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RARE EARTH ELEMENTS IN CHONDRULES FROM THE FELIX (CO3) CHONDRITE: COMPARISON WITH ALLENDE (CV) CHONDRULES

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Abstract: Abundances of REE, Ba, Sr, Rb, K and Ca in five chondrules and one Ca,Al-rich inclusion examined petrographically and whole rock sample from the Felix carbonaceous chondrite (CO3) were precisely determined by mass spectrometric isotope dilution techniques.

The CI-chondrite normalized REE patterns for five chondrules are almost flat but show more or less anomalies of Ce, Eu and Yb. The same REE features are observed in some Allende porphyritic chondrules suggesting that one of the refractory lithophile precursors of CO and CV chondrules had an unfractionated REE pattern with minor irregularities of Ce, Eu and Yb.

The coarse-grained Ca,Al-rich inclusion, which may be assigned to Type B1, exhibits a Group III REE pattern with a large negative Yb anomaly. This is inconsistent with elemental volatilities since Yb is more depleted than Eu, suggesting that a Eu-enriched component may have been added to normal Group III CAI prior to melting the inclusion precursor.

The REE abundance of bulk Felix is unfractionated (1.6–1.7×CI) with ~20% excess of Ce. Anomalies of Ce and/or Yb, commonly observed in carbonaceous chondrites, can be understood as reflecting gas/solid (or liquid) fractionation processes of chondrule precursors as well as those of Ca,Al-rich inclusions.

1. Introduction

Chondrules and Ca,Al-rich inclusions (CAIs) in carbonaceous chondrites, especially CV3 Allende have been extensively and repeatedly studied since it was realized that they preserve a record of fractionation processes in the early solar system. However, relatively little is known about trace element characteristics of chondrules in CO chondrites. OSBORN *et al.* (1974) reported chemical values obtained by instrumental neutron activation analysis (INAA) of ~50 CO chondrules but presented no REE and petrographic data. MCSWEEN *et al.* (1983) suggested that the chondrules in carbonaceous chondrites (CV and CO) can be separated into two distinct populations in terms of redox state and oxygen isotopic composition. Recently, RUBIN and WASSON (1987) analyzed 17 chondrules from Ornans by INAA and suggested possible chondrule precursor components.

Earlier, we demonstrated the existence of REE fractionations among Allende chon-

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drules (MISAWA and NAKAMURA, 1988). To search for a possible fine structure of REE patterns of chondrules, we have undertaken accurate analyses of REE as well as other trace elements by improved mass spectrometric isotope dilution (MSID) techniques. In this paper, precise trace element data along with major element data for the constituents of the Felix (CO) chondrite (chondrules and CAI) are presented and fractionation processes in the solar nebula are discussed.

2. Analytical Method

All chondrules were separated mechanically from a 1.1 g chip of Felix (USNM 235, Smithsonian Inst. NMNH) by freeze-thaw processing in distilled water. Ornans-subtype chondrites are characterized by a high density of small (~0.2 mm in diameter) size-sorted chondrules and inclusions in fine-grained matrix (KING and KING, 1978). The size of chondrules analyzed in this study was from 0.472 to 1.228 mg in total weight. After ultrasonic cleaning in distilled acetone, each chondrule was broken into two parts of approximately equal size using an agate mortar. One half was used for trace element analyses and the residual fragments were used to prepare a thin section for petrographic observations. In addition, a 12 mg-size ultrafine fraction (<50 μm) produced by freeze-thaw processing was analyzed as a "bulk chondrite" sample.

Constituent minerals were identified using a HITACHI S530 scanning electron microscope (SEM) at Kyoto University, equipped with a HORIBA EMAX-2200 energy dispersive X-ray detector (EDX) and operated at 20 kV accelerating voltage and 1.5 nA beam current. The minerals were then analyzed with a JEOL JCXA-733 electron probe microanalyzer (EPMA) at Ocean Research Institute, operated at 15 kV accelerating voltage and 1.2 nA beam current. The bulk chemical compositions of chondrules and CAI were determined, avoiding metal phase, by a defocused beam of 50 μm in diameter, for over 700 s. The analytical data were corrected according to BENCE and ALBEE (1968) and ZAF, with further correction for chondrules by the method of IKEDA (1980).

