We have already seen that groups II and III inclusions formed in separate nebular reservoirs from one another. Thus, the fact that blue spherules exist in both groups implies that similar condensate assemblages accreted to form inclusions in different nebular reservoirs. Furthermore, the fact that mineralogically-different inclusions have the same REE patterns implies that different condensate assemblages were able to accrete within the same nebular reservoir. The fact that group I REE patterns are rare and those indicative of high-temperature, gas-condensed phase REE fraction-

ation processes are so common in refractory inclusions in Murchison suggests that most of the latter stopped equilibrating with the nebular gas at higher temperatures than most Allende coarse-grained inclusions, as is also indicated by the greater abundance of hibonite and, in some cases, corundum in the Murchison inclusions.

Another example of the failure of mineralogical composition to serve as the basis for predicting the REE pattern is BB-5. This inclusion possesses the most refractory phase assemblage seen in any high-temperature inclusion so far, corundum + hibonite + perovskite. It is the type of object for which an ultrarefractory REE pattern like that in SH-2 would be expected; yet, instead, it has a flat REE pattern except for an enigmatic negative Yb anomaly. In trying to understand the relationship between mineralogy and trace element content, the lack of mineralogical data for SH-2 is very unfortunate, making it all the more important to find other inclusions with ultrarefractory REE patterns in order to determine their mineralogical and petrographic characteristics.

Possibility of a liquid origin

KORNACKI and FEGLEY (1984) grouped together a wide range of objects under the heading "spinel-rich chondrules and inclusions". A feature common to all of them is that they are rich in spinel and perovskite. Occasionally, they also contain abundant hibonite that forms radiating sprays of crystals. KORNACKI and FEGLEY (1984) proposed that aggregates of primitive dust were distilled into residues consisting of a spinel-rich solid assemblage and a Ca-rich melt and that "spinel-rich chondrules and inclusions" are merely samples of the solid assemblage remaining after physical removal of the liquid phase. Because REE would have partitioned themselves between the solid assemblage and the liquid phase, the REE patterns of such inclusions would be expected to exhibit characteristic signs of liquid-solid fractionation processes superimposed upon the usual gas-solid fractionation patterns. A comparison of our inclusions with KORNACKI and FEGLEY's (1984) descriptions of "spinel-rich chondrules and inclusions" suggests that those workers would include at least two objects studied here in this category, BB-3 and BB-6. BB-3 has a normal group III and BB-6 a normal group II REE pattern. Both REE patterns are easily interpretable as being the result of gas-solid fractionation processes and neither shows signs of any additional fractionation process. We conclude that BB-3 and BB-6 did not exchange REE with a liquid phase which was later lost and, therefore, that the model of KORNACKI and FEGLEY (1984) is not applicable to such blue spherules. On the other hand, models for explaining REE patterns of three other hibonite-bearing samples studied here, DJ-2, MUCH-1 and BB-5, require the same gas-solid fractionation process that resulted in the group III pattern of BB-3 to be modified by at least one additional constraint.

For DJ-2, it is preferential uptake of light relative to heavy REE that further constrains the model. For BB-5, it is preferential uptake of Eu relative to Yb and for MUCH-1, it is both of these. The modification used earlier in this paper was crystal-chemical control over the partitioning of REE between each of these samples and either the nebular gas or other solid condensates but we cannot use the REE patterns alone to rule out the possibility that the phase with the complementary REE pattern was liquid. Although a liquid phase might be an acceptable carrier of the REE pattern complementary to that in DJ-2, BAR-MATTHEWS et al. (1982) and MACPHERSON et al. (1983) have presented cogent mineralogical and petrographic arguments against the involvement of a liquid phase in the origin of BB-5 and MUCH-1, respectively.

Origin of hibonite fragments

DJ-2 is a hibonite crystal fragment recovered after freeze-thaw disaggregation of a bulk sample of Murchison. MUCH-1 consists of hibonite removed from an inclusion. Although it is not known whether objects like DJ-2 existed as isolated crystals in Murchison or as parts of inclusions containing other phases, MAC-PHERSON et al. (1983) pointed out that the similarity in major and minor element contents between hibonite fragments like DJ-2 and hibonite crystals in MUCH-1 supports the idea that the fragments could have come from inclusions like MUCH-1. From the difference in steepness between the REE patterns of these two hibonite samples, however, it is clear that DJ-2 did not come from an inclusion exactly like MUCH-1.

