Trace Element Constraints on the Origin of Chondrules in Carbonaceous Chondrites

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博士論文

TRACE ELEMENT CONSTRAINTS ON THE ORIGIN OF CHONDRULES IN CARBONACEOUS CHONDRITES

炭素質コンドライト中のコンドリュールの起源に関する微量元素からの制約

１９８８年　１月

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TRACE ELEMENT CONSTRAINTS ON THE ORIGIN OF CHONDRULES IN CARBONACEOUS CHONDRITES

by

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ABSTRACT

Abundances of trace and major elements (REE, Ba, Sr, Rb, K, Mg and Ca) were determined by precise mass spectrometric isotope dilution techniques for 32 petrographically examined individual chondrules from the Allende (CV3) and Felix (CO3) carbonaceous chondrites, and for one Ca,Al-rich inclusion and a whole rock sample from Felix.

The REE abundances in individual Allende chondrules are 2.5-10 x CI for barred olivine chondrules, 2-8 x CI for porphyritic and radial pyroxene chondrules, 0.15-4 x CI for porphyritic olivine and porphyritic olivine-pyroxene chondrules and are more or less similarly fractionated. The REE abundances in individual Felix chondrules are 1.4-4 x CI for porphyritic olivine and porphyritic olivine-pyroxene chondrules. The CI-normalized REE patterns for Felix chondrules are almost flat, however, porphyritic pyroxene chondrule is characterized light REE enrichment (6-12 x CI) relative to heavy REE (∼0.8 x CI).

General REE fractionations (typically for light to heavy REE fractionation) and significantly large (up to 300 %) anomalies of Ce, Eu and Yb are frequently recognized for all textural types of chondrules, particularly for barred olivine and pyroxene-rich chondrules.

The positive correlations of REE with the moderately volatile elements, K and Rb, as well as other refractory elements, Ca, Sr and Ba, are observed independently of textural types and major chemical compositions.

Every type of Allende chondrule has large and systematic abundance variations of K and Rb (Mg-normalized abundance of 0.6-1.7 x CI for barred olivine chondrules, 0.6-2.3 x CI for pyroxene-rich chondrules, and 0.09-0.5 x CI for olivine-rich chondrules), but show a constant K/Rb ratio close to that of CI's.

The coarse-grained Ca,Al-rich inclusion from Felix, 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 the 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 x CI) with ~20 % excess of Ce.

From these results, the following constraints on the chemical characteristics of chondrule precursors and chondrule-forming events are suggested:

(1) Vaporization loss of alkalis accompanied by K/Rb fractionation did not occur during chondrule-formation melting events.

(2) Elemental abundances of chondrules were basically established prior to chondrule-melting events.

(3) Gas/solid (or liquid) processes yielding REE fractionations took place during the formation of refractory chondrule-precursors.

(4) Possible refractory lithophile precursor components of CV and CO chondrules are ultra-refractory residues (or ultra-refractory condensates) and condensates from a gas after removal of ultra-refractory components. These components were alkali-bearing.

(5) Elemental distributions in the chondrule precursor materials had not been established in fractional condensation sequences during cooling from an initially hot gas.

(6) 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.

Table of Contents

The classification of chondrites proposed by WASSON (1974) was utilized in this study. CI, CM, CO and CV refer to the type meteorites -- Ivuna, Mighei, Ornans and Vigarano -- of the four groups of carbonaceous chondrites.

The petrographic labels for chondrules pioneered by GOODING and KEIL (1981) were used in this study. PO, PP, POP, BO, RP for porphyritic olivine, porphyritic pyroxene, porphyritic olivine-pyroxene, barred olivine, radial pyroxene.

I. INTRODUCTION

It is widely believed that chondrules in unequilibrated chondritic meteorites preserve a record of fractionation processes in the primitive solar nebula. In order to make clear the physical and chemical conditions of the early solar system, intensive petrologic, chemical and isotopic studies have been focused on chondrules in unequilibrated chondrites (e.g., DODD, 1971; OSBORN et al., 1973, 1974; CLAYTON et al., 1973; GRAHAM, 1975). The existence of relict mineral grains in chondrules of ordinary chondrites (FREDRIKSSON et al., 1969; CHRISTOPHE MICHEL-LEVY, 1981; NAGAHARA, 1981; RAMBALDI, 1981; RAMBALDI and WASSON, 1982), carbonaceous chondrites (KRACHER et al., 1984) and enstatite chondrites (RAMBALDI et al., 1983) suggested that these chondrules were formed by melting of pre-existing solid precursor materials. The lithophile/siderophile fractionation observed in chondrules of unequilibrated ordinary chondrites (UOCs) also favors chondrule formation by melting of pre-existing materials (GOODING et al., 1980). MCSWEEN (1977a,b) and MCSWEEN et al. (1983) suggested that chondrules in carbonaceous chondrites (CV and CO) can be separated into two distinct populations in terms of redox state. From systematic examinations of chondrules in carbonaceous chondrites, it was found that chondrules with different textural types have characteristic oxygen isotopic compositions (CLAYTON et al., 1983; MCSWEEN, 1985; CLAYTON et al., 1987a,b). In addition, many studies of chondrules from UOCs and enstatite chondrites have been carried out and several candidates for precursor materials of chondrules have been proposed (GOODING et al., 1983; J.N. GROSSMAN and WASSON, 1982, 1983a,b, 1985; J.N. GROSSMAN et al., 1985; KURAT et al., 1984). Nevertheless, problems concerning formation mechanisms of chondrules, chemical characteristics of precursor materials and P, T and f_{O2} conditions of the nebula in a region where chondrule precursors were formed still remain unsolved.

Rare earth elements (REE) have been used to constrain high temperature processes, such as gas/solid or liquid/solid fractionations, and redox conditions in the early solar system (BOYNTON, 1975, 1978). The instrumental neutron activation analysis (INAA) technique has been used for determination of abundances of trace elements including REE in constituents from carbonaceous chondrites, especially from Allende, as well as those from the UOCs and enstatite chondrites, and has brought important contributions for understanding the chemical features of CAIs (L. GROSSMAN, 1972; L. GROSSMAN and GANAPATHY, 1976a,b; L. GROSSMAN et al., 1977, 1979; CONARD, 1976; NAGASAWA et al., 1977; for review, L. GROSSMAN, 1981) and precursor materials of chondrules (OSBORN et al., 1973, 1974; GOODING et al., 1980, 1983; J.N. GROSSMAN and WASSON, 1982, 1985; SMITH et al., 1983; KURAT et al., 1984, 1985; KURAT, 1985; RUBIN and WASSON, 1987b). However, because the sample size of chondrules available for chemical analyses is quite limited, the INAA data do not necessarily give us detailed information on REE fractionation in the chondrules.

Since large amounts of CV Allende were distributed widely, REE compositions of chondrules from this meteorite were studied by many investigators (TANAKA and MASUDA, 1973; OSBORN et al., 1974; KURAT, 1985; KURAT et al., 1985; RUBIN and WASSON, 1986, 1987b). However, relatively little is known about trace element characteristics of chondrules in CO chondrites. OSBORN et al. (1973) reported chemical values obtained by INAA of ∼50 CO chondrules but presented no REE or petrographic data. Recently, RUBIN and WASSON (1987a) analyzed 17 chondrules from Ornans by INAA and suggested possible chondrule precursor components.

The main purpose of this study is to search for possible fine structures of REE patterns in carbonaceous chondrite (CV and CO) chondrules. In order to obtain more precise REE data, I have undertaken the accurate analyses of REE and other trace elements by improved isotope dilution techniques.

In this paper I present precise data of 25 chondrules from the Allende (CV3) chondrite and 7 chondrules from the Felix (CO3) chondrite which clearly demonstrate the existence of REE fractionations among chondrules, and then discuss the chemical characteristics of precursors of Allende (CV) and Felix (CO) chondrules.

Part of the results in this study appeared in MISAWA and NAKAMURA (1986a,b, 1987a,b,c, 1988), and NAKAMURA et al. (1987).

II. EXPERIMENTAL

1. Samples

1-1. Descriptions of samples

Brief descriptions of the samples analyzed in this study are described below.

Allende (carbonaceous chondrite Vigarano-subtype: CV3)

The Allende meteorite fell near Parral, Chihuahua, Mexico, on 8 February 1969. At least two tons of meteoritic stones have been recovered (KING *et al.*, 1969; CLARKE *et al.*, 1970). Metamorphism has affected, to a lesser extent, the Allende meteorite, as evidenced by ferromagnesian mineral equilibration, Fe-enrichment of fine-grained inclusions, and loss of some volatile gases (MCSWEEN, 1977b, 1979). BUNCH and CHANG (1980) suggested that most carbonaceous chondrites underwent some alteration on their parent body and showed that less than 15 % of olivine aggregates in Allende had haloes, as alteration products.

Felix (carbonaceous chondrite Ornans-subtype: CO3)

The Felix meteorite fell at Perry County, Alabama, U.S.A., on 15 May 1900 (GRAHAM *et al.*, 1985).

Felix is not as fresh as the Kainsaz meteorite in appearance. MCSWEEN (1977a) described that the metamorphic grade of the Felix meteorite is in stage II (the metamorphic grade increasing with the stage number), comparable to that of the Ornans and Lance meteorites. An estimate of the redox state of the Felix meteorite (log f_{O2}=-18.6 at 800 ^{o}C) was obtained by BRETT and SATO (1984).

A chip of 1.1 g Felix USNM 235, Smithsonian Inst. NMNH was supplied by courtesy of Dr. J.G. MacPherson.

Peace River (ordinary chondrite, L6)

The Peace River meteorite fell at Alberta, Canada, on 31 March 1963. About 46 kg of meteoritic stones have been recovered (GRAHAM et al., 1985). Two aliquots of powdered sample were used in this study.

1-2. Sample separation

All chondrules were separated mechanically from a 3 g fragment of the Allende meteorite and a 1.1 g chip of the Felix meteorite by combination of excavating with stainless steel tools and freeze-thaw processing in distilled water. They were scraped with tweezers to remove fine-grained adhering matrix material. 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 to prepare a thin section for petrographic observations and the other half was used for trace element analyses. Thirty-two chondrules were selected for chemical analyses from 60 chondrules which had been examined petrographically.

Fine-grained opaque rims (15-50 μm thick) exist in nearly half of the Allende chondrules analyzed. Coarse-grained rims (RUBIN and WASSON, 1987b) were also identified in two barred olivine chondrules (2 and 3 in Table 5). It may be possible that the most friable chondrule rims were crushed during the mechanical separation procedure and thus for many Allende chondrules (3, 4, 7-15, 20 and 21 in Tables 5-7), no significant amounts of the surrounding rims were recognized when they were selected for trace elements analyses.

Ornans-subtype chondrites are characterized by a high density of small ($\sim$0.2 mm in diameter) size-sorted chondrules and inclusions in fine-grained matrix (KING and KING, 1978). Since relatively large samples were selected, the size of chondrules analyzed in this study was from 0.472 to 1.228 mg in total weight. Coarse-grained rims composed of olivine and low-Ca pyroxene (RUBIN, 1984) were not observed in Felix chondrules examined in this study.

In addition, a 12 mg-size ultrafine fraction (<50 μm) produced by freeze-thaw processing was analyzed as a "bulk Felix chondrite" sample.

2. Chemistry

The chemical procedures were generally similar to that of NAKAMURA (1974). Since the sample size was limited, elemental analyses were performed by a modification of an usual method. The analytical sequence is summarized in Fig. 1.

<u>Figure</u> <u>1</u>.

Schematic diagram of the experimental procedure for chemical analyses of chondrules from carbonaceous chondrites.

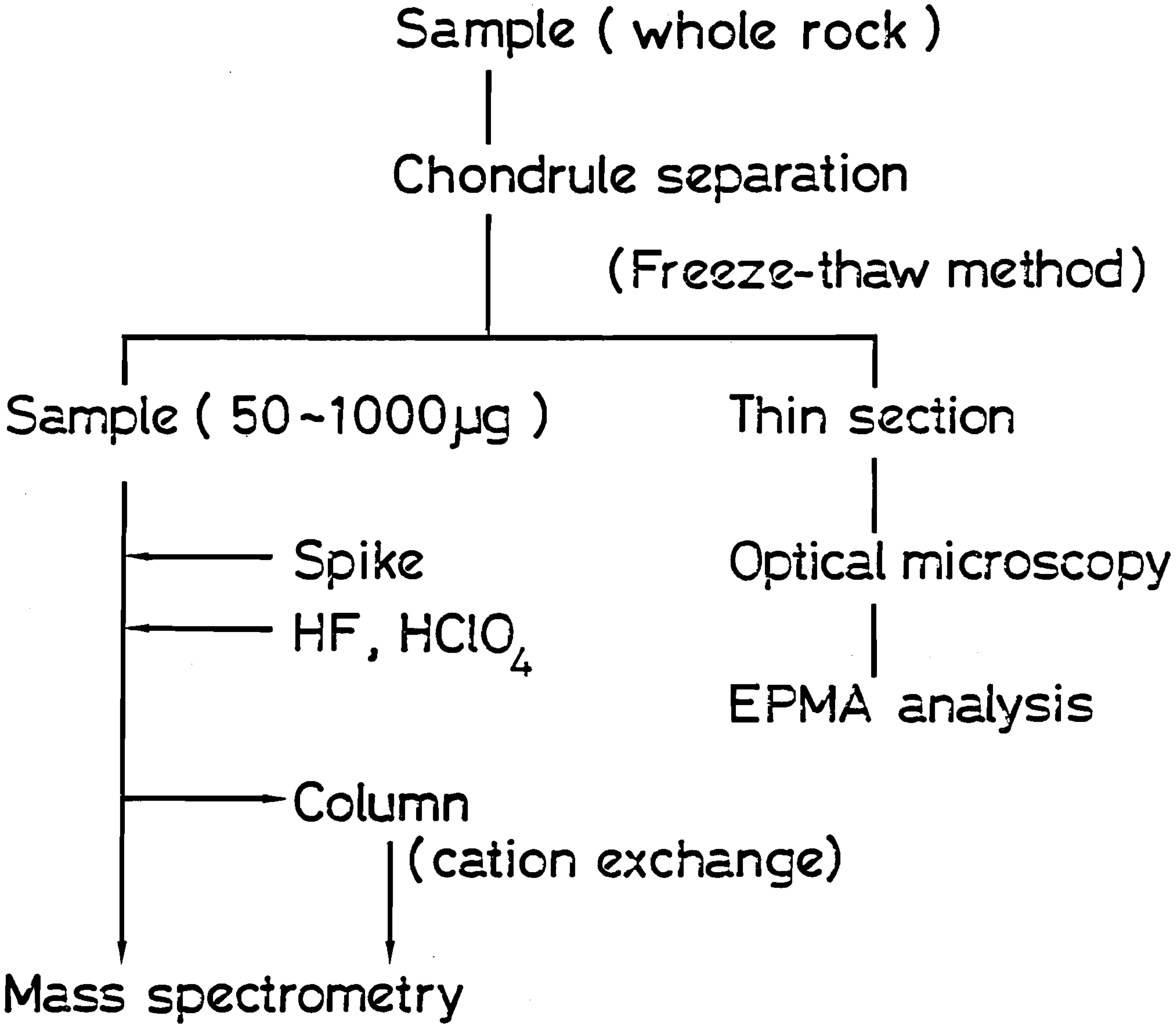

Sample (whole rock)
Chondrule separation
(Freeze-thaw method)
Sample (50~1000µg)
Thin section
Spike
Optical microscopy
HF, HClO4
EPMA analysis
Column
(cation exchange)
Mass spectrometry

Fig. 1

2-1. Dissolution

Splits of each chondrule were weighed by a SARTORIUS 4501-MICRO micro-balance (precision $\pm\sim2$ μg), and then removed into a small teflon bomb. Composite spike solutions (REE, K-Rb-Sr-Ba and Ca-Mg) were added to it. After most of the solution was evaporated to dryness, 3 μl HF and 3 μl $HClO_4$ were added. The sealed teflon bomb was heated in an oven for 8 hours at 170 °C. After decomposition, the sample was evaporated to dryness and then dissolved in 3 μl of concentrated HNO_3 and analyzed by direct-loading mass spectrometry without further chemical treatment.

