



## REE abundances in the matrix of the Allende (CV) meteorite: Implications for matrix origin

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**Abstract**—The trace element distributions in the matrix of primitive chondrites were examined using four least-contaminated matrix specimens from the polished sections of the Allende (CV) meteorite. Analysis of rare earth element (REE), Ba, Sr, Rb, and K abundances by isotope dilution mass spectrometry revealed that the elemental abundances of lithophile elements except for alkali metals (K, Rb) in the specimens of the Allende matrix studied here are nearly CI (carbonaceous Orgueil) chondritic ( $\sim 1 \times \text{CI}$ ). Compared to refractory elements, all the matrix samples exhibited systematic depletion of the moderately volatile elements K and Rb ( $0.1\text{--}0.5 \times \text{CI}$ ). We suggest that the matrix precursor material did not carry significant amounts of alkali metals or that the alkalis were removed from the matrix precursor material during the parent body process and/or before matrix formation and accretion. The matrix specimens displayed slightly fractionated REE abundance patterns with positive Ce anomalies (CI-normalized La/Yb ratio = 1.32–1.65; Ce/Ce\* = 1.16–1.28; Eu/Eu\* = 0.98–1.10). The REE features of the Allende matrix do not indicate a direct relationship with chondrules or calcium-aluminum-rich inclusions (CAIs), which in turn suggests that the matrix was not formed from materials produced by the breakage and disaggregation of the chondrules or CAIs. Therefore, we infer that the Allende matrix retains the REE features acquired during the condensation process in the nebula gas.

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### INTRODUCTION

Matrices in unequilibrated chondritic meteorites, particularly in CV and CO chondrites, are widely believed to preserve a record of the accretion process of the meteorite parent bodies. To tap this information, the mineralogical and textural characteristics and chemical compositions in the matrix of the Allende (CV) chondrite have been studied extensively (e.g., Scott et al. 1988; Brearley 1996; Bland et al. 2003).

While many authors argue that matrix materials are nebula products and experienced extensive astrophysical alteration together with chondrules, calcium-aluminum-rich inclusions (CAIs), and amoeboid olivine aggregates (AOAs) (e.g., Krot et al. 1995), some authors favor an accretion origin from other components, such as chondrules (e.g., Housley and Cirlin 1983).

The results of trace element analyses have been reported

for the major constituent components of the Allende meteorite, such as chondrules, CAIs, and the matrix, and these results have raised important constraints on the condensation origins (Mason and Taylor 1982; Misawa and Nakamura 1988a). However, it seems likely that many chemical analyses of the matrix cannot avoid the effects of contamination from CAIs, chondrules, or isolated minerals that are enriched in refractory trace elements, although some analyses for separated matrix have been reported (Tanaka and Masuda 1973; Rubin and Wasson 1987; Bland et al. 2003).

In this work, the most pure (i.e., least contaminated) matrix material was excavated from sections using a microdrilling apparatus, and precise measurements of the abundances of rare earth elements (REEs) and other lithophile elements were analyzed by isotope dilution mass spectrometry (Nakamura et al. 1989). Based on the abundances of lithophile element in the Allende matrix, we argue that the matrix material is of nebula origin.

## EXPERIMENTAL PROCEDURES

We prepared two polished sections of the Allende (CV) chondrite, labeled *M2* and *M3* (160  $\mu\text{m}$  and 130  $\mu\text{m}$  in thickness, respectively), using resin (petropoxy 154, Maruto) and an adhesive agent. These sections were polished using distilled water and then ultrasonicated in superfine ethanol before trace element analysis.

Backscattered electron scanning electron microscopy (BSE-SEM) was employed to select areas of the matrix material notably lacking in chondrules, CAIs, and isolated mineral grains (i.e., the purest areas of matrix) for analysis. The bulk chemical compositions of four of these pure matrix areas were then determined by electron probe microanalysis (EPMA; 733, JEOL) using a defocused beam (50  $\mu\text{m}$  in diameter) at 15 kV accelerating voltage and 10 nA beam current. The chemical compositions of the constituent silicate phases were elucidated using a focused beam (2  $\mu\text{m}$  in diameter) operated under the same conditions. The Bence-Albee matrix correction method was applied to the results.

After BSE-SEM observations and EPMA analyses, four petrographically characterized areas (*M2-B1*, *M2-B2*, *M3-A1*, *M3-B1*; 0.3 mm radius; 0.10–0.15 mm deep; 73.9–110.5  $\mu\text{g}$  in weight) were selected to excavate matrix samples using a microdrill under a binocular microscope for isotope dilution mass spectrometry. These pure matrix materials are considered to contain the least amounts of contaminants of fragmental CAIs and/or chondrules, although it is still possible that much smaller fragments ( $\ll 100 \mu\text{m}$ ) may be included in the interior of samples. Nevertheless, inclusion of fragmental chondrules and CAIs may not be significant in consideration from REE patterns as mentioned later.

The matrix samples were weighed using a microbalance (precision 0.2  $\mu\text{g}$ ), spiked, acid-decomposed, and then subjected to isotope dilution using a mass spectrometer (JMS-05RB, JEOL). As the individual specimens were too small for conventional chemical procedures, all samples were analyzed for trace elements by direct loading isotope dilution mass spectrometry (DL-IDMS; Nakamura et al. 1989). The analytical precision ( $2\sigma_m$ ) of trace elements was better than  $\sim 3\%$  for alkalis and better than  $\sim 5\%$  (a few cases were  $\sim 10\%$ ) for REEs. Blank effects on the lithophile trace elements in the matrix samples were 1–3% or less, except for barium ( $< 10\%$ ). For REE analyses of whole rock samples, conventional chemical treatment was carried out using cation exchange resin (50W-X12, Dowex; 200–400 mesh).