REFRACTORY SIDEROPHILES

Re, Os, Ir and Ru are often highly enriched relative to C1 chondrites in refractory inclusions in Murchison, as they are in coarse-grained Allende inclusions. Ir, for example, is enriched in seven of the ten samples studied herein, by factors ranging from 2 to 1750 relative to C1 chondrites. Although Allende coarse-grained inclusions are enriched in Ir by a factor of 15.9 relative to C1 chondrites on average (GROSSMAN et al., 1977), the Ir enrichment factor varies considerably from inclusion to inclusion, the maximum observed by GROSSMAN and GANAPATHY (1976a) being 28. Five of the seven Murchison inclusions that are enriched in Ir have enrichment factors greater than this.

In Allende inclusions, group II REE patterns are almost always accompanied by depletions in refractory siderophiles which average a factor of ~4 but which sometimes reach a factor of 100 compared to C1 chondrites (GROSSMAN and GANAPATHY, 1976b). This is frequently not the case in refractory inclusions in Murchison. While one with a group II pattern, BB-6, shows the normal Ir depletion, another, SH-4, with positive Eu and Yb anomalies superimposed on a group II REE pattern, is enriched in Ir by a factor of 30 relative to C1 chondrites. It is interesting that A-

19, one of the Allende inclusions with such a REE pattern, is also enriched in Ir, this one by a factor of 4.3. Another group II inclusion studied herein, M-11, is enriched in Ir by a factor of 8.5 relative to C1 chondrites. DAVIS and GROSSMAN (1979) calculated amounts of REE that must be added in the form of a flat REE pattern to fractionated REE components produced by prior condensation and removal of ultrarefractory REE in order to best match group II patterns observed in Allende fine-grained inclusions. They found a correlation between Ir contents of such inclusions and amounts of REE that must be added in the flat component. The slope of the correlation line in that work suggests a C1 chondritic Ir/REE ratio in the flat component. According to their model, the REE pattern of M-11 is such that essentially all of the Lu, which is enriched by a factor of 9.5 relative to C1 chondrites, was contributed by the flat component. The relatively large Ir enrichment factor in M-11, 8.5, is about what is expected since the model predicts equal enrichment factors for Ir and Lu in this case. While both components are present within each of the Allende inclusions discussed by DAVIS and GROSSMAN (1979), however, there is some question about this in the case of M-11. Because this sample is a mixture of two inclusions, it is conceivable that only one has a group II pattern with the usual low Ir content and that the other has a group III pattern with a high Ir content. The high Ir concentrations in SH-4 and the Allende inclusion A-19, and in M-11 if both of its constituent inclusions have group II patterns, pose a serious obstacle to the model proposed by FEGLEY and KORNACKI (1984) in which group II inclusions form from aggregates of dust which are depleted in refractory noble metals. The two remaining Murchison inclusions that are depleted in siderophiles are MUCH-1 and BB-5, those with large negative Yb anomalies unaccompanied by Eu anomalies of similar size. In both of these inclusions, most refractory lithophiles have higher enrichment factors than the refractory siderophiles relative to C1 chondrites.

In Allende coarse-grained inclusions, refractory siderophiles are found as nuggets of platinum metal alloys (PALME and WLOTZKA, 1976; WARK and LOVERING, 1976; EL GORESY et al., 1978) up to several μm in size. Although such nuggets were only rarely found by MACPHERSON et al. (1983) in Murchison inclusions, no special search was conducted for them and they could have been easily overlooked at the magnifications normally employed in that study. GROSSMAN (1973) predicted that Ru, Os and Ir would condense from the solar nebula in metallic form and calculated what their condensation temperatures would be if each condensed as the pure element. PALME and WLOTZKA (1976) calculated the fraction of each siderophile element that would condense from a gas of solar composition into a common alloy as a function of temperature. From that work, we have constructed Fig. 3 which shows how the Ir/Os and Ru/Re ratios of condensate alloys vary with temperature at a total
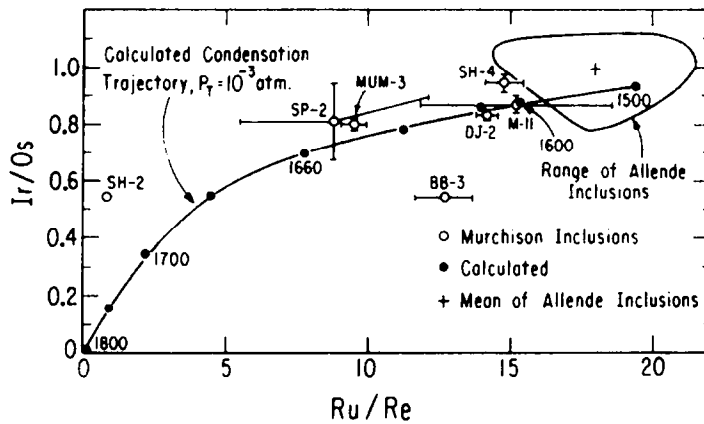
FIG. 3. Refractory siderophile element ratios in refractory inclusions from Murchison compared with those in Allende coarse-grained inclusions and in calculated condensate alloys.