Abundances of REE, Ba, Sr, Rb, K and Ca were determined by MSID techniques (NAKAMURA, 1974; MISAWA and NAKAMURA, 1988). In this study, the conventional chemical treatment was carried out using the cation exchange resin (DOWEX AG 50W-X12, 200–400 mesh). The analytical precision for the elements is considered to be ~3% or better.

3. Results and Discussion

3.1. Petrography

Petrographic descriptions of the Felix chondrules and CAI analyzed for trace elements are presented in Table 1. All chondrules show porphyritic texture with mainly olivine and/or pyroxene. Olivines in each chondrule are Mg-rich, with a large proportion in the range of Fa_{0-10}. Some olivines in chondruels #4 and #5, which are poikilitically enclosed by twinned clinoenstatite, are more fayalitic (~Fa_{25}). Sulfide and metallic Fe, Ni form discrete rims around the chondrules. Coarse-grained rims composed of olivine and low-Ca pyroxene (RUBIN, 1984) were not observed in the chondrules examined in this study.

Table 1. Descriptions of chondrules and CAI used for trace element analyses.

Sample	Petrographic description
#2	Coarse-grained Type B1 Ca,Al-rich inclusion. Melilite (Åk=~17) enclosing a core of Ti,Al-rich pyroxene (TiO_2=~12 wt%, Al_2O_3=~20 wt%) containing abundant spinel. Submicron-sized Pt-group metal nuggets in melilite and perovskite grains in Ti,Al-rich pyroxene.
#4	Porphyritic texture with olivine ($Fa_{0.3-22}$) and pyroxene ($Wo_{0.6-2.8}En_{99.0-91.4}Fs_{0.4-5.8}$).
#5	Poikilitic texture with low-Ca pyroxene oikocrysts ($Wo_{0.7}En_{98.6}Fs_{0.7}$) enclosing small olivine ($Fa_{0.7-24.4}$) grains.
#6	Porphyritic texture with olivine ($Fa_{1.6-7.2}$) and polysynthetically twinning clinoenstatite in minor mesostasis.
#7	Porphyritic texture with olivine ($Fa_{0.5-5}$) and low-, and high-Ca pyroxene ($Wo_{1-5}En_{99-93}Fs_{0-2}$, $Wo_{44}En_{56}$).
#30	Porphyritic texture with euhedral olivine ($Fa_{0.8-3}$) in glassy mesostasis. Minor metallic Fe,Ni and sulfide.

3.2. Major and minor element composition

The bulk chemical compositions of the chondrules and CAI are listed in Tables 2 and 3. The major element compositions of the chondrules are almost within the range

Table 2. Bulk chemical compositions of the Felix chondrules obtained by EPMA defocused beam analyses (values in wt%).

Chdl	#4	#5	#6	#7	#30
SiO_2	45.35	49.44	45.16	43.82	41.48
Al_2O_3	6.95	2.87	4.93	2.00	3.11
Cr_2O_3	0.67	0.82	0.86	0.38	0.53
FeO	4.51	4.44	5.49	1.94	4.72
MnO	0.09	0.09	0.18	0.06	0.05
MgO	35.30	36.99	37.99	47.27	43.26
CaO	3.67	1.81	3.12	1.99	2.10
Na_2O	0.47	0.08	0.07	0.03	0.97
Total	97.01	96.54	97.80	97.49	96.22

Table 3. Bulk chemical composition of Type B1 Ca,Al-rich inclusion #2 from Felix obtained by EPMA defocused beam analyses (values in wt%).

	CAI #2
SiO_2	23.15
TiO_2	2.55
Al_2O_3	33.44
FeO	0.28
MgO	9.43
CaO	28.70
Cr_2O_3	0.12
Total	97.67

Table 4. Bulk chemical compositions of chondrules and CAI from Felix obtained by mass spectrometric isotope dilution analyses (values in ppm, otherwise stated).