In this study, the resin and adhesive agent were also analyzed to estimate the effect of contamination on the matrix compositions. A careful inspection indicated that the matrix samples analyzed here contained significant amounts of resin and very minor amounts of adhesive agent. Based on binocular microscope observation and densities, we estimated that the resin made up about 5% by weight of the sample, and the adhesive agent made up much less than 1%. To estimate

the effects of these contaminants on the trace element data of the matrix, the remaining and unused resin and adhesive agent were also analyzed. The obtained concentrations (in ppm) were: K = 35, Rb = 0.057, Sr = 0.11, Ba = 0.63, La = 0.34, Ce = 0.91, Nd = 0.17, Sm = 0.18, Eu = 0.0056, Gd = 0.041, Dy = 0.034, Er = 0.016, and Lu = 0.0048 in the resin and La = 0.024, Ce = 0.11, Nd = 0.016, Sm = 0.018, and Gd = 0.0055 in the adhesive agent. The effects of the trace elements in the resin were: K 0.5–1.8%, Sr 0.5% or less, Ba 1% or less, La 4–5%, Ce 4%, Nd 1.5–2%; Eu  $\sim 0.5\%$  or less, and other elements  $< 0.5\%$ . The effect of the adhesive agent was negligible. Therefore, the effects of these contaminants mostly fell within the precision of mass spectrometry and/or procedural blanks. Although the estimated amounts of resin and adhesive agent include some uncertainty, careful observations of thin sections and drilled matrix materials suggested that the amount of resin contaminant in the matrix specimens is never more than 10%. In addition, the concentrations of La and Ce in the resin are similar to those in the pure matrix. Thus, even if larger amounts of resin contaminant are assumed, the REE patterns of the matrix should not be affected significantly by these contaminants. All trace element data discussed in this work have been corrected for these contaminants.

For evaluation of the possible redistribution of REEs between the matrix and chondrules during alteration processes, the degree of alteration of 24 chondrules was also determined. The REE abundances in several chondrules studied here have been determined previously (Misawa and Nakamura 1988a).

## RESULTS AND DISCUSSION

### Petrography

All four specimens of the Allende matrix are porous and consist of fine-grained aggregates of primarily Fe-rich olivine ( $\text{Fo}_{50.6}$  average) with minor amounts of Ca-rich pyroxene ( $\text{Fs}_{14-35}\text{Wo}_{43-50}$ ), andradite, nepheline, sodalite, iron-nickel (Fe-Ni) metals, pyrrhotite, and pentlandite, consistent with the observations of Scott et al. (1988) and Krot et al. (1998).

One representative area (*M3-A1*) chosen for IDMS analysis is shown in Fig. 1, and the bulk chemical compositions of the matrix specimens obtained by defocused beam analysis are listed in Table 1. The chemical compositions of the matrix are Fe-rich and Mg-poor compared with the Allende chondrules' composition (Brearley 1996). Although the bulk composition of the four matrix specimens were similar to those of McSween and Richardson (1977) and Zolensky et al. (1993), the Fe/(Fe + Mg) ratios obtained here (0.51–0.52) are slightly higher than in previous studies (Fe/(Fe + Mg) = 0.470, McSween and Richardson 1977; 0.500, Zolensky et al. 1993; 0.44, Clarke et al. 1970) (see Table 1). This may suggest that the present matrix samples are the least contaminated by Mg-rich

Table 1. Bulk chemical compositions (wt%) of the “pure” matrix from the Allende (CV) chondrite determined by defocused beam analysis.

	<i>M2</i>		<i>A1</i>	<i>M3</i>		Previous <sup>a</sup>	
	<i>B1</i>	<i>B2</i>		<i>B1</i>		<i>MR77</i>	<i>Zol93</i>
SiO <sub>2</sub>	28.66	28.46	26.87	27.86	28.00	29.56	
TiO <sub>2</sub>	b.d. <sup>b</sup>	b.d.	b.d.	b.d.	0.09	0.09	
Al <sub>2</sub> O <sub>3</sub>	2.12	2.38	1.61	1.64	2.30	1.69	
Cr <sub>2</sub> O <sub>3</sub>	0.48	0.38	0.43	0.24	0.38	0.49	
FeO	37.01	34.55	36.60	36.12	31.9	36.86	
NiO	1.60	1.59	1.66	1.57	1.83	0.63	
MnO	0.21	0.20	0.22	0.21	0.21	0.2	
MgO	19.17	18.03	19.30	19.19	20.2	20.65	
CaO	1.57	3.14	1.24	1.11	2.37	0.22	
Na <sub>2</sub> O	0.15	0.21	0.05	0.32	0.22	0.05	
K <sub>2</sub> O	b.d.	b.d.	b.d.	b.d.	0.01	0.0	
P <sub>2</sub> O <sub>5</sub>	0.16	0.23	0.21	0.03	n.d. <sup>c</sup>	0.15	
SO <sub>3</sub>	2.20	1.93	2.05	2.05	2.82	1.13	
Cl	b.d.	b.d.	b.d.	b.d.	n.d.	n.d.	
Total	93.33	91.1	90.24	90.34	90.33	91.72	
Fe(Fe + Mg) <sup>d</sup>	0.520	0.518	0.515	0.514	0.470	0.500	

<sup>a</sup>*MR77*: McSween and Richardson (1977); *Zol93*: Zolensky et al. (1993).

<sup>b</sup>b.d. = below detection limits (3 $\sigma$ ): 0.05 for K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>, 0.07 for TiO<sub>2</sub>.

<sup>c</sup>n.d. = not determined.

<sup>d</sup>FeO/(FeO + MgO) mol%.