2-2. Column chemistry

For larger samples (e.g., > 0.5 mg), the conventional chemical treatment was carried out. The REE separation column, which was made of quartz glass and was 3 mm in inside diameter, was filled to a height of 16 mm with Dowex AG 50-X12, 200-400 mesh, cation exchange resin. Before an elution, the resin was prepared by passing through it 20 ml of 6N HCl. This was followed by 300 µl of 1N HCl for conditioning. The decomposed sample, evaporated to dryness, was dissolved in 20 µl of 1N HCl and loaded onto the resin using a microsyringe with teflon tube. After the sample solution was allowed to pass through the column, 650 µl of 2N HCl, 150 µl of 6N HCl and 250 µl of 6N HCl were added separately and each effluent was collected. The solution containing Na, K, Mg, Fe and Ca was dried up and was then ready to be loaded on the Mg separation column. A typical elution curve is shown in Fig. 2. The separation of alkaline earth and REE by this elution procedure is not efficient. However, the decrease of the amount of cation exchange resin decreases the contribution of blanks.

For REE measurements of Sr-, Ba-rich samples such as plagioclase, Sr^+Sr^+, Ba^+, BaO^+ and $BaCl^+$ peaks interfere REE in the same mass regions. In order to minimize these interferences, REE were separated from Sr and Ba using 2N HNO_3 and 6N HCl as eluant in the REE column. The sample solution was loaded in the same way as described above. The 800 µl of 2N HNO_3 eluant was allowed to pass through the column, then 800 µl of 6N HCl was added and the effluent was collected. This is evaporated to dryness and is allowed to pass through the REE column.

In addition, a significant interference of Na is observed during Mg measurement in alkali-rich chondrules. In order to minimize the Na contribution, Mg was, as much possible as, separated from Na using a major element column which is made of quartz glass and is 2.5 mm in inside diameter and filled to a height of 18 mm with Dowex AG 50-X12, 200-400 mesh, cation exchange resin. Before an elution the resin was prepared as described the REE column chemistry. This was followed by 150 µl of 1N HCl. The sample dissolved by 20 µl of 1N HCl was loaded. After the sample solution was allowed to pass through the column, 600 µl of 1N HCl was added. After the eluant was allowed to pass through, 300 µl of 2N HCl was added and effluent was collected. A typical elution curve is also shown in Fig. 2.

Figure 2.

Typical elution curves for Na, Mg, Fe, Ca and Sr (upper) and K, Ca and Sr (lower) from the Mg separation and REE separation cation exchange columns.

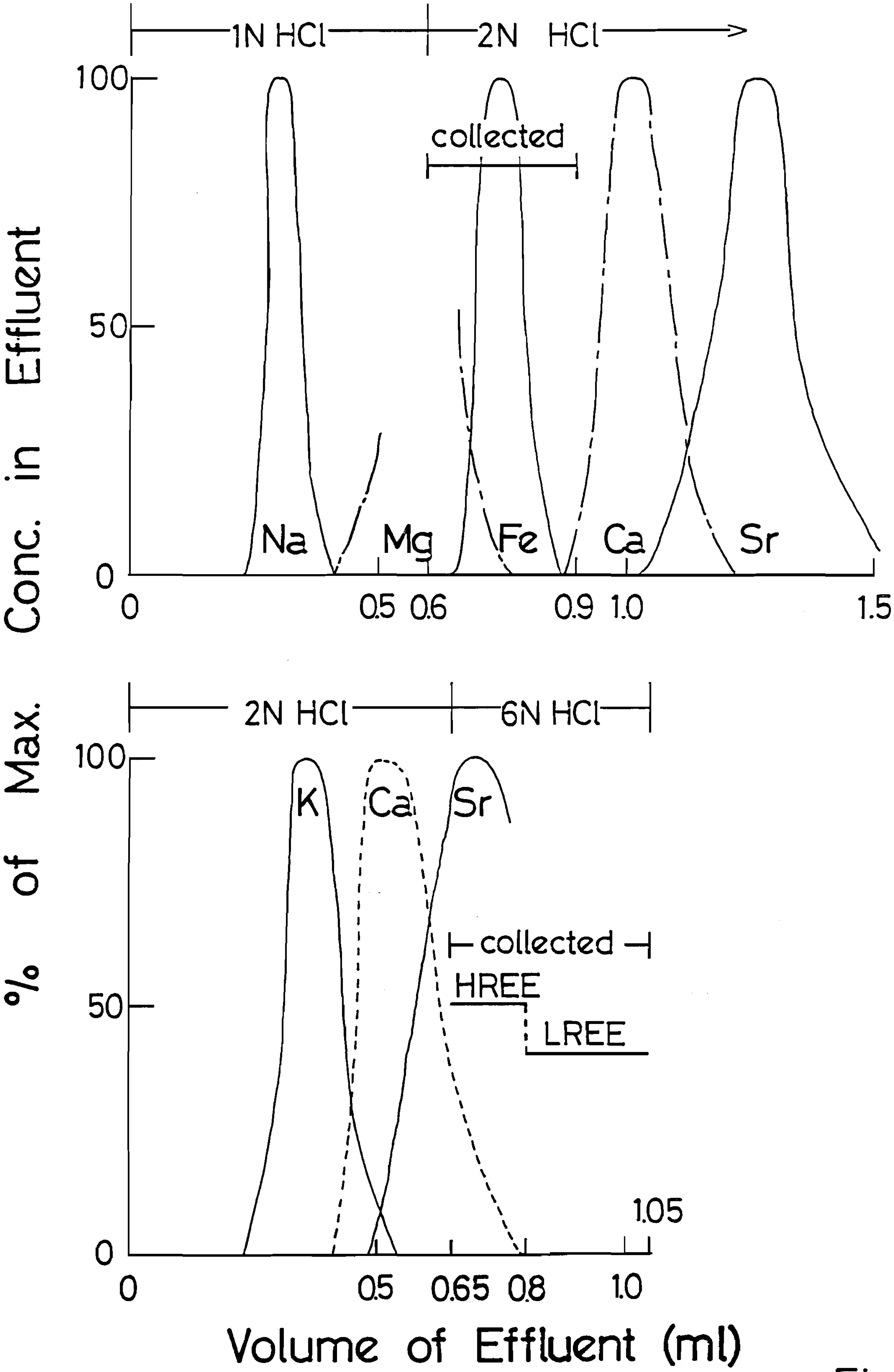

1N HCl
2N HCl
100
50
0
Na
Mg
Fe
Ca
Sr
collected
0
0.5
0.6
0.9
1.0
1.5
2N HCl
6N HCl
K
Ca
Sr
collected
HREE
LREE
1.05
0
0.5
0.65
0.8
1.0
% of Max. Conc. in Effluent
Volume of Effluent (ml)

Fig. 2

2-3. Blanks

Reagents used in this study is as follows. H_2O was distilled twice in still following a cation exchange treatment. Acetone was distilled once in SiO_2 still. HCl was prepared by bubbling HCl gas in H_2O. HNO_3 was distilled twice in SiO_2 still. HF was four times distilled in teflon bottle. $HClO_4$ was four times distilled in SiO_2 still.

Total chemistry blank was measured during the course of the work. Contribution of blanks from the Ca-Mg spike solution is not included in the procedural blanks listed in Table 1, but were measured separately and found to be negligible for most elements except for Ba. The contribution of Ba blank to the sample was about 20 %. All data in Tables 11, 12 and 16 are corrected for blanks.

Table 1.

Laboratory contamination levels.

	Total blank Direct-loading (pg)	Total blank Column chemistry* (pg)	Ca-Mg spike solution (p.p.m.)
K	260		1.2×10^{-2}
Rb	0.33		2.4×10^{-5}
Sr	4.5		2.3×10^{-4}
Ba	43		1.4×10^{-2}
La	1.7	3.4	1.3×10^{-5}
Ce	1.1	---	1.3×10^{-5}
Nd	0.34	2.0	8.5×10^{-6}
Sm	0.16	0.36	2.4×10^{-6}
Eu	0.11	0.13	5.7×10^{-7}
Gd	---	---	1.6×10^{-6}
Dy	---	0.51	7.5×10^{-6}
Er	---	0.39	---
Yb	---	---	---
Lu	0.057	0.093	1.5×10^{-6}

* Cation exchange treatment was performed for REE separation. Dashes denote "not determined".

3. Mass spectrometry

Rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb and Lu), Ba, Sr, Rb, K, Ca and Mg were determined on a JEOL JMS 05RB mass spectrometer equipped with an electron multiplier. A double Re-Ta filament assembly was used for analyses of alkalis, alkaline earths, Ce, Nd, Sm, Eu, Yb and Lu; a single Re filament assembly for La, Nd, Gd, Dy and Er. Lanthanum, Ce, Nd, Gd, Dy and Er were measured as the oxide-ion species and the other elements were measured as the metal-ion species.

Several technical problems must be overcome to make precise determination of trace element abundances with the mass spectrometer. For Mg and REE measurements in direct-loaded samples, it was necessary to hold at relatively low temperature until the intensities of Na and Ca were significantly reduced. It was also essential that "dirty" samples were brought up slowly to the emission temperature until the isobaric interferences such as from BaO^+ and $BaCl^+$ were substantially reduced. These conditions typically lasted for 5 hours or longer. The problems of mutual interferences among REE isobars were minimized by controlling the emission temperature of the filament and the oxygen partial pressure in the ion source as $\sim 1 \times 10^{-5}$ torr using a needle valve.

4. Analytical precision and reproducibility

In order to test the accuracy of the direct-loading mass spectrometry for chondritic samples, the homogenized L6 ordinary chondrite, Peace River was used.

Analytical results of a 135 μg Peace River II sample by the direct-loading mass spectrometry technique are given in Table 2 and Fig. 3. They are compared with the results of 135 μg and 275 μg analyses of Peace River II samples, which were carried out by the REE column chemistry described above, and with the results of 100 mg-sized Peace River samples, which were performed by conventional large column chemistry. From above results, a new procedure allows the precise determination (± ~3 % for most elements) of 50 pg quantities of REE (i.e., 100 μg chondritic material).

Table 2.

Analytical results of the Peace River (L6) chondrite (values in p.p.m.).

	Peace River I (108.0 mg)*	Peace River II (223.5 mg)+	135 µg** direct loading	135 µg** column chemistry	275 µg** column chemistry
La	0.3112 ±.0017	0.3660 ±.0033	0.379 ±.005	0.383 ±.008	0.384 ±.005
Ce	0.8143 ±.0021	0.9824 ±.0080	0.978 ±.030	1.05 ±.04	1.00 ±.02
Nd	0.6056 ±.0014	0.7194 ±.0037	0.743 ±.005	0.782 ±.017	0.741 ±.003
Sm	0.1940 ±.0005	0.2324 ±.0015	0.229 ±.003	n.d.	0.239 ±.003
Eu	0.06574 ±.00020	0.07985 ±.00073	0.0818 ±.0017	0.0850 ±.0022	n.d.
Gd	0.2594 ±.0050	0.3105 ±.0045	0.316 ±.009	0.327 ±.010	0.325 ±.010
Dy	0.3057 ±.0018	0.3691 ±.0042	0.380 ±.003	0.384 ±.007	0.378 ±.007
Er	0.2040 ±.0032	0.2465 ±.0035	0.244 ±.013	0.259 ±.016	0.249 ±.013
Yb	0.2047 ±.0021	0.2459 ±.0035	n.d.	n.d.	n.d.
Lu	0.03143 ±.00009	0.03739 ±.00033	n.d.	0.0398 ±.0009	0.0390 ±.0017

* Sample resolved. About 105 mg aliquot was used for REE analyses.
\+ Sample resolved. A 84.4 mg aliquot was used for REE analyses.
** Spiked Peace River II solution was spilit into several fractions.
n.d. = not determined.

Figure 3.

Chondrite normalized REE patterns of Peace River I, Peace River II and fraction II/fraction I (upper).

Sample normalized to Peace River II REE contents (obtained from conventional column chemistry) for comparison between results obtained by direct-loading and small column chemistry procedures for Peace River II fraction (lower).

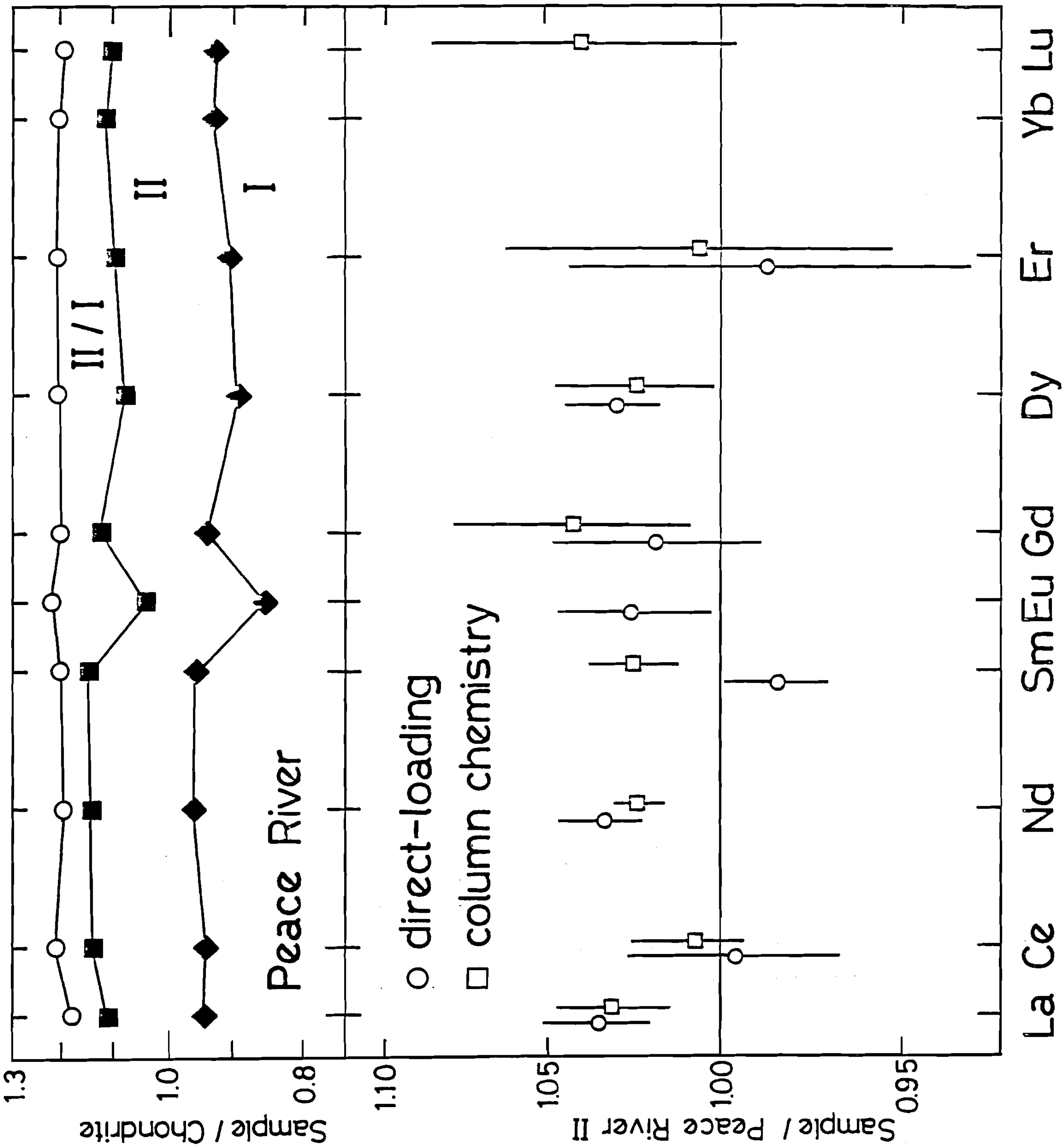

Peace River
○ direct-loading
□ column chemistry
II / I
II
I
La
Ce
Nd
Sm
Eu
Gd
Dy
Er
Yb
Lu
Sample / Chondrite
1.3
1.0
0.8
Sample / Peace River II
1.10
1.05
1.00
0.95

Fig. 3

Repeated analyses for different portions of the same chondrules (Allende chondrules 1 and 2, in Figs. 14 and 15) suggest that one half of a chondrule may be considered as representative of the whole chondrule in terms of the trace element chemical composition, though this would not be the case for chondrules with extremely low trace element abundances like the Allende chondrule 18 (Fig. 23). Thus, most of the chondrules in this study were analyzed using roughly half of the chondrule.