	#2	#4	#5	#6	#7	#30	bulk**
Sample wt (μg)	850	1175	>1056*	569	1228	472	1.1 (g)
Dissolved wt (μg)	545	674	555	334	493	181	11.974 (mg)
Ca (%)	20.7	2.14	2.00	2.07	1.59	2.99	n.d.
K	44.5	659	503	363	222	461	n.d.
Rb	0.173	2.12	1.83	1.31	0.870	1.80	n.d.
Sr	155	42.8	36.4	42.5	25.8	9.52	n.d.
Ba	16.4	4.81	4.86	12.3	5.06	8.18	n.d.
La	4.33	0.728	n.d.	n.d.	0.347	0.511	0.434
Ce	11.0	1.96	1.83	n.d.	0.950	1.35	1.31
Nd	8.89	1.45	1.05	n.d.	0.688	1.02	0.797
Sm	3.03	0.464	0.356	n.d.	0.227	0.334	0.255
Eu	1.09	0.119	0.107	n.d.	0.0921	0.150	0.0948
Gd	3.89	0.624	0.467	n.d.	0.301	0.440	0.337
Dy	4.80	0.735	0.483	n.d.	0.365	0.552	0.421
Er	3.08	0.467	0.313	n.d.	0.246	0.359	0.276
Yb	1.96	0.426	0.318	n.d.	0.250	0.371	0.281
Lu	0.527	0.0714	0.0528	n.d.	0.0392	0.0565	0.0447

* Sample #5 is fragment of chondrule.
** Fine-grained (<50 μm) fraction produced by freeze-thaw processing.
n.d.=not determined.

of those of ferromagnesian chondrules analyzed by SIMON and HAGGERTY (1980) and MCSWEEN *et al.* (1983). Coarse-grained CAI #2 may be assigned to Type B1 (WARK and LOVERING, 1977) from its texture, constituent mineral assemblage and chemical composition. The results of MSID analyses for the chondrules, CAI and fine-grained fraction of the "bulk chondrite" are given in Table 4.

3.3. *REE fractionation*

In Figs. 1 and 2, CI-normalized REE abundance patterns for the "bulk chondrite", chondrules and CAI are shown. The REE abundance of "bulk chondrite" is 1.6–1.7 ×CI and is consistent with INAA results (KALLEMEYN and WASSON, 1981), except that a significantly large positive Ce anomaly (~20%) is found in this study. Minor irregularities at Ce and/or Yb have been reported for many carbonaceous chondrites (*e.g.*, TANAKA and MASUDA, 1973; MASUDA *et al.*, 1973; NAKAMURA, 1974; EVENSEN *et al.*, 1978). These REE irregularities are generally explained as the heterogeneous distribution of anomalous REE component(s) in carbonaceous chondrites. From the REE abundance pattern of bulk Felix, a specific object with positive Ce anomaly is expected.

Rare earth abundances in individual chondrules are 1.5–4×CI and show positive or negative Eu anomalies. In several cases, minor irregularities at Ce (chondrules #4 and #7) and Yb (chondrules #4, #5 and #7) are observed. Since solid/liquid partitioning of elements under planetary conditions cannot produce such anomalies (SCHNETZLER and PHILPOTTS, 1970), gas/solid (or liquid) processes in the nebula may have been