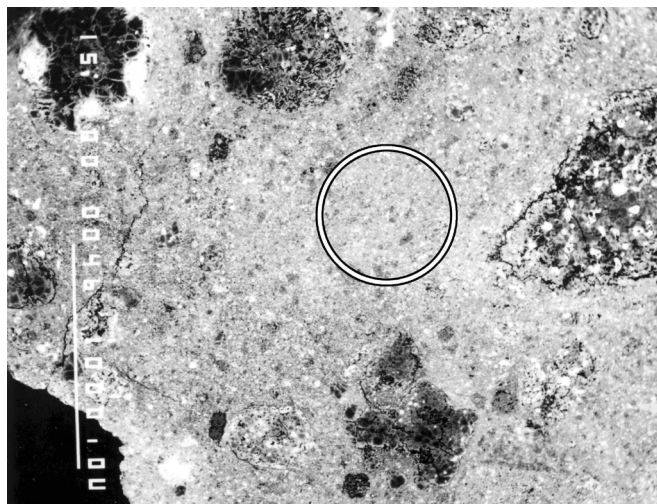


Fig. 1. Backscattered electron image of the matrix of the Allende chondrite *M3-A1*. The excavated area is indicated by a circle (0.6 mm diameter). This area does not contain any fragments of chondrules or minerals but does contain some Ca-rich pyroxene grains (fine gray). The width of the photograph is 3 mm.

chondrules or fragments. The higher content of Ca in *M2-B2* is due to the heterogeneous distribution of Ca-rich pyroxene, as noted in Fig. 1. The alkali content (Na and K) in the matrix is variable (0.05–0.3 wt% for Na<sub>2</sub>O and <0.02% for K<sub>2</sub>O).

### Depletion of Alkali Metals in the Matrix

Table 2 shows the results of DL-IDMS. The lithophile element abundances in the matrix specimens are normalized

to those of the CI chondrite Orgueil (K, Rb, Sr, Ba [Anders and Grevesse 1989], REE [Nakamura 1974; Fig. 2]). Except for K and Rb, the chondrite-normalized lithophile element abundance patterns for the specimens from sections *M2* and *M3* are essentially flat at the CI-chondritic level ( $\sim 1 \times \text{CI}$ ) but have slightly elevated La, Ce, Ba, and Sr abundances. As shown in Fig. 2, all the matrix specimens exhibit systematic depletions of the moderately volatile alkali metal elements K and Rb ( $0.1\text{--}0.5 \times \text{CI}$ ) compared to refractory elements. CAIs and some chondrules are enriched in REEs and alkali metals (Mason and Taylor 1982; Misawa and Nakamura 1988a; Matsuda et al. 1990). As mentioned previously, this feature is consistent with the Na data in Table 1 obtained by EPMA. The alkali abundances previously reported for the matrix are higher (K  $0.4\text{--}0.5 \times \text{CI}$ ; REE  $1.0\text{--}1.8 \times \text{CI}$  by INAA; Rubin and Wasson 1987) than obtained here, possibly due to the admixture of components that are relatively enriched in alkalis, such as alteration products, and some types of CAIs and chondrules. Variable abundances of K and Rb ( $0.1\text{--}0.5 \times \text{CI}$ ) in the matrix specimens reflect the inhomogeneous distribution of alkali metal carriers (mainly nepheline).

The origin of the matrix material can be inferred by comparing the trace element abundances (particularly REEs and alkali metals) of the matrix with those of chondrules (and CAIs).

Figure 3 compares the abundances of K and Rb in the matrix with those in the Allende chondrules (Misawa and Nakamura 1988a). Here, most of the rim material adhering to the chondrules was removed from the specimen during sample processing. The alkali (particularly Rb) abundances in the majority of chondrules ( $0.2\text{--}3 \times \text{CI}$ ) are much higher than

Table 2. Lithophile trace element abundances of the matrix and whole rock samples from the Allende meteorite.<sup>a</sup>

wt <sup>b</sup> (μg)	<i>M2-B1</i>	<i>M2-B2</i>	<i>M3-A1</i>	<i>M3-B1</i>	<i>Mean</i> <sup>c</sup>	<i>W.R.</i> <sup>d</sup>
	107.6	110.5	98.4	73.9		
K (ppm)	71.0 ± 0.5	150 ± 3	68.2 ± 0.8	336 ± 4	n.d. <sup>e</sup>	265
Rb (ppm)	0.249 ± 0.002	0.479 ± 0.007	0.242 ± 0.003	0.543 ± 0.012	n.d.	n.d.
Sr (ppm)	7.40 ± 0.20	7.83 ± 0.15	14.7 ± 0.6	10.9 ± 0.3	n.d.	n.d.
Ba (ppm)	2.64 ± 0.04	3.35 ± 0.10	4.43 ± 0.07	5.31 ± 0.15	n.d.	4.85
La (ppm)	0.369 ± 0.029	0.322 ± 0.001	0.389 ± 0.012	0.362 ± 0.017	0.373	0.507
Ce (ppm)	0.983 ± 0.029	n.d.	1.15 ± 0.04	0.971 ± 0.107	1.035	1.33
Nd (ppm)	0.492 ± 0.021	0.508 ± 0.021	0.518 ± 0.021	0.426 ± 0.009	0.479	1.00
Sm (ppm)	n.d.	n.d.	n.d.	n.d.	n.d.	0.330
Eu (ppm)	0.0607 ± 0.0035	0.0704 ± 0.0140	0.0569 ± 0.0019	0.0532 ± 0.0029	0.0569	0.113
Gd (ppm)	0.187 ± 0.015	n.d.	0.193 ± 0.014	0.177 ± 0.018	0.186	0.414
Dy (ppm)	0.225 ± 0.024	n.d.	0.280 ± 0.090	0.180 ± 0.028	0.228	0.504
Er (ppm)	n. d.	n.d.	0.161 ± 0.011	n. d.	0.154	0.303
Yb (ppm)	0.186 ± 0.012	n.d.	0.177 ± 0.006	0.146 ± 0.020	0.169	0.315
Lu (ppm)	n.d.	n.d.	n.d.	n.d.	n.d.	0.0465

<sup>a</sup>All concentration data were blank and resin corrected.