The small sample sizes and low abundance levels yield uncertainties of ∼5 % for heavy REE in a few cases. It is pointed out that the absolute elemental concentration in small chondrules (i.e., 50 µg) contains relatively large uncertainties (∼5 %) due to weighing errors, but this is not relevant to the later discussion because it is mainly concerned with the relative abundances of the elements.

5. Electron probe microanalysis

Major and minor elements of the constituent minerals were analyzed with a JEOL JXA-5A microprobe at the Institute for Study of the Earth's Interior, Okayama University, and a JEOL JCXA-733 microprobe at the Ocean Research Institute, University of Tokyo. They were both operated at 15 kV accelerating voltage and 20 nA or 0.9 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 seconds. The analytical data are corrected according to BENCE and ALBEE (1968) with further correction for bulk chemical compositions of chondrules by the method of IKEDA (1980).

Constituent minerals were also 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 analytical data were corrected according to ZAF. Bulk chemical composition of a Felix chondrule #8 was also obtained by SEM-EDS modal recombination. In Table 3, results of EPMA defocused beam analyses and SEM-EDX modal recombination for the Felix chondrule #8 are shown. They are in good agreement with each other except for FeO, MgO and Na_2O. Disagreement between EPMA defocused beam analyses and SEM-EDX modal recombination is considered to be mainly due to the detection of Fe-sulfides phases and due to the loss of alkalis during the electron beam bombardments.

Table 3.

Comparison of EPMA defocused beam analysis and SEM-EDX modal recombination (values in wt %, recalculated to 100 %).

	Felix chondrule #8	
	EPMA defocused*	SEM-EDX**
SiO_2	50.9	52.5
TiO_2	n.d.	0.3
Al_2O_3	15.5	13.8
FeO	5.8	2.8
MnO	0.44	0.3
MgO	14.7	18.9
CaO	8.63	6.5
Na_2O	2.93	3.8
K_2O	n.d.	0.2
Cr_2O_3	1.18	0.8

* Avoiding opaque phases.
** Excluded opaque phases.
n.d. = not determined.

III. ALLENDE RESULTS

1. Petrography

Petrographic descriptions of the Allende chondrules analyzed for trace elements are presented in Tables 4-6. Chondrules 19, 23, 24 were lost during thin section preparation. The chondrules are classified into three types based on trace element abundances, constituent minerals and textures (GOODING and KEIL, 1981): barred olivine (BO) chondrules (barred olivine type); porphyritic pyroxene (PP) and radial pyroxene (RP) chondrules (pyroxene-rich type); porphyritic olivine (PO) and porphyritic olivine-pyroxene (POP) chondrules (olivine-rich type). Detailed petrographic classifications of chondrules in the Allende and the other CV chondrites were presented by CLARKE *et al.* (1970), MCSWEEN (1977b), SIMON and HAGGERTY (1980) and COHEN *et al.* (1983). According to these studies, the porphyritic olivine chondrules are by far the most abundant, and the barred olivine and pyroxene-rich chondrules make up only 10 % of the total chondrules. Although chondrules analyzed in this work cover most classes of Allende chondrules given by CLARKE *et al.* (1970) and SIMON and HAGGERTY (1980), our sampling appears to have a bias toward the barred olivine and pyroxene-rich types compared to the actual populations of the Allende chondrules.

Table 4. Petrographic descriptions of Allende barred olivine chondrules.

Chdl	Fa[@]	Texture
1	8.3	Barred texture with ol and px in glassy mesostasis.
2	1.4	Barred texture with ol and minor sp in fibrous mesostasis.
3	3.4	Barred texture with ol and fine-grained slender px.
4	5.6	Barred texture with ol, minor high-Ca px and minor interstitial plg.
5	3.6	Barred texture with ol in glassy mesostasis.
6	3.6	Barred texture with ol in glassy mesostasis.
7	29.6	Barred texture with ol and px in glassy mesostasis.

@ Fayalite mole % in olivine.
ol: olivine, px: pyroxene, plg: plagioclase, sp: spinel.

Table 5. Petrographic descriptions of Allende pyroxene-rich chondrules.

Chdl	Fa(Fs)[@]	Texture
8	14.5(9.4)	Porphyritic texture with prismatic low-Ca px and minor ol in minor mesostasis.
9	12.5(0.4)	Microporphyritic texture with subhedral low-Ca px, fine-grained ol, interstitial plg and abundant irregular opaque particles of metal-sulfide ?
10	4.6(0.7)	Poikilitic texture with low-Ca px oikocrysts enclosing small ol grains.
11	(1.1)	Porphyritic texture with prismatic to blocky low-Ca px and minor ol in glassy mesostasis.
12	33.4	Microporphyritic texture with very fine-grained px, minor ol and abundant irregular particles of metal-sulfide ?
13	8.1(1.2)	Radiating texture with low-Ca px laths, minor ol and high-Ca px.

@ Fayalite mole % in olivine and ferrosilite mole % in low-Ca pyroxene.
ol: olivine, px: pyroxene, plg: plagioclase.

Table 6. Petrographic descriptions of Allende olivine-rich chondrules.

Chdl[*]	Fa[@]	Texture
14	3.8	Porphyritic texture with anhedral ol, px and chromian hercynite.
15	4.7	Porphyritic texture with euhedral ol, high-, and low-Ca px and spherical metallic Fe-Ni particles.
16	10.2	Porphyritic texture with euhedral ol and prismatic low-Ca px in abundant glassy mesostasis.
17	n.a.	Porphyritic texture with euhedral to subhedral ol and minor low-Ca px in glassy mesostasis.
18	0.6	Porphyritic texture with anhedral ol and very minor mesostasis.
19[**]	n.a.	Porphyritic texture with ol.
20	2.3	Porphyritic texture with euhedral to subhedral ol in glassy mesostasis.
21	0.7	Porphyritic texture with subhedral ol in glassy mesostasis.
22	11.1	Porphyritic texture with skeletal ol and chromian hercynite in fine-grained mesostasis. Ol exhibits coincidental extinction and contains abundant sp grains.
25	12.6	Granular texture with fine-grained anhedral ol.

[*] Chondrules 19, 23 and 24 were lost during the thin section preparation.

[**] Chondrule 19 is classified as olivine-rich type from a preliminary examination.

[@] Fayalite mole % in olivine.

ol: olivine, px: pyroxene, sp: spinel, n.a.: not analyzed.

2. Mineral chemistry

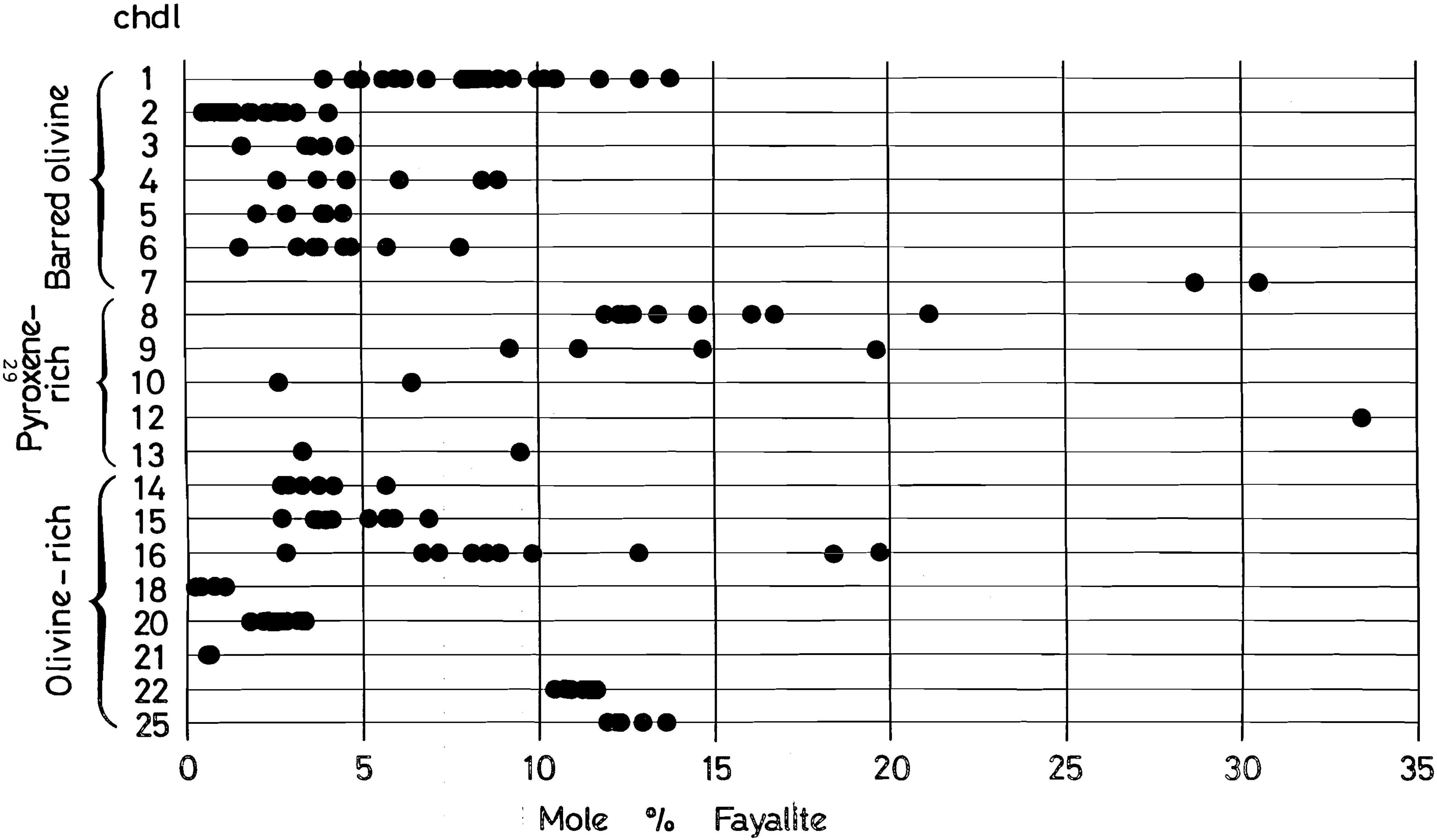
Olivine

The results of electron microprobe analyses of olivines are shown in Fig. 4. Most of olivines show that they are predominantly Mg-rich, with the large proportion having composition in the range of Fa_{0-10} . Olivines in chondrules 7, 8, 12, 22 and 25 are FeO-rich (*i.e.*, Fa_{10-33}). These features are in good agreement with the results of Allende chondrules obtained by SIMON and HAGGERTY (1979).

Figure 4.

Compositions of olivines in Allende chondrules, by petrographic type. Most analyses fall within the range Fa_{0-10} .

Fig. 4


chdl
Barred olivine
Pyroxene-rich
Olivine-rich
1
2
3
4
5
6
7
8
9
10
12
13
14
15
16
18
20
21
22
25
0
5
10
15
20
25
30
35
Mole % Fayalite

Pyroxene

The results of electron microprobe analyses of low-Ca pyroxenes are shown in Figs. 5-7. Most of pyroxenes are Fe-poor (Fs_{0-5}). Representative analyses of Al-rich pyroxene are given in Table 7.

Figure 5.

Compositions of pyroxenes in Allende barred olivine chondrules. Most analyses fall within the range Fs_{0-5} .

Figure 6.

Compositions of pyroxenes in Allende pyroxene-rich chondrules. Most analyses fall within the range Fs_{0-5} .

Figure 7.

Compositions of pyroxenes in Allende olivine-rich chondrules. The pyroxene in chondrule 22 is the most Fe-rich among this study.