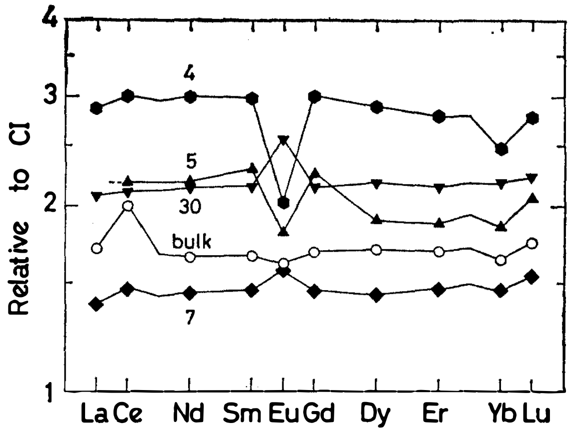

Fig. 1. CI-normalized REE patterns of individual chondrules from Felix (numbers correspond with those in Tables 1, 2 and 4). The abundance pattern for a fine-grained fraction of the "bulk chondrite" is also shown in open symbol. Normalization factors are taken from the Orgueil data (NAKAMURA, 1974).

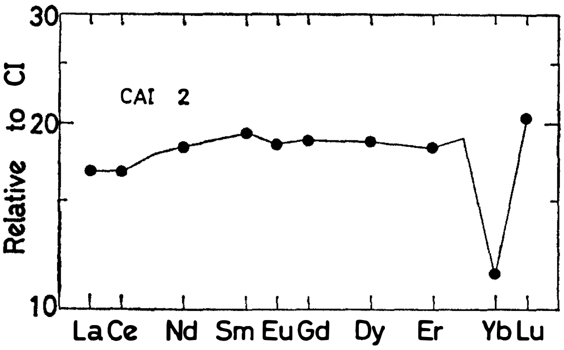

Fig. 2. CI-normalized REE abundance pattern of coarse-grained CAI from Felix.

responsible for the observed REE fractionations in the chondrules. Besides the five chondrules under consideration, two unique Al- and Ca-rich chondrules ($Al_2O_3 > 7$ wt%, $CaO > 5$ wt%) show large positive Ce anomalies (40–50%; unpublished data), which substantiate the REE pattern for the "bulk chondrite".

Calcium,Al-rich inclusion #2 shows a nearly flat REE pattern with an enrichment factor of $17–21 \times$CI and a large negative Yb anomaly. This may be classified as a Group III REE pattern but the Eu abundance appears unusual. The negative Yb anomaly is not accompanied by a Eu anomaly of comparable size. From the condensation calculations, it is suggested that Eu is more volatile than Yb (KORNACKI and FEGLEY, 1986). Thus, one of the possible explanations of this pattern is that the precursor material of CAI #2 originally had negative Eu and Yb anomalies of equal magnitude (like the normal Group III pattern) with Eu being added to it as a later stage condensate. This would leave the relative abundances of trivalent REE unaffected. Alternatively, the REE pattern represents complicated history or non-equilibrium origin of the inclusion precursors. Similar Group III REE patterns having lower CI-normalized Yb abundances than that of Eu were observed in meteoritic hibonites, especially in CM2 Murchison (*e.g.*, FAHEY *et al.*, 1987).

3.4. *Moderately volatile lithophile elements, K and Rb*

Abundances of alkalis in the Felix chondrules vary from 0.4 to $1.2 \times$CI but alkalis in CAI #2 are strongly depleted ($\sim 0.08 \times$CI). In Fig. 3, Rb is plotted against K for the Felix chondrules. Regardless of different bulk chemical compositions, the chondrules have a constant K/Rb ratio, close to that of CI's. The most straightforward interpretation for this observation in the Felix (CO) and Allende (CV) chondrules is that evaporative loss of alkalis accompanied by K/Rb fractionation was not significant