<sup>b</sup>Weights of samples dissolved for isotope dilution.

<sup>c</sup>The mean composition of *M2-B1*, *M3-A1*, and *M3-B1*.

<sup>d</sup>The mean composition of two whole rock samples.

<sup>e</sup>n.d. = not determined.

those in matrix materials, and K and Rb in the matrix are clearly depleted compared to the chondrules, suggesting that the matrix precursor material did not carry significant amounts of alkali metals or that alkalis were removed from the precursor during the parent body processes (Krot et al. 1995 and 2003) and/or before matrix formation and accretion (Kimura and Ikeda 1995).

As demonstrated here, the low alkali metal abundances in the pure matrix give a important hint in terms of understanding the parent body alteration processes that may have produced high-Fe olivine (Krot et al. 2003). If alteration occurred under aqueous conditions, alteration fluids might also be accompanied by high alkali metals, which may yield high alkalis in the matrix. However, this is not the case for the Allende matrix. We suspect that alkali metals were removed from the matrix and transferred to the chondrules or CAIs during parent body alteration. This interpretation is consistent with younger Rb-Sr model ages of most chondrules and some CAIs (Gray et al. 1973; Tatsumoto et al. 1976). Alternatively, alteration occurred under dry conditions, and alkali fluids were introduced locally into the matrix at a later time. However, this interpretation appears to be less consistent with the fact that the whole rock Rb-Sr isotopic system of the Allende meteorite has been closed since its formation (Gray et al. 1973).

### REE Fractionation and Origin of Matrix

As shown in Figs. 2a and 2b, the chondrite-normalized Sr concentrations are slightly but systematically less than those of Ba, which are relatively similar to those of La. The abundances of La, Nd, and Eu in *M2-B2* are mostly in agreement with those in *M2-B1*. *M3-A1* has REE abundances

quite similar to those in *M3-B1*, although a minor systematic difference is observed between the two specimens. *M2-A1*, *M2-B1*, and *M3-A1* exhibit a uniformly flat pattern from Nd to Lu, with significant enrichment in La and Ce relative to heavy REEs (CI-normalized La/Yb ratio = 1.32–1.65) accompanying relatively high Ba and Sr. Although small Ce variability relative to La and Nd (Ce anomaly) is common in chondritic materials, typically CAIs, and chondrules (e.g., Tanaka and Masuda 1973; Misawa and Nakamura 1988a), the enrichment of both La and Ce is rare. Thus, the reliability of the present observations was carefully examined, but we found no errors in our data analyses. All three matrix samples exhibit slight but significantly higher relative abundances of Ce compared with La, resulting in an apparent Ce anomaly. The degree of positive Ce anomaly calculated from Ce/Ce\* is 16–28% (Ce\* is the normal value interpolated from abundances of La-Nd). The positive Ce anomaly obtained here is clearly resolvable even if the very largest analytical errors for La and Nd are considered. The Ce abundance may be anomalous for materials formed in oxidizing conditions through nebula processes (Boynnton 1975). On the other hand, if La depletion relative to Ce (a negative La anomaly) is assumed, the negative La anomaly is calculated to be 20–32% from the ratio La/La\* (La\* is the normal abundance extrapolated from Ce and Nd). However, such a systematic La depletion is not readily understandable except for a few cases in lunar highland samples, which was explained by a late crystallization sequence of the lunar magma ocean (Tanimizu and Tanaka 2002). Under oxidizing conditions, Ce can exist in the (IV) oxidation state, therefore, we suspect that the data reflect the anomalous behavior of Ce compared to trivalent REE. The observed positive Ce anomaly is considered to have derived directly from the REE-carrier materials in the Allende

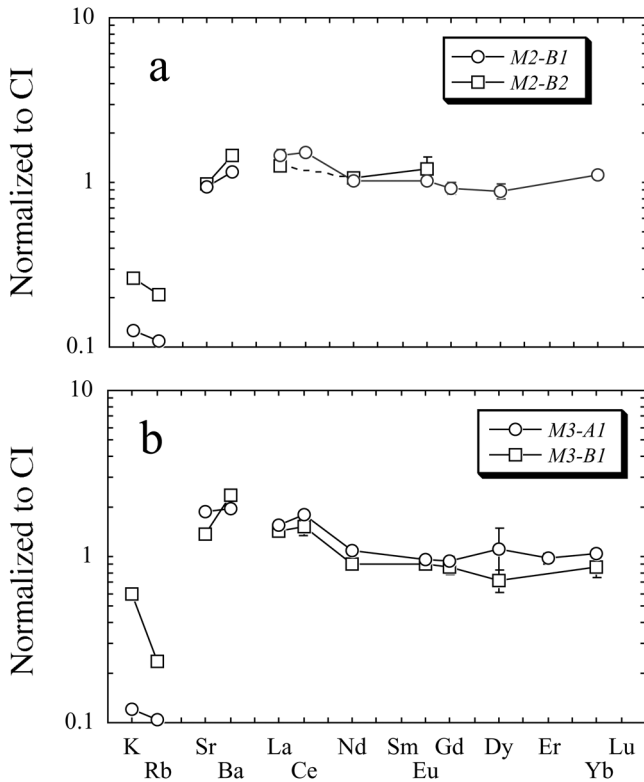


Fig. 2. CI chondrite-normalized lithophile element abundances in matrix materials of the Allende chondrite: a) *B1* and *B2* samples from section *M2*; b) *A1* and *B1* samples from section *M3*. The error bars are those of mass spectrometric measurement. The analytical errors in most elements are smaller than or equal to the symbol sizes.