Fig. 5

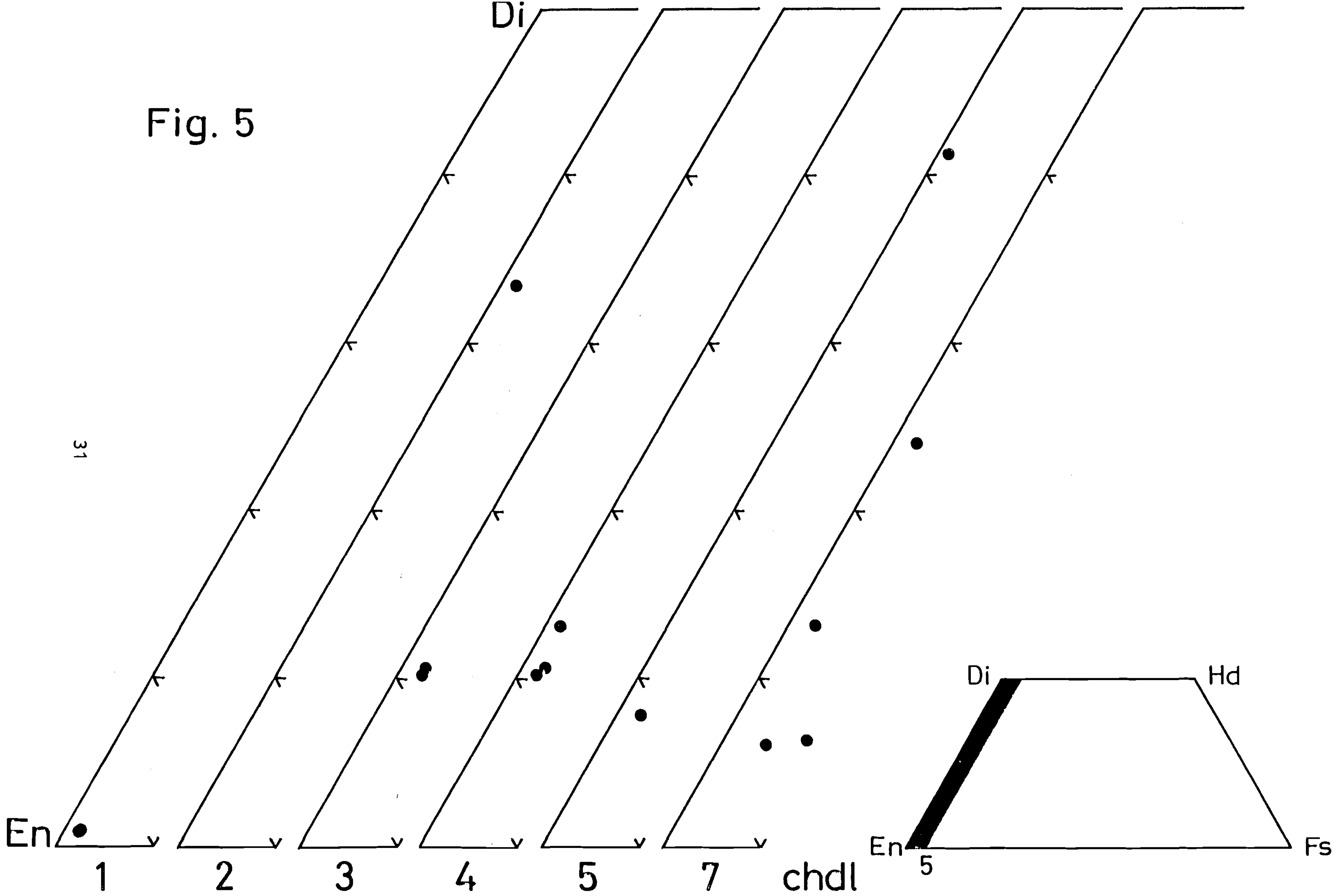
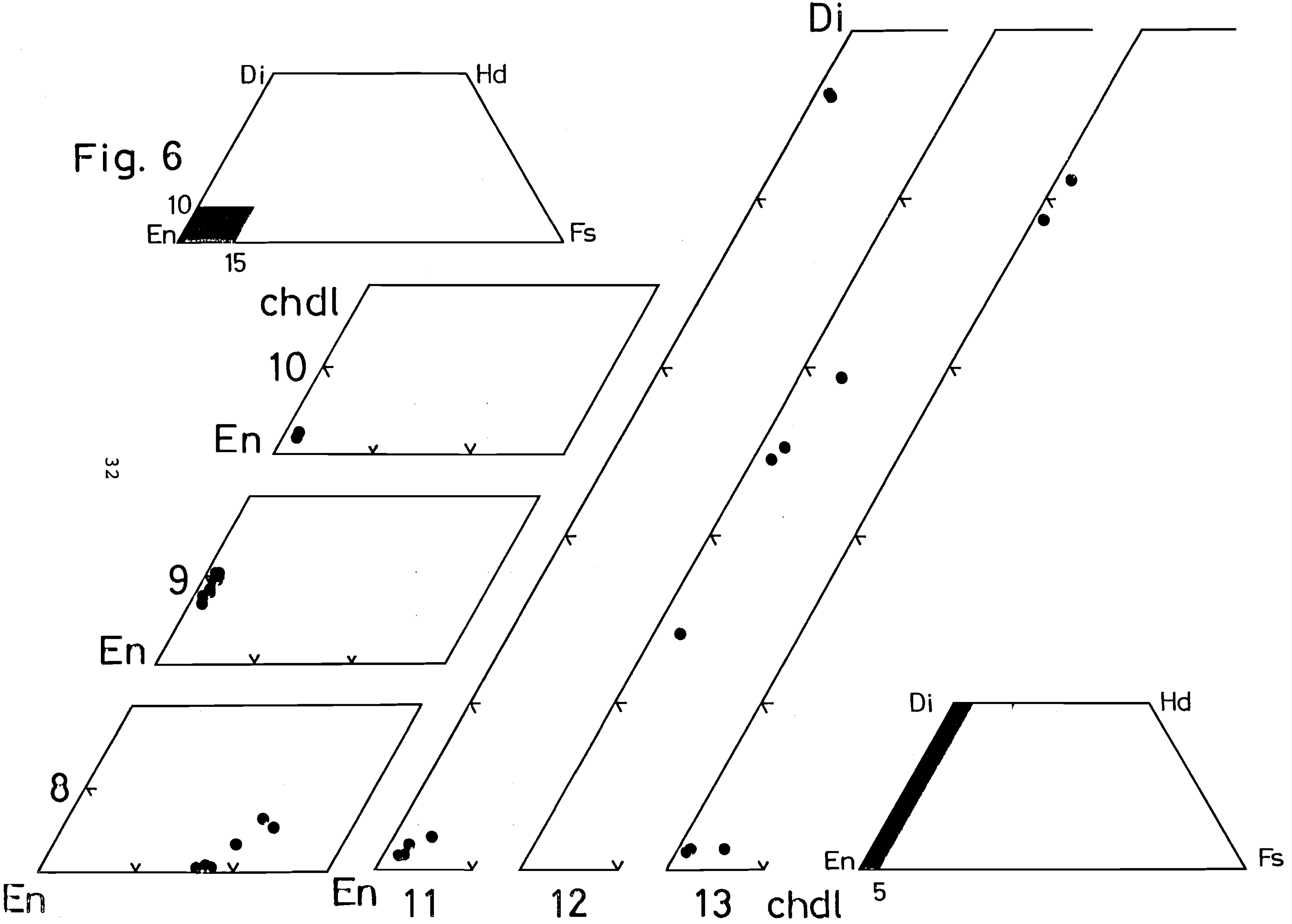


Fig. 6



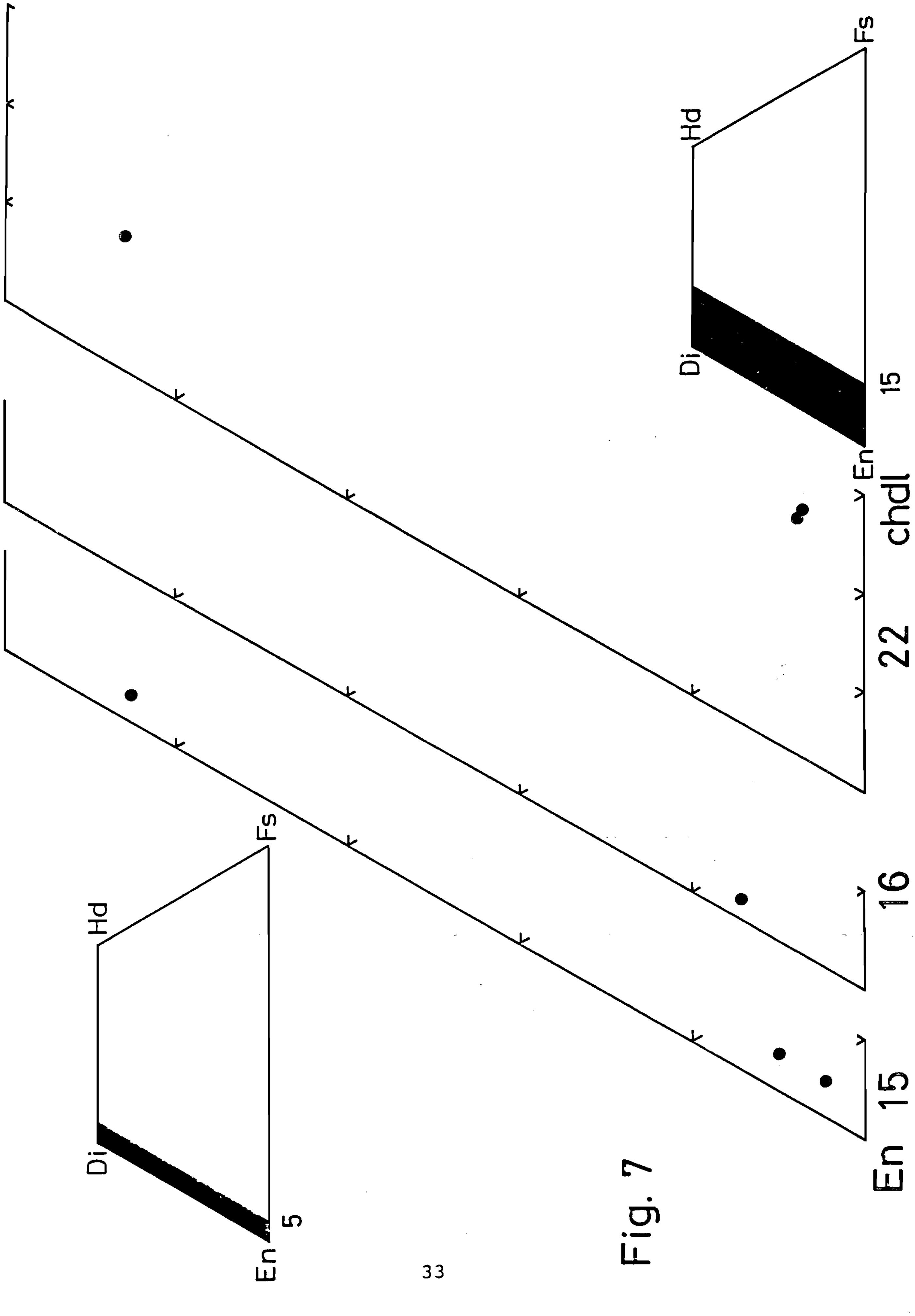


Fig. 7

Table 7.

Representative analyses of Al-rich pyroxene from the Allende chondrules (values in wt %).

	1	2	3	4	5
SiO_2	47.33	48.05	44.58	46.19	49.02
TiO_2	0.71	1.40	1.93	1.27	1.16
Al_2O_3	12.65	10.81	12.55	10.00	7.95
FeO	0.35	0.39	0.35	0.79	3.74
MnO	0.17	0.45	0.01	0.63	0.23
MgO	16.29	16.75	14.13	17.87	16.32
CaO	21.19	20.20	23.98	18.91	19.24
Na_2O	0.07	0.06	0.02	0.06	0.03
K_2O	0.01	n.d.*	0.01	0.01	n.d.
Cr_2O_3	1.02	1.40	0.66	2.17	2.01
Total	100.07	99.53	98.28	98.04	99.72

Cations per 6 Oxygens

Si	1.696	1.733	1.648	1.701	1.788
Ti	0.019	0.038	0.054	0.035	0.032
Al	0.534	0.460	0.547	0.434	0.342
Fe	0.010	0.012	0.011	0.024	0.114
Mn	0.005	0.014	0.000	0.020	0.007
Mg	0.871	0.901	0.797	0.981	0.887
Ca	0.814	0.781	0.950	0.746	0.752
Na	0.005	0.004	0.001	0.004	0.002
K	0.001		0.001	0.000	
Cr	0.029	0.040	0.019	0.063	0.058
Total Cations	3.992	3.981	4.012	4.014	3.982

[1] chdl 1; [2] chdl 11; [3] chdl 14; [4] chdl 15; [5] chdl 22. n.d.* = not detected.

Spinel

Representative analyses of spinels are given in Table 8. Spinels in the chondrule 1 are poor in FeO and Cr_2O_3. In chondrules 14 and 22, on the other hand, spinels contain abundant FeO and Cr_2O_3. These features may be reflect their higher oxidation states.

Table 8.

Representative chemical composition of spinel in the Allende chondrules (values in wt %).

	1	2	3	4	5	6	7	8	9	10
SiO_2	0.08	0.05	0.05	0.40	0.30	0.30	0.32	0.40	0.07	0.11
TiO_2	0.28	0.32	0.28	--	--	--	--	--	0.41	0.45
Al_2O_3	67.96	68.25	67.66	57.37	58.22	59.13	58.74	61.93	22.71	20.69
FeO	1.23	1.15	1.10	9.66	6.17	8.42	6.59	4.52	19.28	21.56
MnO	0.01	0.05	0.01	--	--	--	--	--	0.32	0.31
MgO	26.40	26.08	26.28	20.48	22.76	20.79	22.48	24.23	10.37	8.58
CaO	0.02	n.d.*	0.03	0.02	0.02	0.02	0.02	0.01	0.05	0.12
Cr_2O_3	2.76	2.70	3.20	9.95	11.33	10.13	11.69	10.31	44.96	45.34
V_2O_3	0.09	0.05	0.09	--	--	--	--	--	0.36	0.28
Total	98.90	98.69	98.75	97.88	98.80	98.79	99.84	101.39	98.54	97.45
Cations per 32 Oxygens										
Si	0.016	0.008	0.008	0.084	0.062	0.062	0.066	0.078	0.016	0.032
Ti	0.040	0.048	0.040						0.080	0.088
Al	15.576	15.656	15.536	14.174	14.068	14.369	14.075	14.382	6.768	6.352
Fe	0.200	0.184	0.176	1.694	1.058	1.452	1.120	0.745	4.072	4.696
Mn	0.000	0.008	0.000						0.072	0.064
Mg	7.656	7.568	7.632	6.399	6.958	6.389	6.813	7.117	3.584	3.336
Ca	0.008	---	0.008	0.004	0.004	0.003	0.004	0.002	0.016	0.032
Cr	0.424	0.416	0.496	1.650	1.836	1.652	1.879	1.606	8.984	9.344
V	0.016	0.008	0.016						0.072	0.056
Total Cations	23.944	23.912	23.928	24.005	23.986	23.927	23.957	23.928	23.992	24.008

[1-3] chdl 2; [4-8] chdl 14; [9,10] chdl 22.
*n.d. = not detected. Dashes denote "not determined".

Glass

Representative analyses of chondrule glasses are given in Table 9. There seems that two types of glass (*i.e.*, alkali-rich and alkali-poor) occurred in chondrules. Since alkaline elements are mobile during the post accretionary aqueous alteration in a parent body, the effect may have been affected alkali abundances in chondrule 2 which contains the green (hydrated ?) silicate phase ('spinach phase' termed by FUCHS *et al.*, 1973).

Table 9.