nebular pressure of 10^{-3} atm. Both Os and Re are totally condensed above 1800°K but it is only below this temperature that a significant fraction of the Ir and Ru condense. Thus, the Ir/Os and Ru/Re ratios increase together with falling temperature until the Ir and Ru are also totally condensed at 1500°K, at which point the condensate alloy has Ir/Os and Ru/Re ratios equal to their C1 chondritic values.

Also plotted in Fig. 3 are the Ir/Os and Ru/Re ratios of seven of the Murchison inclusions studied herein as well as the field defined by eight Allende coarse-grained inclusions studied by GROSSMAN and GANAPATHY (1976a) and GROSSMAN et al. (1977). It is seen that the Allende inclusions cluster around the 1500°K calculated point, where these ratios have their C1 chondritic values. As mentioned above, this has been interpreted to mean that each of these elements was totally condensed when Allende coarse-grained inclusions formed, implying that the alloy into which the refractory siderophiles condensed stopped equilibrating with the solar nebular gas at 1500°K or slightly higher, if the total pressure was 10^{-3} atm. In contrast to these, the Murchison inclusions do not cluster around the 1500°K point but have significantly lower Ir/Os and Ru/Re ratios than Allende inclusions, implying that the refractory siderophile condensate alloys in the former have higher equilibration temperatures than those in the latter. Four of the Murchison inclusions lie along the composition trajectory for condensate alloys and three of these, SH-4, DJ-2 and M-11, plot near 1600-1620°K, at the high temperature edge of the field of Allende inclusions. MUM-3 falls very close to the condensate trajectory but clearly distinct from and at a higher temperature, ~1650°K, than all Allende inclusions. These temperatures are compatible with the equilibration temperature of the condensate host phase that contributed REE to DJ-2, M-11 and MUM-3 in that the REE patterns of these inclusions have negative Yb anomalies, indicating that the REE-bearing condensate phase last equilibrated with the solar nebular gas above 1575°K. Two inclusions, SH-2 and BB-3, have drastically lower Ir/Os and Ru/Re

ratios than C1 chondrites and also deviate strongly from the condensate trajectory. Individual metal particles with Ir/Os and Ru/Re ratios very similar to the ratios in SH-2 have been reported from an Allende coarse-grained inclusion by BLANDER et al. (1980). The simplest explanation for the deviations is condensation of the refractory siderophiles remaining in the gas after prior condensation and removal of some of the Os and Re, the most refractory of these elements. Not only will the Ir/Os and Ru/Re ratios of the resulting alloys be higher than their C1 chondritic values after total condensation of the remainder of these four elements but also these ratios will be higher at any given equilibration temperature than in the case of no prior removal. According to this explanation, SH-2 formed after prior removal of much of the Os and BB-3 after removal of some of the Re and possibly some of the Os as well. The refractory siderophile components in both inclusions have much higher equilibration temperatures than those in Allende coarse-grained inclusions. It is interesting that unusually high equilibration temperatures are indicated for both the refractory lithophile and the refractory siderophile components in SH-2. If inclusions such as SH-2 represent a significant fraction of the refractory siderophiles in the reservoir in which they formed, this reservoir must have been distinct from the one in which those inclusions formed that lie along the calculated trajectory in Fig. 3, as the fractionations that give rise to SH-2 would not, in general, lead also to compositions along the trajectory. Thus, just as in the case of the refractory lithophiles, removal of a portion of each of the most refractory siderophiles in an early, very high-temperature condensate is necessary to produce the fractionations observed in some Murchison inclusions and occurred in reservoirs distinct from those that produced the refractory siderophile components in other Murchison inclusions.