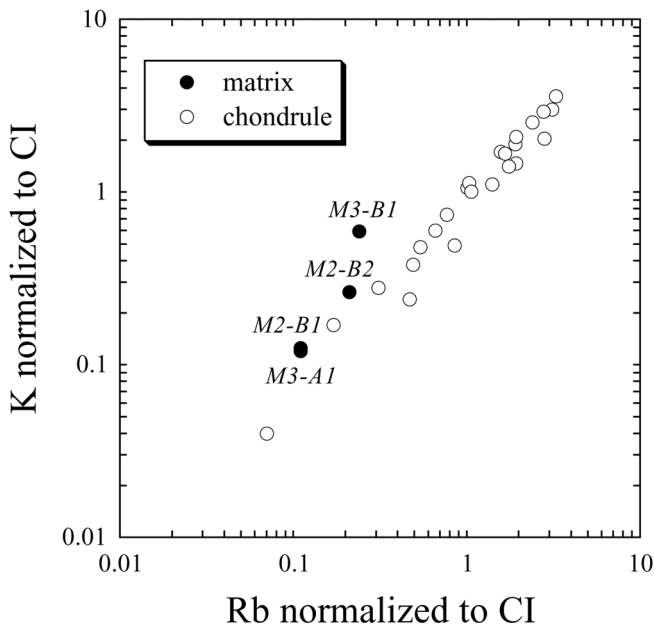


Fig. 3. Relationship between K and Rb in matrix and chondrule specimens from the Allende meteorite. The chondrule data discussed here is taken from Misawa and Nakamura (1988a).

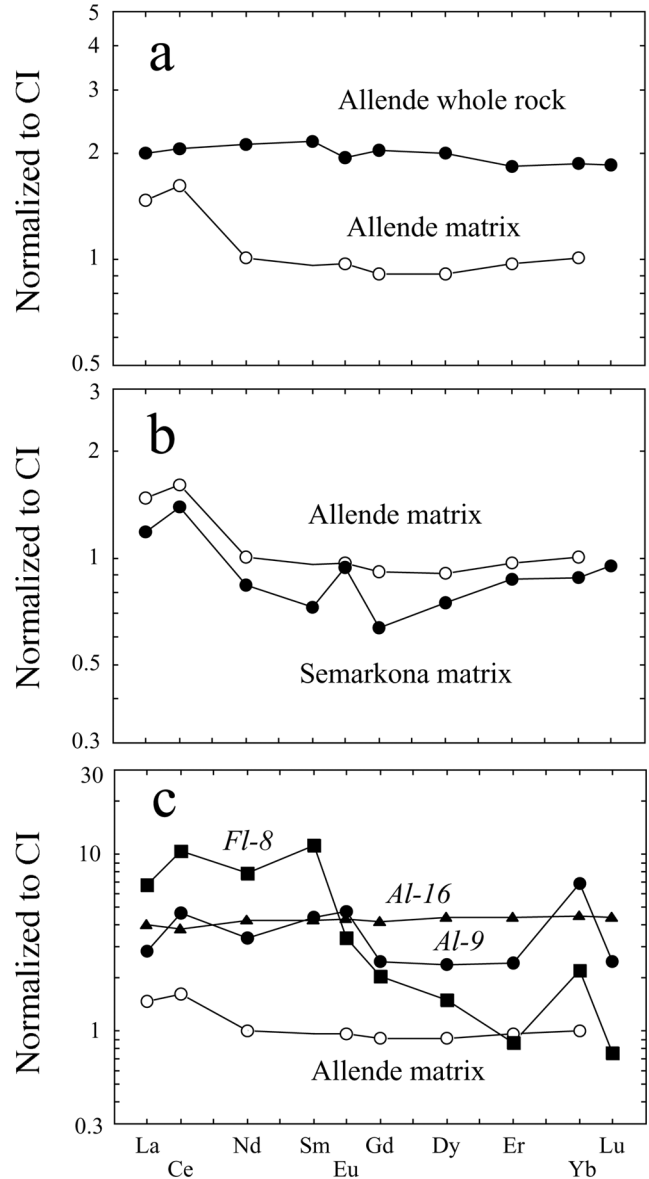


Fig. 4. CI-normalized REE abundance patterns of: a) matrix (mean composition from specimens *M2-B1*, *M3-A1*, and *M3-B1*) and whole rock samples from the Allende meteorite; b) the matrix of the unequilibrated ordinary chondrite Semarkona (LL3) (Alexander 1995); and c) chondrules from Allende (*Al-9* and *-16*; Misawa and Nakamura 1988a) and Felix (*Fl-8*; Misawa and Nakamura 1988b). Sm abundance of the matrix is the normal value interpolated from Nd and Gd.

matrix. As also noted in Fig. 2, none of the four matrix materials exhibit significant Eu anomalies.

Although there are some omissions in the REE data in Fig. 2, the REE abundances in the four matrix specimens are largely consistent, suggesting that the mean composition of *M2-B1*, *M3-A1*, and *M3-B1* can be taken as representative of the pure Allende matrix. The mean REE pattern of the Allende matrix is shown in Fig. 4 (La/Yb = 1.47; Ce/Ce\* = 1.21; Eu/

Table 3. Index of anhydrous alteration and lithophile element abundance ratios.