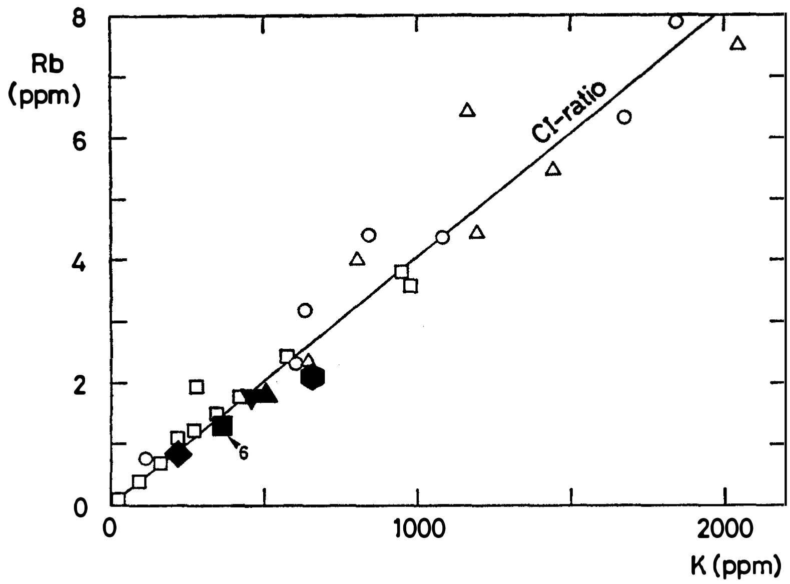

Fig. 3. Rb vs. K variation of chondrules in Felix. Symbols are the same as in Fig. 1. Chondrule ♯6 was analyzed for alkalis and alkali earths only. Open symbols represent the Allende chondrules; circles barred olivine type; triangles, pyroxene-rich type; squares; olivine-rich type after MISAWA and NAKAMURA (1988). Chondrules from CO and CV chondrites show a linear trend which correlates with the CI K/Rb ratio.

during the melting event (MISAWA and NAKAMURA, 1988). In addition, the lack of a correlation between alkali abundance and chondrule mass is also considered to support the interpretation that alkali loss from chondrules was minor.

Figure 4 shows a plot of K *vs.* Sm for the Felix chondrules. As is the case for the Allende chondrules, K is positively correlated with Sm. The correlation between alkalis and REE was also observed in Ornans (CO) chondrules (RUBIN and WASSON, 1987). From the above results, it is suggested that elemental distributions in the precursor materials had not been established by the sequential fractional condensation, and that the refractory lithophile precursor component of CO and CV chondrules was alkali-bearing. This component was probably formed by the reaction of refractory lithophiles with alkali-rich gas in the solar nebula prior to chondrule formation.

3.5. Refractory lithophile elements, Sr, Ba and Ca

Abundances of alkaline earths in the Felix chondrules vary from 1.2 to 5.4×CI. In Figs. 4 and 5, plots of Ca *vs.* Sm, Sr *vs.* Sm and Ba *vs.* Sm for the Felix chondrules are shown along with those for Allende. Refractory lithophile Ca, Sr and Ba are positively correlated with REE. In the Felix chondrules, Sm-Sr data points deviate from the CI ratio, and Sr is enriched relative to REE as also observed in some Allende chondrules. The presence of Sr-rich refractory lithophile precursors could be a possible explanation for these enrichments. High Sr and Ba concentrations were reported in a CAI from Essebi (CM2) (EL GORESY *et al.*, 1984). In any case, further study may be required to confirm this explanation.