NON-REFRACTORY ELEMENTS

GROSSMAN and GANAPATHY (1976a) divided the concentration of every non-refractory element in each

Allende coarse-grained inclusion which they studied by its abundance in the bulk meteorite. They found that Fe, Co and Mn consistently had the lowest normalized abundances of all the non-refractories, attributed them to contamination by Allende matrix material during excavation of inclusion samples from the meteorite and attributed the higher normalized abundances of the remaining non-refractories to indigenous concentrations of these elements in the inclusions. Normalizing the concentrations of non-refractory elements in the inclusions studied in this work to their respective concentrations in bulk Murchison reveals many of the same characteristics but the normalized abundances of Fe, Co and Mn are frequently lower than those in Allende coarse-grained inclusions, resulting in lower average values for each of them, as seen in Table 3. Although the Allende inclusions and five of those from Murchison were dug from their matrices, the other five Murchison samples were obtained by freeze-thaw disaggregation which tends to separate inclusions from matrix more cleanly. As might be expected, the mean normalized abundances in the entire sample of Murchison inclusions are lower than those in the subset which was obtained by excavation. Nevertheless, even when the Allende inclusions are compared to the subset of those from Murchison which were excavated, the former have much higher average normalized abundances of non-refractory elements. It is difficult to believe that we were able to excavate these samples from Murchison more cleanly than those which we dug from Allende and which are one thousand times larger. We thus conclude that the concentrations of even Fe, Co and Mn in the Allende coarse-grained inclusions studied by GROSSMAN and GANAPATHY (1975, 1976a) are largely indigenous, that the Murchison inclusions studied here tend to have lower indigenous concentrations of non-refractory elements than the Allende inclusions and that the levels of matrix contamination in our μgm-sized Murchison inclusions seldom exceed a few percent.

The different concentrations of non-refractory elements in refractory inclusions from the two meteorites are conveniently summarized in Fig. 4 which shows the Cl chondrite-normalized abundances of Na, Cr, Mn, Fe, Co and Ni in the Murchison inclusions along with corresponding literature data for Allende coarse-grained inclusions. Refractory inclusions in both meteorites are generally depleted in these elements relative to Cl chondrites but those in Murchison are more depleted than those in Allende. Except for Cr, the
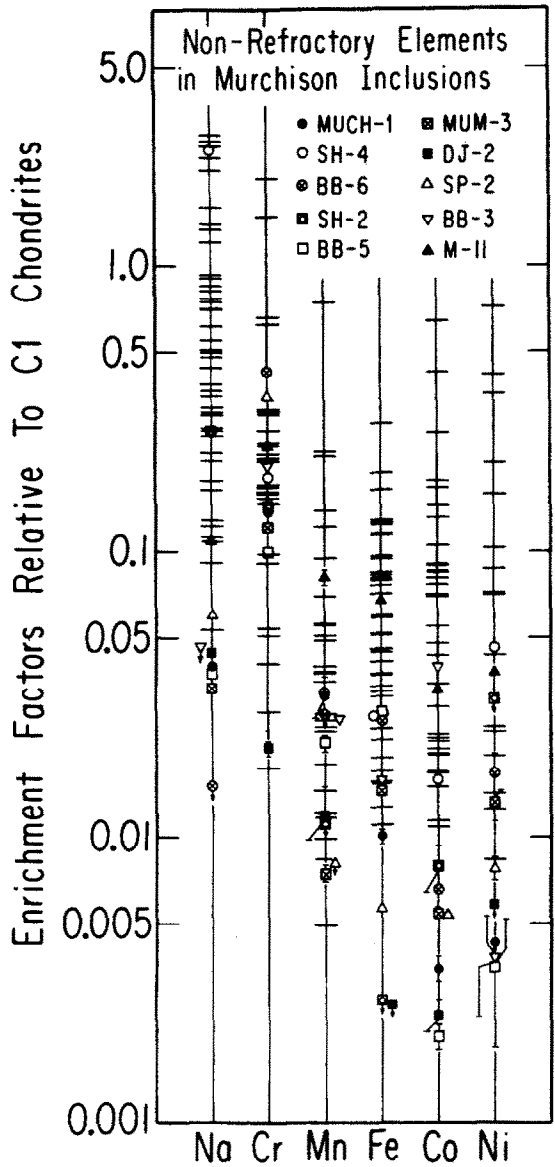

FIG. 4. Most non-refractory elements have lower concentrations in most refractory inclusions from Murchison than in Allende coarse-grained inclusions. The data for Allende coarse-grained inclusions are marked by horizontal lines and are taken from the references listed in Fig. 8 of DAVIS et al. (1982).

concentration range for each non-refractory element in the Murchison inclusions extends from the low end of the concentration range for the same element in Allende coarse-grained inclusions to below it. While Allende inclusions are seldom depleted in non-refractory elements by as much as a factor of one hundred, this is frequently the case for Murchison inclusions.