	Textural type <sup>b</sup>	Index of alteration					CI-normalized <sup>a</sup>		
		gls <sup>c</sup>	nph <sup>c</sup>	sdl <sup>c</sup>	mss. <sup>d</sup>	alt. <sup>d</sup>	Na/Ca	La/Yb	Ce/(Ce*)
<i>Al-A</i>	BO	o	o	×	20	10	0.17	n.d.	n.d.
<i>Al-B</i>	PO	o	o	×	10	50	0.22	n.d.	n.d.
<i>Al-22<sup>c</sup></i>	PO	o	o	×	5	50	0.15	0.97	0.99
<i>Al-5<sup>c</sup></i>	PO	o	o	×	10	60	0.37	0.93	0.97
<i>Al-C</i>	POP	o	o	×	10	70	0.24	n.d.	n.d.
<i>Al-D</i>	PO	o	o	×	5	70	0.44	n.d.	n.d.
<i>Al-E</i>	PO	o	o	o	5	80	0.17	n.d.	n.d.
<i>Al-F</i>	PO	o	o	×	5	80	0.17	n.d.	n.d.
<i>Al-G</i>	PO	o	o	o	10	80	0.27	n.d.	n.d.
<i>Al-9<sup>c</sup></i>	POP	o	×	o	10	80	0.32	0.44	1.54
<i>Al-H</i>	POP	o	o	×	5	90	0.33	n.d.	n.d.
<i>Al-I</i>	POP	o	o	o	5	90	0.46	n.d.	n.d.
<i>Al-10<sup>c</sup></i>	POP	o	o	×	10	90	0.27	0.97	0.99
<i>Al-J</i>	POP	o	o	×	10	90	0.33	n.d.	n.d.
<i>Al-K</i>	POP	o	o	×	10	90	0.56	n.d.	n.d.
<i>Al-L</i>	PO	o	o	×	10	90	0.65	n.d.	n.d.
<i>Al-M</i>	POP	o	o	×	10	90	1.44	n.d.	n.d.
<i>Al-N</i>	PO	×	o	×	5	100	0.19	n.d.	n.d.
<i>Al-O</i>	POP	×	o	o	5	100	0.65	n.d.	n.d.
<i>Al-16<sup>c</sup></i>	POP	×	o	o	10	100	0.26	0.95	0.90
<i>Al-P</i>	PO	×	o	×	10	100	0.43	n.d.	n.d.
<i>Al-Q</i>	PO	×	o	o	10	100	0.51	n.d.	n.d.
<i>Al-4<sup>c</sup></i>	BO	×	o	o	10	100	0.51	0.81	1.05
<i>Al-R</i>	PO	×	o	×	10	100	0.63	n.d.	n.d.

<sup>a</sup>CI-normalized abundance ratios; Na, Ca data were obtained by EPMA in this study; and La, Ce and Yb data are from Misawa and Nakamura (1988a).

<sup>b</sup>BO = barred olivine; PO = porphyritic olivine; POP = porphyritic olivine pyroxene.

<sup>c</sup>gls = glass; nph = nepheline; sdl = sodalite; o = existence; × = no existence in chondrule mesostasis.

<sup>d</sup>vol% of mesostasis in the chondrule and altered portion in mesostasis.

<sup>e</sup>The sample number corresponds to the chondrules studied by Misawa and Nakamura (1988a).

Eu\* = 1.05) compared with Allende whole rock (Fig. 4a), Semarkona matrix (Alexander 1995) (Fig. 4b), and Allende chondrules (Misawa and Nakamura 1988a, b) (Fig. 4c).

#### Possible Origin of Matrix from Chondrules

Current formation models for the origin of the matrix broadly state that the matrix is either a product of secondary processes acting on chondrules (Alexander et al. 1989) or of pristine or processed condensates formed in the solar nebula (Kornacki and Wood 1984; Brearley 1993; Krot et al. 1995; Grossman and Fedkin 2003). As noted by Misawa and Nakamura (1988a), the majority of Allende chondrules are slightly enriched in heavy REEs (CI-normalized La/Yb ratio <1) and display Eu depletion (Eu/Eu\* <1; Eu\* indicates normal value), while some CAIs with the group II pattern (Mason and Taylor 1982) generally exhibit light/heavy REE fractionation (La/Yb >1) with a negative Eu anomaly, indicative of high-temperature nebula fractionation processes (Boynnton 1975). In Fig. 5, the degree of light/heavy REE fractionation are plotted for the matrix, chondrules (data of our laboratory) (Misawa and Nakamura 1988a), CAIs (Mason and Taylor 1982), and the whole rock specimen (this study) from the Allende meteorite. Although the data for the matrix is still limited, the values clearly plot outside the range of the chondrules (and possibly

CAIs). Therefore, the REE abundance features of the Allende matrix appear to have no direct geometrical relationship with those of the chondrules (or CAIs), which in turn suggests that the matrix was not directly produced by the breakage and desegregation of the chondrules or CAIs. This is supported by oxygen-isotopic data (Clayton et al. 1987) and chemical compositions (Palme et al. 1992; Palme 1992), which does not reconcile with the chondrule origin of the matrix material.

#### Possible Redistribution of REEs

Although the matrix material, the most abundant constituent (57 vol%; Clarke et al. 1970) in the Allende meteorite, exhibits enrichment in Ce and La, the typical whole rock samples analyzed in this study and previously reported (Nakamura 1974) do not display such features (i.e., grossly flat, REE ~2 × CI; CI-normalized La/Yb ratio = 1.07; Ce/Ce\* ratio = 1.01) (Fig. 4a). As shown in Fig. 5, the REE patterns of the matrix material, particularly the fractionation of light/heavy REEs, seems to be complementary to the fractionation in the chondrules. The REE patterns of the matrix display smooth, light REE enriched fractionation (CI-normalized-La >Nd >Dy <Yb; CI-normalized La/Yb ratio = 1.32–1.65), while the chondrules are depleted in light REEs (La <Nd <Dy <Yb; La/Yb = 0.41–1.09) (Misawa and Nakamura 1988a).