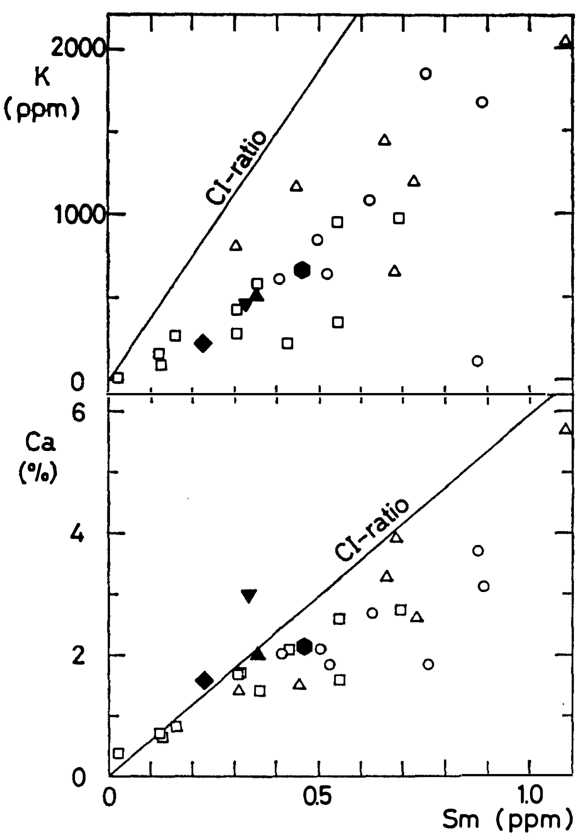

Fig. 4. (Upper) K vs. Sm variation of chondrules in Felix. The refractory trace element, Sm, and moderately volatile K correlate positively in the Felix chondrules.
(Lower) Ca vs. Sm variation of chondrules in Felix. The refractory major element, Ca, and the refractory trace elements, Sm, correlate positively in the Felix chondrules. Open symbols represent the Allende chondrules (MISAWA and NAKAMURA, 1988). Symbols are the same as in Figs. 1 and 3.

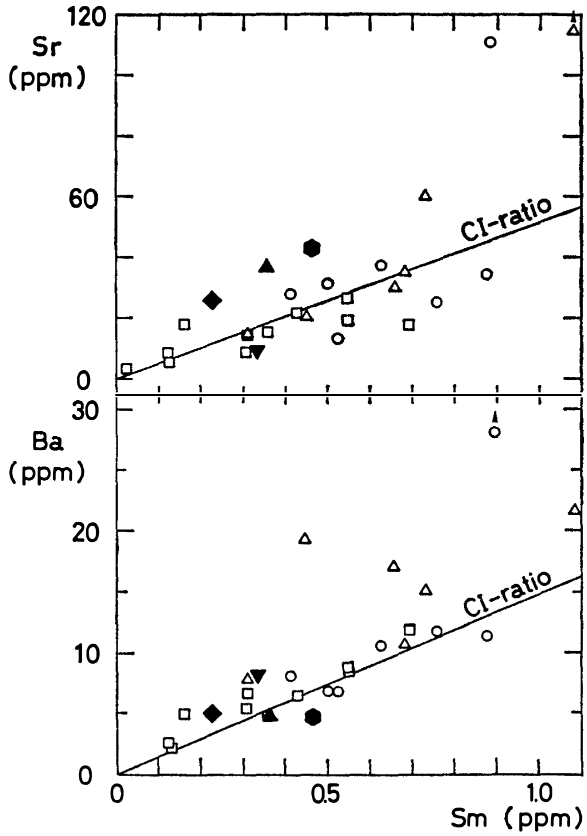

Fig. 5. Sr vs. Sm variation (upper) and Ba vs. Sm variation (lower) of chondrules in Felix. For Felix (CO) and Allende (CV) chondrules, positive correlations are observed among refractory trace elements, Sr, Ba and Sm. Open symbols represent the Allende chondrules (MISAWA and NAKAMURA, 1988). Symbols are the same as in Figs. 1 and 3.

4. Summary and Conclusions

The trace element characteristics of the Felix chondrules described here do not differ from the most common feature found in the Allende chondrules (MISAWA and NAKAMURA, 1988).

Regardless of different bulk chemical compositions and chondrule mass, the Felix chondrules have a constant K/Rb ratio, close to that of CI's suggesting that evaporative alkali loss during chondrule-forming melting events was not significant.

As is the case of the Allende chondrules, REE abundances for individual Felix chondrules range from 1.5 to $4\times$CI and show minor anomalies of Eu, Ce and Yb, indicating that gas/solid (or liquid) processes generating specific REE fractionations took place during formation of refractory precursors, and also that these fractionation processes were ubiquitous in the region of the nebula where CO and CV chondrule precursors formed.

From the positive correlation between alkalis and REE in CO and CV chondrules, we conclude that elemental distributions in the precursor materials had not been established in fractional condensation sequences during cooling from an initially hot gas and that one of the refractory lithophile precursor components was alkali-bearing.

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