We have seen that the higher concentrations of non-refractory elements in Allende coarse-grained inclusions are due mostly to greater indigenous amounts of these elements than in the refractory inclusions in Murchison. This is a surprising result, as it is generally believed that non-refractory elements were introduced into these high-temperature condensate assemblages

Table 3. Means and standard deviations of normalized abundances of some non-refractory elements in high-temperature inclusions.

	Mean Concentration in Allende Coarse-Grained Inclusions ÷ Concentration in Bulk Allende	Mean Concentration in Murchison Refractory Inclusions ÷ Concentration in Bulk Murchison	
		Excavated Only	All
Fe	.051 ± .046	.027 ± .019	.020 ± .015
Co	.072 ± .088	.011 ± .009	.010 ± .011
Mn	.064 ± .079	.054 ± .027	.034 ± .026

during relatively low-temperature secondary alteration processes which would be expected to have produced more severe effects on the Murchison inclusions because of their smaller sizes and greater porosities than most of the Allende inclusions. Apparently, the conditions of alteration were more intense and/or their duration longer in the case of Allende coarse-grained inclusions. Of the five samples studied herein which were also studied by BAR-MATTHEWS *et al.* (1982) and MACPHERSON *et al.* (1983), SH-4 and MUCH-1 show the most, and BB-5 the least, petrographic evidence of low-temperature metasomatism. This is confirmed in the present work for SH-4 and BB-5 in that, for each non-refractory element, SH-4 and BB-5 are consistently among the few Murchison inclusions with the highest and lowest concentrations, respectively. Despite petrographic indications that MUCH-1 was altered, however, the hibonite removed from this inclusion and studied herein shows little evidence of this, judging from its very low concentrations of non-refractory elements. DJ-2 is one of the lowest and M-11 one of the highest inclusions in non-refractory elements. Although no direct petrographic information is available for either of these, we may conclude that DJ-2 was not significantly affected by secondary alteration but that M-11 was altered extensively.

Cr is the only non-refractory element which has similar concentrations in Allende and Murchison refractory inclusions but the fact that its C1 chondrite-normalized abundance is higher than those of other non-refractory elements may indicate that, unlike the latter, it was not incorporated during low-temperature alteration of refractory inclusions but, instead, is a primary constituent. Indeed, calculations suggest that small amounts of Cr may condense from a gas of solar composition above $1450°K$ at a total pressure of 10^{-3} atm. by entering into solid solution in spinel.

GROSSMAN and GANAPATHY (1976b) pointed out that a characteristic of Allende fine-grained inclusions is the coexistence therein of group II REE patterns and concentrations of non-refractory elements such as Na, Mn and Fe which are five to ten times higher than in Allende coarse-grained inclusions. Thus, although M-11 and BB-6 have group II REE patterns, they can be distinguished chemically from Allende fine-grained inclusions by their much lower concentrations of these non-refractory elements.

CONCLUSIONS

Refractory inclusions in Murchison fall into four trace element categories. Those in the first have group II REE patterns (M-11, BB-6) or a group II pattern modified by enrichment, rather than depletion, in Eu and Yb (SH-4). Those in the second have group III patterns (MUM-3, BB-3) or a group III pattern modified by preferential uptake of light relative to heavy REE (DJ-2). Those in the third (BB-5, MUCH-1) have large negative Yb anomalies unaccompanied by correspondingly large negative Eu anomalies. It may be

that these condensed originally with group III patterns and preferentially took up Eu in later exchange processes under reducing conditions. Finally, SH-2 has an ultrarefractory REE component in it that has been mixed with a REE component that condensed at lower temperature.

Inclusions with similar petrographic and mineralogical characteristics, such as BB-6 and BB-3, have different REE patterns, indicating that similar refractory assemblages formed in different nebular reservoirs. Also, inclusions with no apparent petrographic similarities to one another, such as MUM-3 and BB-3, have similar REE patterns, indicating that a variety of types of refractory assemblages formed within the same reservoir. The frequency of highly fractionated REE patterns and absence of group I patterns suggest that refractory inclusions in Murchison stopped equilibrating with the nebular gas at higher temperatures than most Allende coarse-grained inclusions which usually have group I patterns. Similarly, the lower Ir/Os and Ru/Re ratios of some Murchison inclusions compared to those of Allende coarse-grained inclusions indicate that noble metal alloys in these Murchison inclusions also stopped equilibrating with the nebular gas at higher temperatures than their Allende counterparts. Murchison inclusions tend to be lower in non-refractory elements than Allende coarse-grained inclusions, suggesting that, on average, the former underwent less severe secondary alteration than the latter.

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