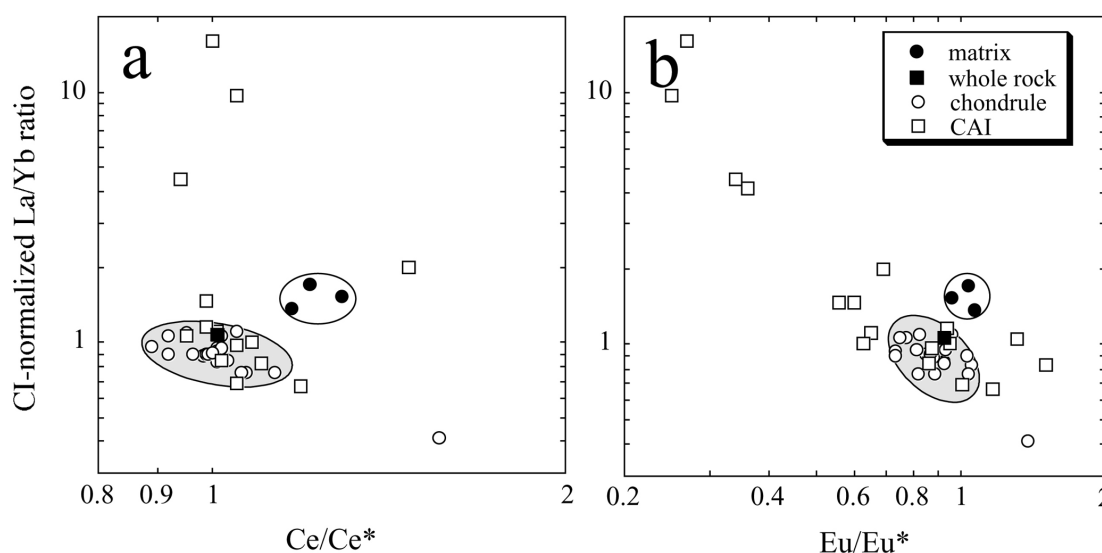


Fig. 5. Plot of CI-normalized La/Yb ratio versus (a) Ce/Ce\* and (b) Eu/Eu\* ratios for the matrix, chondrules (data of our laboratory) (Misawa and Nakamura 1988a), CAIs (Mason and Taylor 1982), and whole rock samples (this study) from the Allende meteorite. La/Yb > 1 observed in four chondrules is due to a negative Yb anomaly rather than light REE enrichment. Ce\* and Eu\* are the normal values interpolated from the abundances of La-Nd and Sm-Gd, respectively. The circles and shaded areas denote the degree of REE fractionation of the matrix and chondrules, respectively.

The Allende meteorite is extensively altered compared to reduced CVs (Kimura and Ikeda 1995; Krot et al. 1995). Notably, the REE (particularly light REE) fractionation of matrices from the unequilibrated ordinary chondrites Semarkona (LL3.0), Bishunpur (LL/L3.1), Chainpur (L/LL3.4), and Krymka (LL3.1) are similar to the present results, including various degrees of Eu anomaly (Eu/Eu\* = 0.48–2.13) (Fig. 4b). These REE features have been explained as being due to the existence of secondary minerals such as phosphate (and plagioclase for Eu) formed during metamorphic processes (Alexander 1995). Therefore, the REE abundances in the matrix of Allende also may have been influenced by elemental redistribution (partial preferential release of Ce and La from the chondrules accompanying the Ca) in the parent body or the nebula.

To discuss the effects of alteration reactions in chondrules, we compare the degree of mesostasis alteration and light/heavy REE fractionation on the basis of the CI-normalized La/Yb abundance ratios for the Allende chondrules, as previously reported by Misawa and Nakamura (1988a) (Table 3). Since mesostasis is highly enriched in REEs (Kennedy et al. 1993), the degree of mesostasis alteration may be related to the redistribution of REEs in chondrules.

The degree of alteration is defined as the volume fraction of altered mesostasis—a modification of the definition of alteration of chondrules by Ikeda and Kimura (1995). Despite the wide range of major chemical compositions, the chondrules with the least altered mesostasis (*Al-22*, *Al-A*, and *Al-B*; altered volume of mesostasis <50% by BSE-SEM) seem to have relatively low Na/Ca abundance ratios (<~0.2), reflecting a lower abundance of secondary nepheline and/or

sodalite compared to other chondrules (>50 vol% altered mesostasis). However, differing from the case of alkali metals, one chondrule (*Al-9*) exhibiting La and Nd depletion and a positive Ce anomaly (CI-normalized La/Yb ratio = 0.41; Ce/Ce\* = 1.56) (Fig. 4c) is not altered (80 vol%) to a notably further extent than the others (90–100 vol%). The chondrules from CO chondrites such as Felix (CO3.4) are generally much less altered compared to the Allende (CV3) chondrules. It is also noteworthy that one Felix chondrule (*F1-8*) exhibits heavy REE enrichment (Fig. 4c; Misawa and Nakamura 1988b), although, strictly speaking, chondrules from these two meteorites have rather different alteration histories. In addition, CAIs from the Allende meteorite, which are considered to have experienced more extensive alteration compared to chondrules, do not show signs of the preferential release of light REEs (Fig. 5). Therefore, no clear evidence exists of direct REE exchange between the matrix and chondrules (or CAIs), although a more detailed investigation will be required to clarify REE fractionation during alteration.