Representative chemical composition of glass from the Allende chondrules (values in wt %).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO_2	42.49	42.30	48.52	48.78	48.38	47.85	48.45	38.85	38.49	41.50	36.41	37.35	43.79	44.90
TiO_2	1.04	0.70	0.91	0.83	1.03	1.19	0.17	0.21	0.16	n.d.	0.49	1.39	1.11	1.30
Al_2O_3	27.88	27.62	24.03	22.87	23.69	24.27	19.63	22.27	26.57	31.62	25.43	29.80	24.55	24.76
FeO	0.86	0.85	0.50	0.45	0.38	0.46	0.29	7.17	2.70	0.83	7.88	0.26	0.87	0.40
MnO	0.11	0.08	0.05	0.07	0.04	0.04	0.15	0.12	0.11	0.03	0.09	0.01	0.04	0.02
MgO	4.32	4.13	5.74	7.60	6.59	6.41	14.80	15.08	6.59	1.58	12.82	7.83	4.83	5.12
CaO	6.28	5.62	17.14	15.83	16.54	16.78	11.73	1.08	2.33	11.10	4.90	17.70	19.93	20.03
Na_2O	12.31	11.83	1.73	1.64	1.55	1.41	1.17	12.81	14.90	8.02	6.11	2.66	0.84	0.96
K_2O	1.62	1.58	0.01	0.01	n.d.	0.02	0.06	1.27	1.67	0.85	0.80	0.37	0.01	0.01
Cr_2O_3	0.59	0.30	0.18	0.35	0.27	0.25	0.43	0.08	0.10	0.07	0.45	0.11	0.37	0.38
V_2O_3	n.d.*	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
P_2O_5	0.06	n.d.	--	--	--	--	0.03	0.07	0.05	n.d.	--	0.05	0.05	0.05
Total	97.58	95.00	98.81	98.44	98.48	98.69	96.91	99.04	93.65	95.62	95.38	97.57	96.39	97.92

[1,2] chdl 1; [3-6] chdl 2; [7] chdl 3; [8,9] chdl 8; [10] chdl 13; [11] chdl 16; [12] chdl 18; [13,14] chdl 21. n.d.* = not detected. Dashes denote "not determined".

3. Bulk chemical compositions

Normalization factor

In the past most investigators used several reference concentration sets and adoption of only one agreed set of chondrite-normalizing concentrations has not occurred. In Table 10, REE concentrations in chondritic meteorites used for normalization are given.

Table 10.

Rare earth element abundances in chondritic meteorites used for normalization.

Element	Orgueil average	Orgueil average	CI average	CI	Av. of 10 O-chondrites	Leedy '73	Leedy '84
	Nakamura (1974)	Beer et al. (1984)	Evensen et al. (1978)	Anders & Ebihara (1982)	Nakamura (1974)	Masuda et al. (1973)	Shimizu & Masuda (1986)
La	0.253	0.2365	0.2446	0.236	0.329	0.378	0.322
Ce	0.645	0.612	0.6379	0.616	0.865	0.976	0.835
Nd	0.476	0.467	0.4738	0.462	0.630	0.716	0.603
Sm	0.154	0.153	0.1540	0.142	0.203	0.230	0.1964
Eu	0.0587	0.0580	0.05802	0.0543	0.0770	0.0866	0.0825
Gd	0.204	0.2055	0.2043	0.196	0.276	0.311	0.270
Dy	0.252	0.254	0.2541	0.242	0.343	0.390	0.331
Er	0.166	0.1655	0.1660	0.160	0.225	0.255	0.226
Yb	0.168	0.170	0.1651	0.166	0.220	0.249	0.233
Lu	0.0253	0.02535	0.02539	0.0243	0.0339	0.0387	0.0362

In Fig. 8, each REE concentrations are normalized by the average of 10 ordinary chondrites (NAKAMURA, 1974). It appears that abundances of heavy REE obtained by NAKAMURA (1974), EVENSEN *et al*. (1978), and BEER *et al*. (1984) are in good agreement one another, except for Yb abundance. On the other hand, they are similarly fractionated among La-Sm. As a result, about 7 % of differences of relative REE abundances with different CI-normalization set are occurred. In this study, REE are after NAKAMURA (1974), alkalis and alkaline earths are after ANDERS and EBIHARA (1982).

Figure 8.

Rare earths abundance patterns of Leedy '73 (MASUDA *et al*., 1973), Leedy '84 (SHIMIZU and MASUDA, 1986), Orgueil (NAKAMURA, 1974), avg. of CI (EVENSEN *et al*., 1978), Orgueil (BEER *et al*., 1984) and CI (ANDERS and EBIHARA, 1982) are normalized by average of 10 ordinary chondrites (NAKAMURA, 1974).

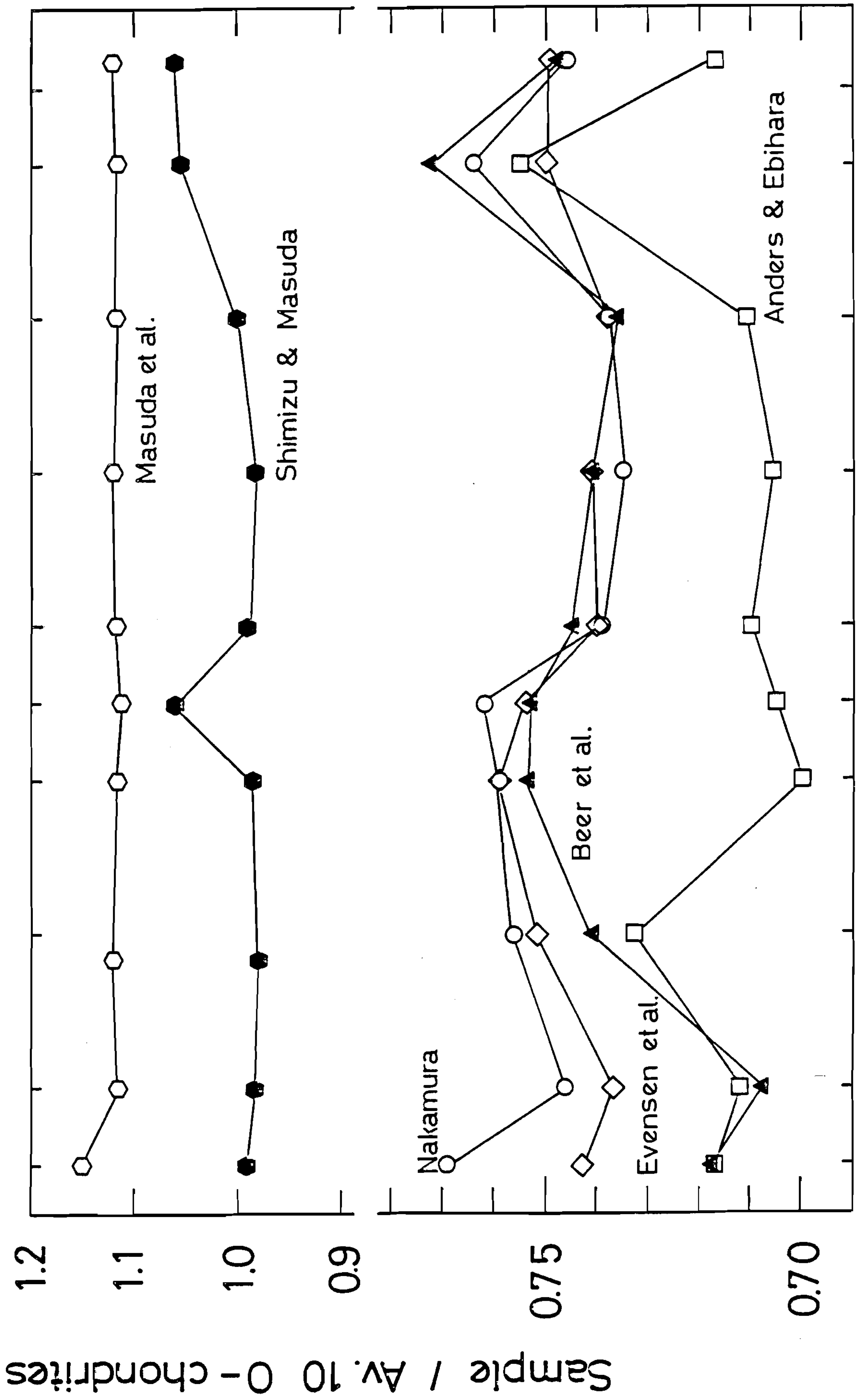

Sample / Av. 10 O-chondrites
1.2
1.1
1.0
0.9
0.75
0.70
Masuda et al.
Shimizu & Masuda
Nakamura
Evensen et al.
Beer et al.
Anders & Ebihara
La
Ce
Nd
Sm
Eu
Gd
Dy
Er
Yb
Lu

Fig. 8

The results of isotope dilution analyses for 25 Allende chondrules are given in Tables 11 and 12, and shown in Figs 9-10. The elemental abundances are normalized to CI-chondrite and then further normalized to Mg = 1.0 and plotted in the order of REE, alkaline earths and alkalis, and increasing volatility expected from a gas of solar composition (KORNACKI and FEGLEY, 1986). Here I point out that "volatility", in the sense I use it, is equivalent to equilibrium partitioning between gas and a condensed phase. Magnesium contents obtained for the Allende chondrules range from 14.2 to 28.6 wt % (Table 11). Since Si was not determined in this work, Mg is used for normalization. The difference of relative elemental abundances with different normalization was discussed by J.N. GROSSMAN *et al*. (1985).

Table 11. Bulk chemical compositions of Allende chondrules.

chdl	weight dissolved (mg)	Mg (%)	Ca (%)	K (ppm)	Rb (ppm)	Sr (ppm)	Ba (ppm)
1-1	0.572	21.4	1.72	1570	6.32	20.1	10.4
1-2	0.511	19.8	1.84	1840	7.95	25.3	11.8
2-1	0.684	17.9	4.03	164	1.35	39.3	12.9
2-2	1.050	18.8	3.71	114	0.794	34.4	11.4
3	0.158	19.0	2.02	603	2.33	27.8	8.12
4	0.167	18.4	2.68	1080	4.39	37.3	10.6
5	0.977	23.7	2.09	839	4.43	31.3	6.92
6	0.832	21.5	1.84	633	3.21	13.4	6.88
7	0.052	17.3	3.12	1670	6.36	111	43.3
8	0.690	18.2	1.40	802	4.03	14.8	7.83
9	0.315	16.1	3.91	644	2.36	35.0	10.7
10	0.173	18.1	2.59	1190	4.45	60.2	15.1
11	0.053	14.2	3.27	1440	5.50	30.0	17.1
12	0.056	14.8	5.67	2040	7.53	124	21.6
13	0.079	21.6	1.50	1160	6.46	20.4	---
14	0.141	22.9	2.58	343	1.51	26.6	8.58
15	0.536	21.0	1.68	419	1.78	14.9	6.79
16	0.230	17.9	2.73	973	3.61	17.7	11.9
17	0.176	28.6	0.710	162	0.704	8.60	---
18-1	0.684	---	0.392	29.2	0.201	2.55	1.03
18-2	0.448	22.4	0.386	14.9	0.103	3.33	---
19	0.206	20.7	0.824	271	1.24	18.0	5.04
20	0.698	21.2	1.41	573	2.44	15.3	4.90
21	2.607	17.9	0.648	94.6	0.402	5.41	2.30
22	0.637	24.2	1.69	280	1.96	8.94	5.50
23	0.143	20.7	2.09	219	1.12	21.9	6.57
24	0.218	25.2	1.58	948	3.82	19.4	8.85
25	0.774	23.3	2.51	351	1.73	9.61	3.22
CI#		9.55	0.902	569	2.30	7.91	2.27

CI values are after Anders and Ebihara (1982).

Table 12. REE contents of Allende chondrules.

La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Dy (ppm)	Er (ppm)	Yb (ppm)	Lu (ppm)	chdl
1.05	2.83	2.18	0.730	0.193	0.924	1.20	0.967	0.642	0.190	1-1
1.15	3.07	2.33	0.759	0.231	0.936	1.24	1.00	0.741	0.203	1-2*
1.35	3.34	2.71	0.860	0.264	1.11	1.32	1.44	0.765	0.254	2-1
1.35	3.36	2.72	0.878	0.269	1.08	1.31	1.41	0.884	0.253	2-2*
0.633	1.65	1.24	0.412	0.166	0.549	0.656	0.448	0.506	0.0784	3
1.00	2.72	1.89	0.626	0.234	0.738	0.838	0.512	0.874	0.0845	4
0.761	1.95	1.53	0.503	0.166	0.678	0.812	0.550	0.576	0.0889	5*
0.826	2.11	1.62	0.525	0.172	0.679	0.816	0.553	0.616	0.0881	6*
1.41	3.69	2.76	0.894	0.245	1.15	1.34	0.886	0.993	0.141	7
0.455	1.23	0.931	0.314	0.111	0.422	0.506	0.340	0.356	0.0526	8
0.715	3.02	1.59	0.684	0.281	0.509	0.597	0.404	1.15	0.0631	9*
1.08	2.83	2.17	0.716	0.224	0.891	1.09	0.647	0.780	0.0981	10
1.04	2.65	2.00	0.662	0.185	0.877	1.13	0.761	0.772	0.114	11
1.66	4.85	3.24	1.09	0.404	1.73	1.94	1.28	1.45	0.219	12
0.675	---	1.35	0.451	0.141	0.502	0.546	0.330	---	0.0482	13
0.958	2.13	1.71	0.548	0.171	0.737	0.893	0.601	0.664	0.102	14
0.479	1.30	0.939	0.309	0.112	0.405	0.489	0.324	0.289	0.0482	15
1.02	2.43	2.03	0.659	0.256	0.854	1.11	0.735	0.755	0.112	16
0.198	0.488	0.371	0.121	0.0456	0.166	0.213	0.163	---	0.0268	17
---	0.264	0.126	---	---	---	0.0563	---	---	---	18-1
---	0.0819	0.0613	0.0227	0.0130	---	---	0.0229	---	---	18-2
0.243	0.677	0.502	0.170	0.0534	0.231	0.284	0.199	0.213	0.0356	19
0.527	1.41	1.08	0.358	0.127	0.473	0.549	0.359	0.368	0.0575	20
0.199	0.493	0.384	0.125	0.0403	0.153	0.188	0.141	0.148	0.0237	21*
0.461	1.21	0.935	0.306	0.102	0.411	0.489	0.327	0.336	0.0520	22*
0.659	---	1.33	0.428	0.155	0.596	0.717	0.490	0.523	0.0808	23
0.845	2.03	1.71	0.548	0.155	0.719	0.853	0.569	0.529	0.0983	24
0.801	2.22	1.58	0.493	0.206	0.624	0.751	0.498	0.482	0.0776	25*
0.253	0.654	0.476	0.154	0.0587	0.204	0.252	0.166	0.168	0.0253	CI#

* Cation exchange treatment was performed for REE separation.
# CI values sre after Nakamura (1974).
Dashes denote "not determined".

Figure 9.

CI-normalized abundances of lithophile elements in barred olivine type and pyroxene-rich type chondrules from Allende (abundances are normalized to Mg in the sample and then renormalized to CI). Elements are arranged in the order of REE, alkaline earths and alkalis, and increasing volatilities from the left to the right.

Figure 10.

CI-normalized abundances of lithophile elements in olivine-rich type chondrules from Allende. Plots are the same manner as in Fig. 9.