#### Nebula Condensates and REEs

As shown in Fig. 5, the REE abundance features (La/Yb, Ce/Ce\*, and Eu/Eu\* ratios) of the matrix and chondrules exhibit a complementary relationship. This chemical complementarity was also observed in Cr and Ni, implying a closed local system in the nebula (Palme 1992; Palme et al. 1992). The present REE results for the matrix materials are more reasonably understandable as having retained the features of the nebula gas during the condensation process, and the precursor materials of the chondrules and matrix in Allende may have formed in a closed region.

Tanaka and Masuda (1973) determined the REE abundances in the Allende matrix (grain size,  $<74 \mu\text{m}$ ; density,  $3.32 \text{ g/cm}^3$ ) and obtained a smoothly fractionated REE pattern ( $\text{La/Yb} = 1.76$ ) along with high Ba abundance ( $\sim 73 \times \text{CI}$ ), which was explained as reflecting nebula condensate material with highly fractionated REE and enriched Ba. The present REE results are similar to those for a Ba-rich matrix except for the positive Ce anomaly. However, judging from the REE abundances of Ba-rich components (REE;  $<3.5 \times \text{CI}$ ; Tanaka et al. 1976; Tanaka and Okumura 1977), a very minute amount of such micro-components ( $<2 \text{ wt}\%$  in this matrix estimated from the Ba abundance) cannot give rise to the observed La and Ce enrichment. Recently, Bland et al. (2003) claimed that the matrix of Allende exhibited a marked decrease in trace element abundances with decreasing condensation temperature and suggested an incomplete condensation origin of the matrix.

As to the inclusions in Allende, the REE-Ba pattern of a giant olivine chondrule (7 mm in diameter) (CI-normalized  $\text{La/Yb}$  ratio = 1.44;  $\text{Ce/Ce}^* = 6.56$ ;  $\text{Eu/Eu}^* = 2.26$ ), which was explained to have formed as a later-stage condensate in the nebula (Tanaka et al. 1975), also has features more similar to those of the matrix than the CAIs and typical chondrules, as mentioned above. As pointed out by Tanaka and Masuda (1973) and Nakamura (1974), while a representative Allende whole rock shows a fractionated light to heavy REE but unfractionated light REE (or slightly light REE depleted) pattern, some Allende whole rock samples indicate a light REE enriched pattern similar to those of matrix. It is also noteworthy that one of the AOAs (sample 2; Grossman et al. 1979) has a very unusual REE pattern for an Allende inclusion; enrichments drop steadily from La to Ce to Eu and rise sharply from Yb to Lu. The general trend of the REE pattern of sample 2 is similar to those of Allende matrix and whole rock samples reported here and by Tanaka and Masuda (1973). Therefore, we considered that some unknown components carrying light REE enrichment exist in Allende that might be related in some way to AOAs formed in a low-temperature nebula gas (Grossman et al. 1979). Therefore, the matrix material (precursor) may be composed of an assemblage of various interstellar dusts. As for REE fractionations in the nebula, the most plausible candidates giving rise to the complementary features are high-temperature products such as chondrule precursors and CAIs ( $>1500 \text{ K}$ ; Hewins 1988).

If the REE patterns of the matrix represent the residual fraction of nebula gas during removal of chondrules and/or CAIs in a closed system, chondrules and CAIs will possibly exhibit a light REE depletion and negative Ce anomaly as compensation for the light REE enrichment in the matrix. However, chondrules and CAIs from carbonaceous chondrites generally do not display negative Ce anomalies, except in some rare cases (Misawa and Nakamura 1988a; Mason and Taylor 1982). Thus, we suggest that the REE precursors of

matrix materials do not represent direct condensates after the removal of chondrules and CAIs and that matrix REE fractionations were produced at later stages. Mass balance constraints would require Ce-depleted components, and these REE fractions would be expected for primitive chondrites. Therefore, the search for such a component would be important for evaluating the late-stage nebula processes.

In conclusion, we suggest that the light REE enrichment, together with a positive Ce anomaly, is common for the matrix materials from the carbonaceous and ordinary chondrites, indicating that the nebula oxidizing conditions were prevailing during formation of late-stage components of carbonaceous and ordinary chondrites. The alkali depletion and REE fractionations observed here appear to be reconciled with the high-Fe olivine of matrix materials. Further detailed search would be required to obtain a stronger connection among these results.

## SUMMARY AND CONCLUSIONS

We excavated the most pure matrix material from sections of the Allende meteorite and precisely analyzed the abundances of REE and other lithophile elements by isotope dilution mass spectrometry. Based on these results, we obtained the following implications about the origin of the Allende matrix.

1. The bulk compositions of matrix obtained in this study are relatively Fe-rich compared to previous data on the Allende (CV) matrix. A  $\text{FeO}/(\text{FeO} + \text{MgO})$  ratio of  $\sim 52 \text{ mol}\%$  is consistent with the average Fo value in matrix olivine. We suggest that the matrix specimens we obtained and analyzed in this study are less contaminated with Mg-rich chondrules or fragments than those of other studies.
2. The matrix is depleted in K and Rb ( $0.1\text{--}0.5 \times \text{CI}$ ) compared to the chondrules ( $0.2\text{--}3 \times \text{CI}$ ), suggesting that the matrix precursor materials did not carry significant amounts of alkali metals or that alkalis were removed from the precursor materials in the parent body and/or before the accretion of the matrix onto the Allende parent body.
3. The least-contaminated matrix material exhibits light REE enrichment with a positive Ce anomaly. Except for Ce, the pattern of enrichment for the matrix is complementary to that of the chondrules. The precursor materials of matrix from Allende may, therefore, have formed in oxidizing conditions at later stages after removal of chondrules and CAIs. The REE patterns suggest that the matrix materials formed from the nebula gas through the condensation process.

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