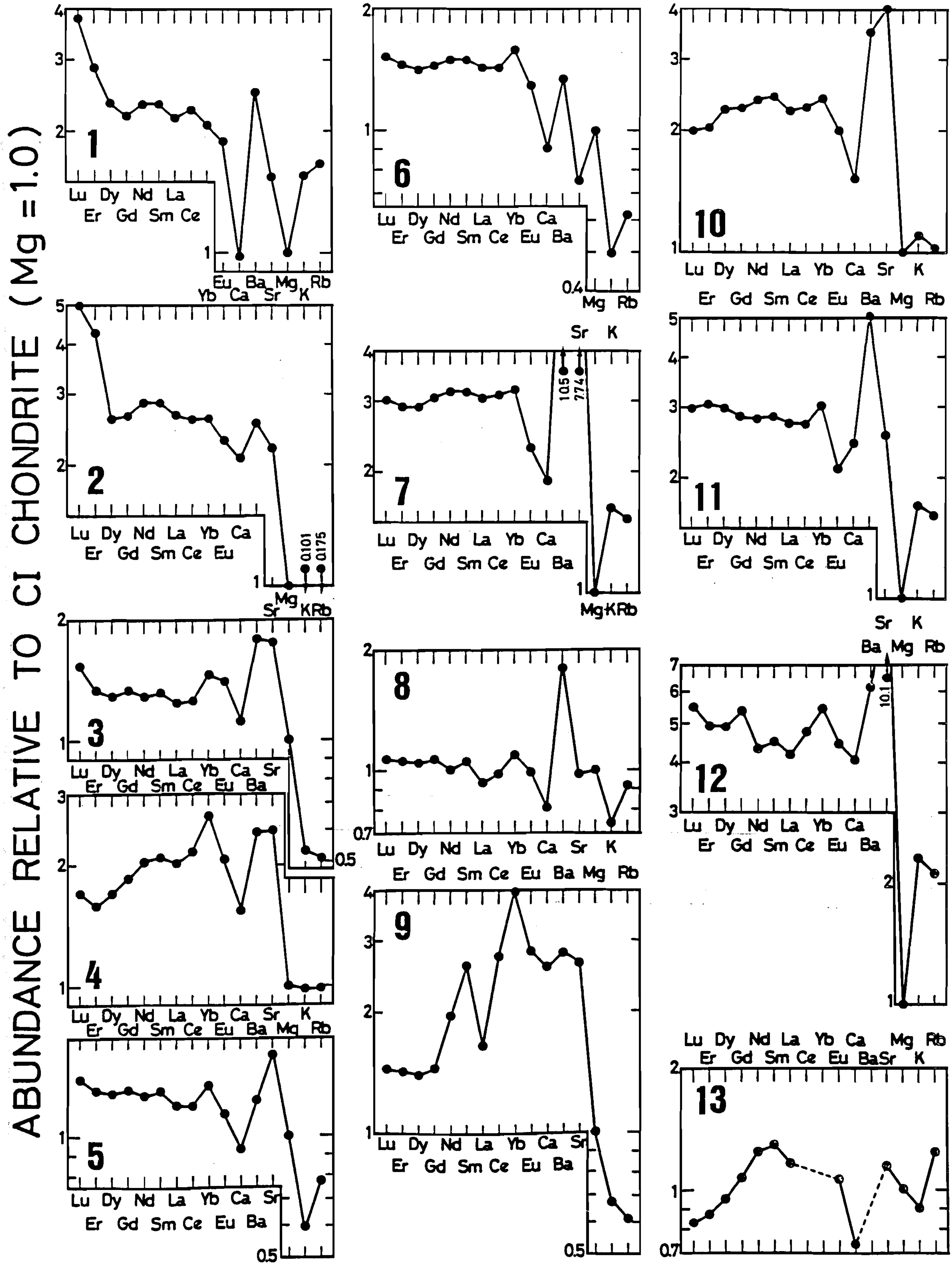
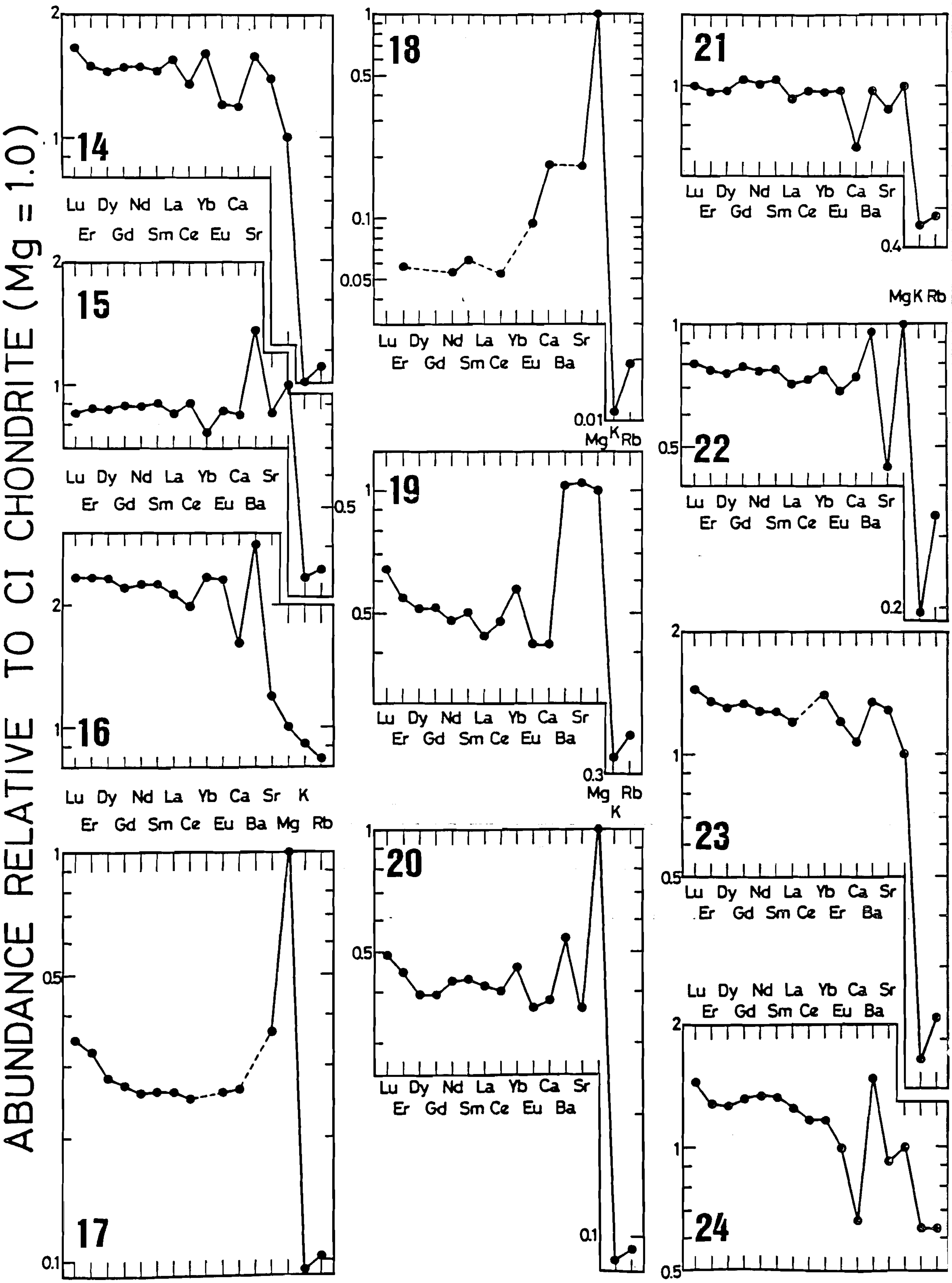

ABUNDANCE RELATIVE TO CI CHONDRITE (Mg = 1.0)
1
Lu Dy Nd La
Er Gd Sm Ce
Eu Ba Mg Rb
Yb Ca Sr K
2
Lu Dy Nd La Yb Ca
Er Gd Sm Ce Eu
0.101
0.175
Sr Mg K Rb
3
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
0.5
4
Lu Dy Nd La Yb Ca Sr K
Er Gd Sm Ce Eu Ba Mg Rb
5
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
0.5
6
Lu Dy Nd La Yb Ca
Er Gd Sm Ce Eu Ba
0.4
Mg Rb
7
Sr K
10.5
77.4
Lu Dy Nd La Yb Ca
Er Gd Sm Ce Eu Ba
Mg K Rb
8
Lu Dy Nd La Yb Ca Sr K
Er Gd Sm Ce Eu Ba Mg Rb
0.7
9
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
0.5
10
Lu Dy Nd La Yb Ca Sr K
Er Gd Sm Ce Eu Ba Mg Rb
11
Lu Dy Nd La Yb Ca
Er Gd Sm Ce Eu
Sr K
Ba Mg Rb
12
10.1
Lu Dy Nd La Yb Ca
Er Gd Sm Ce Eu Ba
Lu Dy Nd La Yb Ca Mg Rb
Er Gd Sm Ce Eu Ba Sr K
13
0.7

Fig. 9



ABUNDANCE RELATIVE TO CI CHONDRITE (Mg = 1.0)
14
2
1
Lu Dy Nd La Yb Ca
Er Gd Sm Ce Eu Sr
15
2
1
0.5
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
16
2
1
Lu Dy Nd La Yb Ca Sr K
Er Gd Sm Ce Eu Ba Mg Rb
17
1
0.5
0.1
18
1
0.5
0.1
0.05
0.01
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
Mg K Rb
19
1
0.5
0.3
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
Mg Rb
K
20
1
0.5
0.1
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
21
1
0.4
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
Mg K Rb
22
1
0.5
0.2
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
23
2
1
0.5
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Er Ba
Lu Dy Nd La Yb Ca Sr
Er Gd Sm Ce Eu Ba
24
2
1
0.5

Fig.10

3-1. Alkalis and alkaline earths

Abundances of the moderately volatile elements, K and Rb, show large variations, ranging from 0.03 to 3.5 x CI (Table 11). The variations are found to be rather characteristic for the chondrule types, when the abundances are normalized to Mg = 1.0 (Figs. 9-10): barred olivine and pyroxene-rich types have higher K and Rb abundances (0.5-2 x CI except for chondrule 2), while the majority of olivine-rich type chondrules have lower K and Rb abundances (< 0.5 x CI). These results are consistent with the observation of Na abundances for the Allende chondrules (SIMON and HAGGERTY, 1980). Low chondrite-normalized alkali abundances in olivine-rich chondrules may be due to inefficient scavenging of alkali-rich component in this type of chondrules.

In Fig. 11, Rb is plotted against K for the Allende chondrules. Regardless of textural or bulk chemical differences, the chondrules have a constant K/Rb ratio close to that of CI's. These features are consistent with the results of relatively large Mg-rich Allende chondrules (2-12 mm in diameter) analyzed by TATSUMOTO _et_ _al_. (1976).

Figure _11_.

Relationship between K/Mg _vs_. Rb/Mg in individual chondrules from Allende. Solid circles: barred olivine type, solid triangles: pyroxene-rich type, solid squares: olivine-rich type, open circles: unclassified.

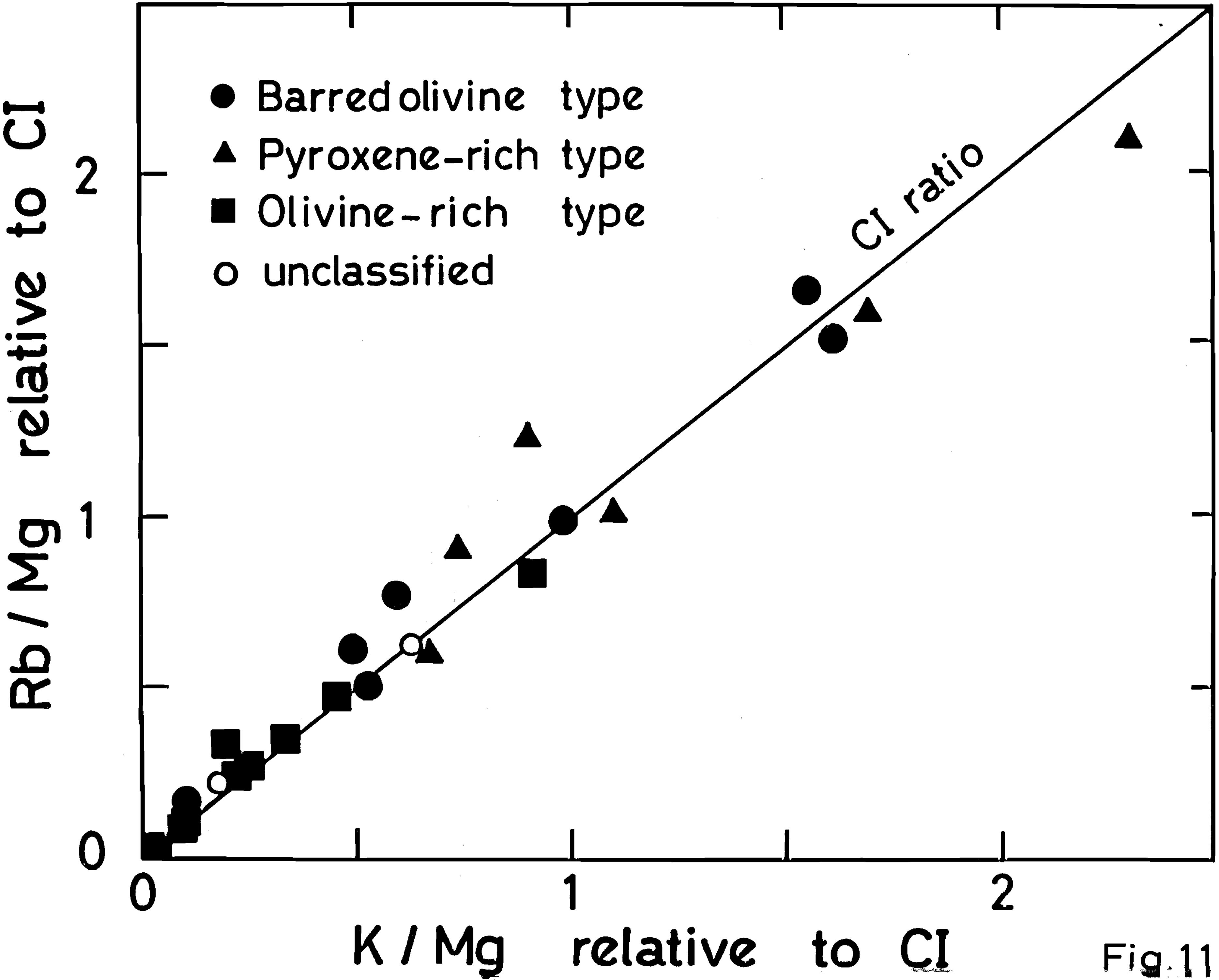

Barredolivine type
Pyroxene-rich type
Olivine-rich type
unclassified
CI ratio
Rb / Mg relative to CI
K / Mg relative to CI
0
1
2
0
1
2

Fig.11

As shown in Figs. 9 and 10, the relative abundances of Sr and Ba show a general trend among chondrules; olivine-rich type < barred olivine type pyroxene-rich type, and are considerably scattered in some BO and PP chondrules (*e.g.*, 7 and 12).

In Figs. 12 and 13, K *vs.* Sm, Ca *vs.* Sm, Sr *vs.* Sm, and Ba *vs.* Sm variations of Allende chondrules are shown. Abundances of Ca ranging from 0.18 to 4.3 x CI are parallel with those of REE (0.26-4.6 x CI) and a positive correlation of Ca with Sm is clearly observed for different types of chondrules (Fig. 12). The slope of the total trend is 0.6. It is mainly controlled by the barred olivine chondrules, indicating that these chondrules show a systematic depletion of Ca relative to REE, as illustrated in Fig. 9. The relative depletion of Ca is consistent with the observation that relative Ca abundances in the barred olivine chondrules from CV and CO chondrites are lower than those of other refractory elements with similar volatilities (J.N. GROSSMAN and WASSON, 1983b). Similar trends are also found for correlations of Sm with Sr and Ba (Fig. 13) but Sr and Ba tend to be enriched relative to Sm. These results for refractory trace and major elements are partly in agreement with the observations of OSBORN *et al.* (1974). In chondrules 7 and 12, Sr and/or Ba are highly enriched relative to other refractory lithophiles.

Figure 12.

Plots of K/Mg *vs.* Sm/Mg and Ca/Mg *vs.* Sm/Mg for Allende chondrules.

Figure 13.

Plots of Ba/Mg *vs.* Sm/Mg and Sr/Mg *vs.* Sm/Mg for Allende chondrules.

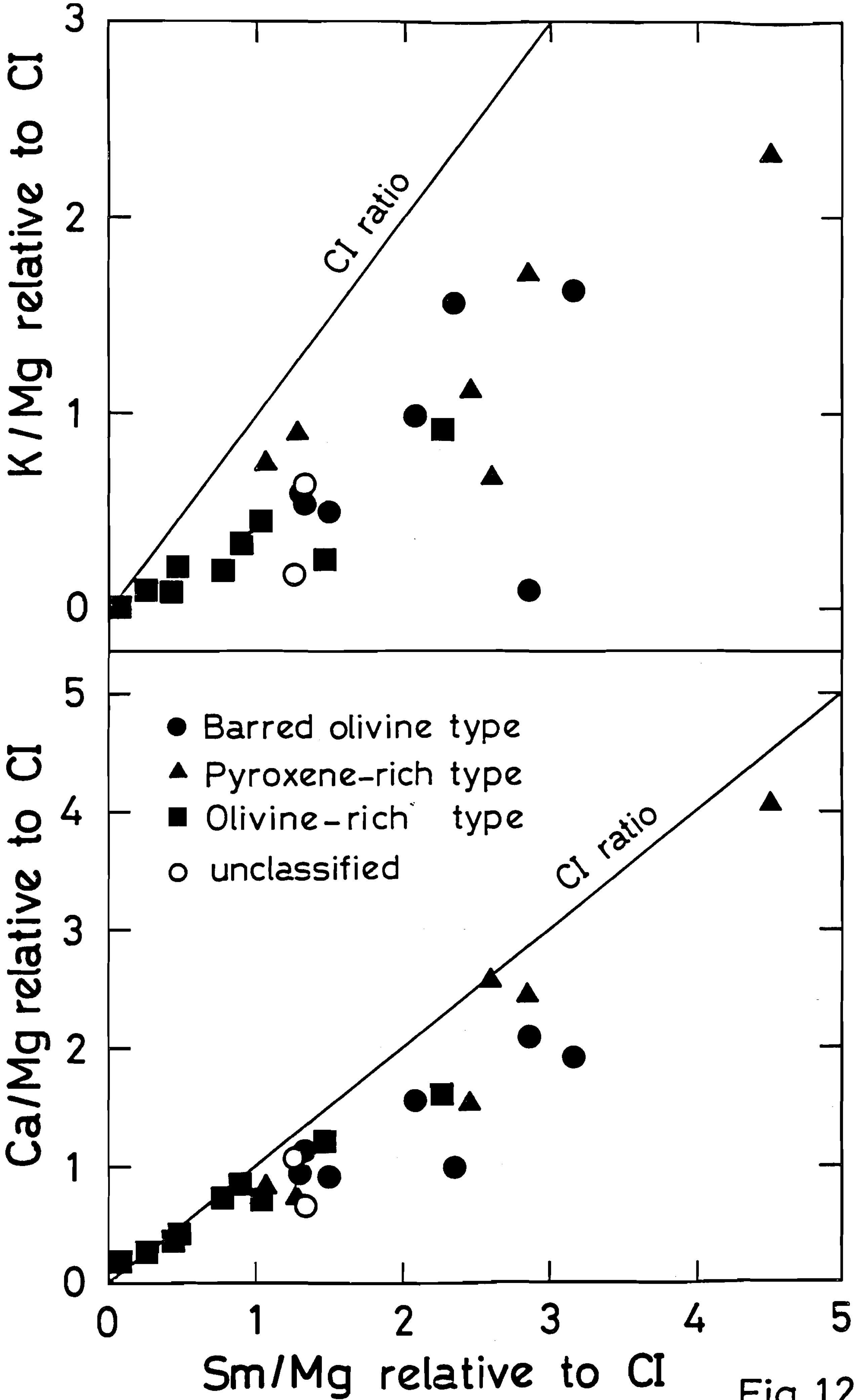

3
2
1
0
K / Mg relative to CI
CI ratio
5
4
3
2
1
0
Ca/Mg relative to CI
● Barred olivine type
▲ Pyroxene-rich type
■ Olivine-rich type
○ unclassified
CI ratio
0
1
2
3
4
5
Sm/Mg relative to CI

Fig.12

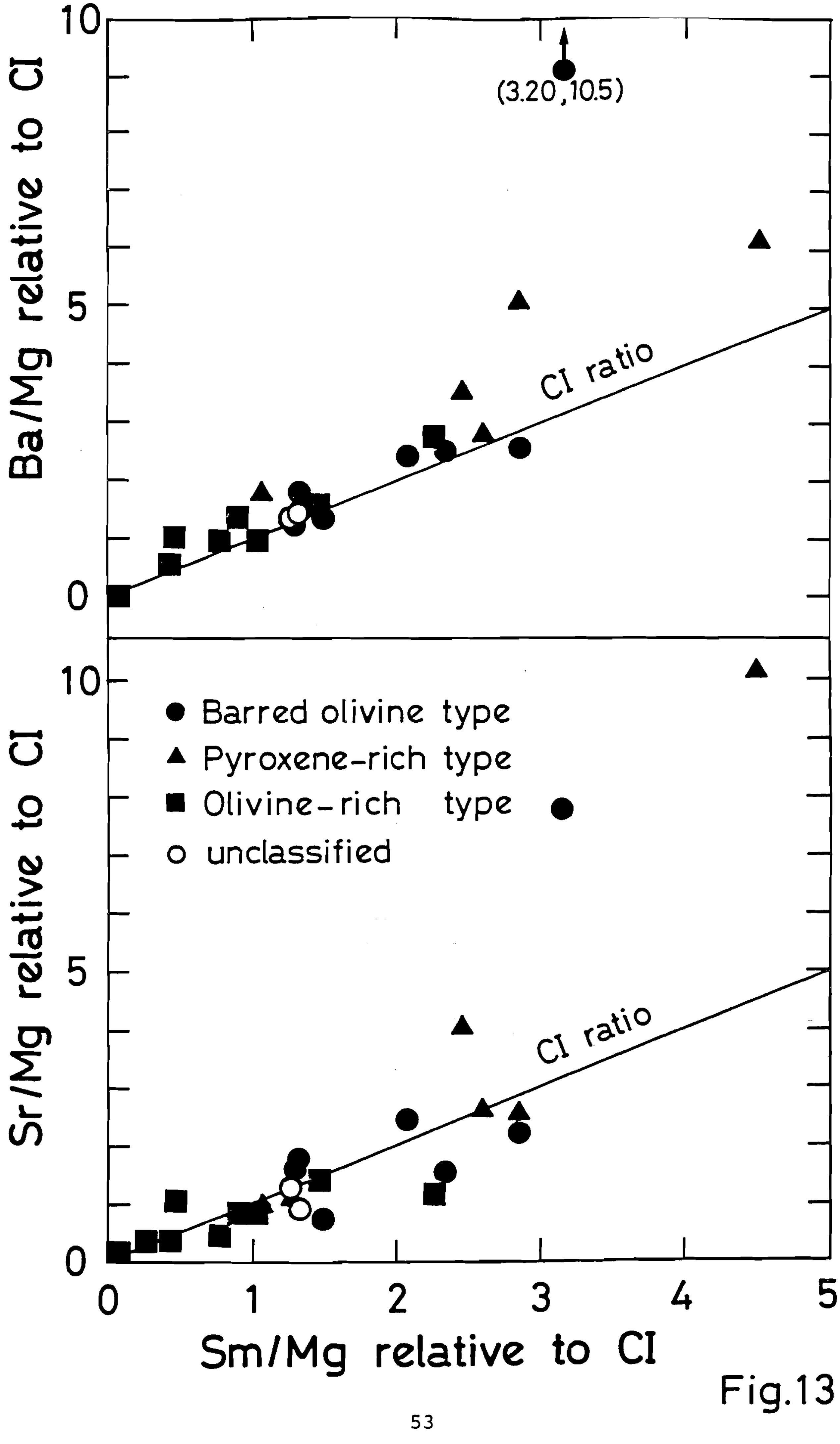

10
5
0
Ba/Mg relative to CI
(3.20, 10.5)
CI ratio
10
5
0
Sr/Mg relative to CI
● Barred olivine type
▲ Pyroxene-rich type
■ Olivine-rich type
○ unclassified
CI ratio
0
1
2
3
4
5
Sm/Mg relative to CI

Fig.13

In Fig. 12, there is a positive correlation between K and Sm. RUBIN and WASSON (1987b) showed that Na and K only correlate moderately with Al in Allende chondrules and suggested a refractory-free, alkali-rich nebular component. They analyzed mainly PO and POP chondrules. Sodium abundances in 10 of the 20 chondrules and K abundances in 15 of the 20 chondrules were below CI levels. In this study, by contrast, K and Rb abundances in 15 of the 24 chondrules were above CI levels . If alkali-poor BO chondrule 2 is excluded, K positively correlates with Sm (r=0.865, n=24; r=correlation coefficient, n=number of samples) and moderately correlates with Ca (r=0.658, n=24), suggesting similar behavior of the moderately volatile elements and the refractory elements as a single nebular component. The close correlations of the alkaline elements Na and/or K with REE has been reported for the Qingzhen (EH) and Ornans (CO) chondrules (J.N. GROSSMAN *et al.*, 1985; RUBIN and WASSON, 1987a). In Allende, alkali-rich CAIs and CAIs' rims were also found (L. GROSSMAN *et al.*, 1975; L. GROSSMAN and STEEL, 1976; L. GROSSMAN *et al.*, 1979; WARK and LOVERING, 1977).

3-2. Rare earths

In Figs. 14-25, REE abundance patterns for Allende chondrules are shown. The abundances are normalized to the Orgueil CI chondrite. Analytical errors are usually within or nearly equal to the symbol size.

Figures 14-25.

REE abundance patterns (plots of relative abundances *vs*. atomic number) for Allende chondrules. REE patterns are drawn based on the following criteria;

(1) each data point is weighted equally,
(2) light and heavy REE are treated separately and thus the pattern is composed of two segments (i.e., light REE and heavy REE),
(3) each segment consists of a smoothly curved line which is apploximately drawn among three or four data points. As a results, data points which deviate more than 5 % from the fitting line are regarded as "anomalous".

Figure 14.

CI-normalized REE patterns of Allende barred olivine chondrule 1. Sample 1-1 was analyzed by the direct-loading technique. Sample 1-2 was performed column chemistry for REE separation.

Figure 15.

CI-normalized REE patterns of Allende barred olivine chondrule 2. Sample 2-1 was analyzed by the direct-loading technique. Sample 2-2 was performed column chemistry for REE separation.

Figure 16.

CI-normalized REE patterns for Allende barred olivine chondrules 3 and 4.

Figure 17.

CI-normalized REE patterns for Allende barred olivine chondrules 5, 6 and 7.

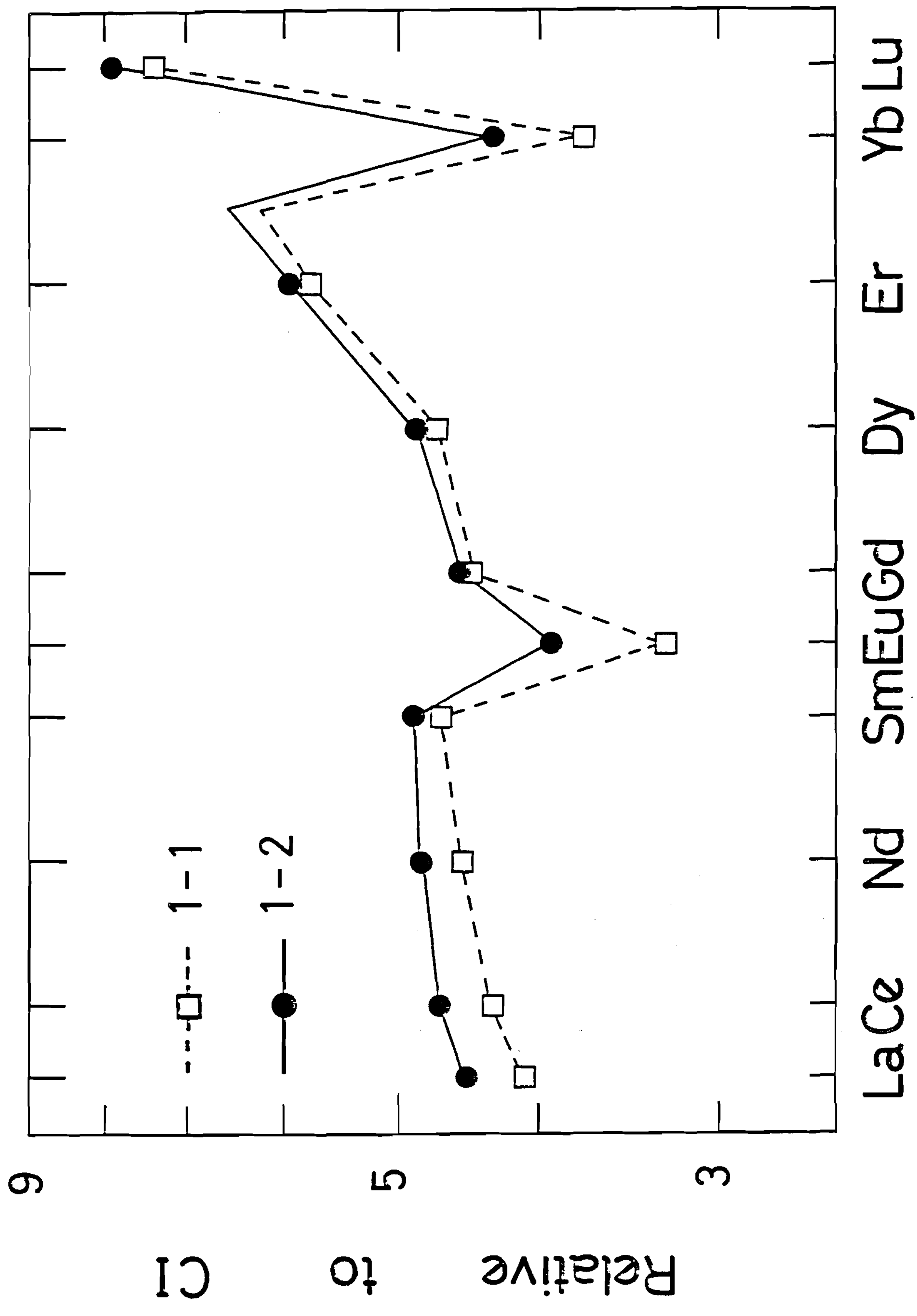


Fig. 14

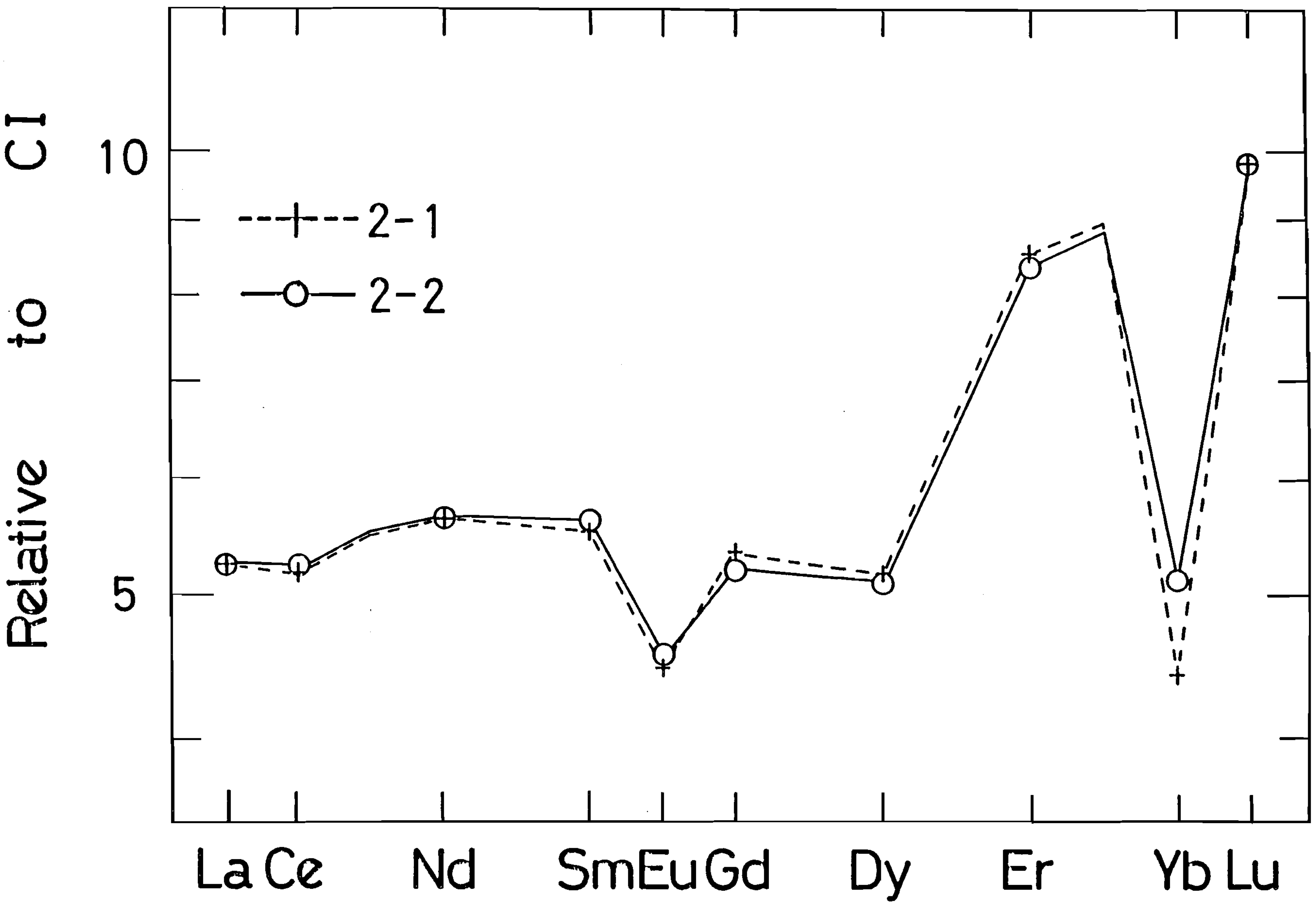


Fig.15

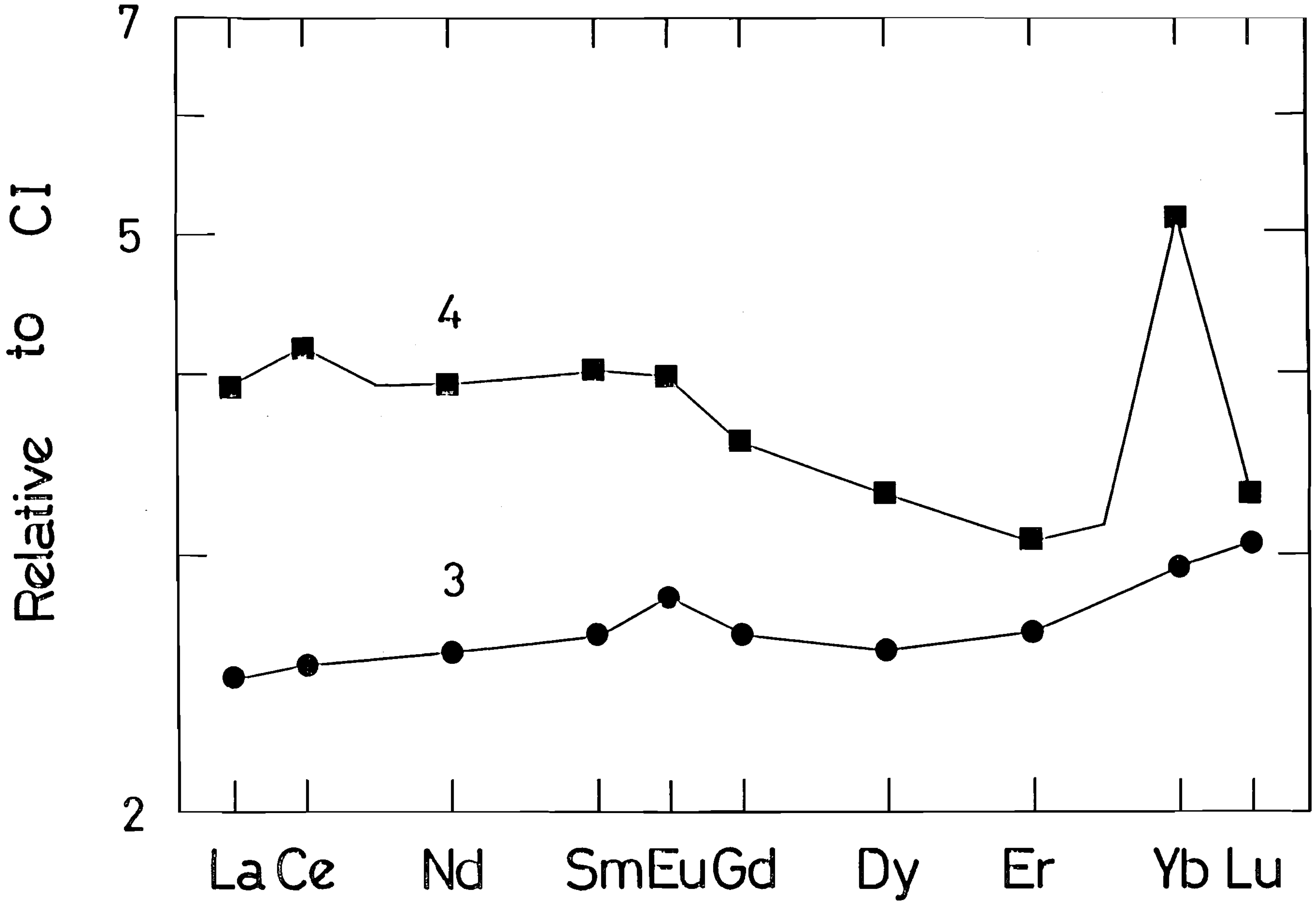


Fig.16

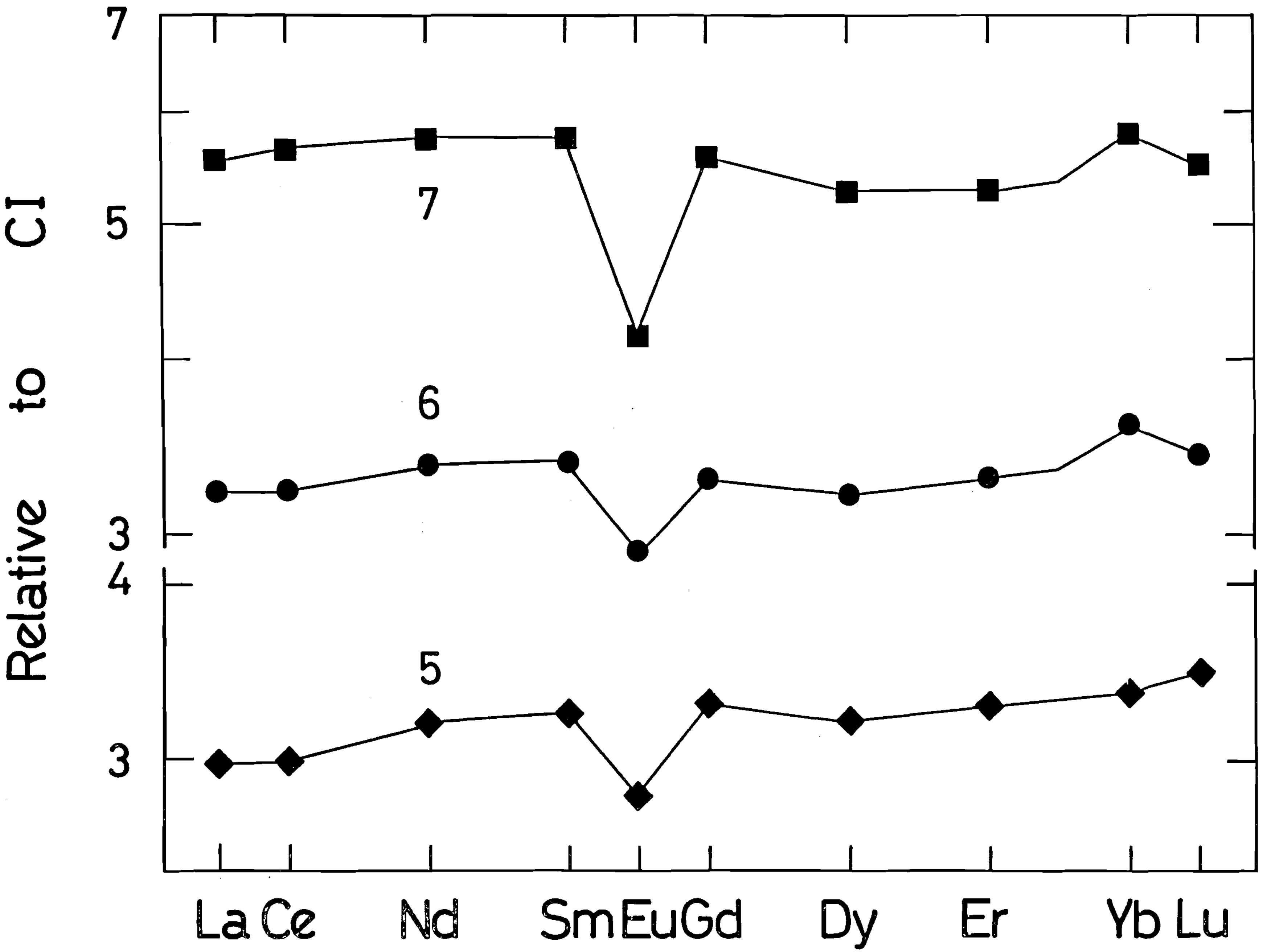


Fig.17

Figure 18.

CI-normalized REE patterns for Allende pyroxene-rich chondrules 8 and 9.

Figure 19.

CI-normalized REE patterns for Allende pyroxene-rich chondrules 10 and 11.

Figure 20.

CI-normalized REE patterns for Allende pyroxene-rich chondrules 12 and 13.

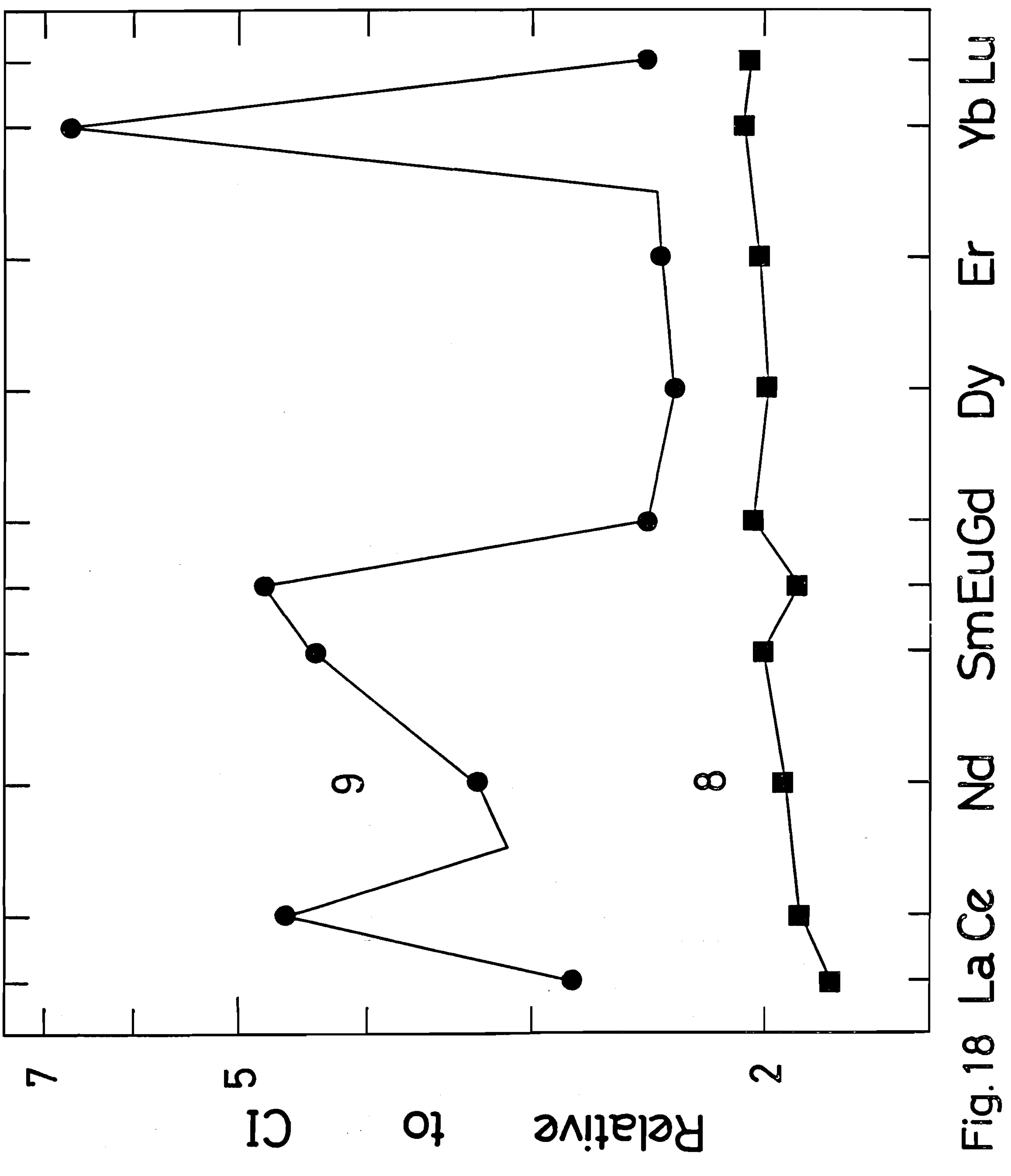


Fig.18

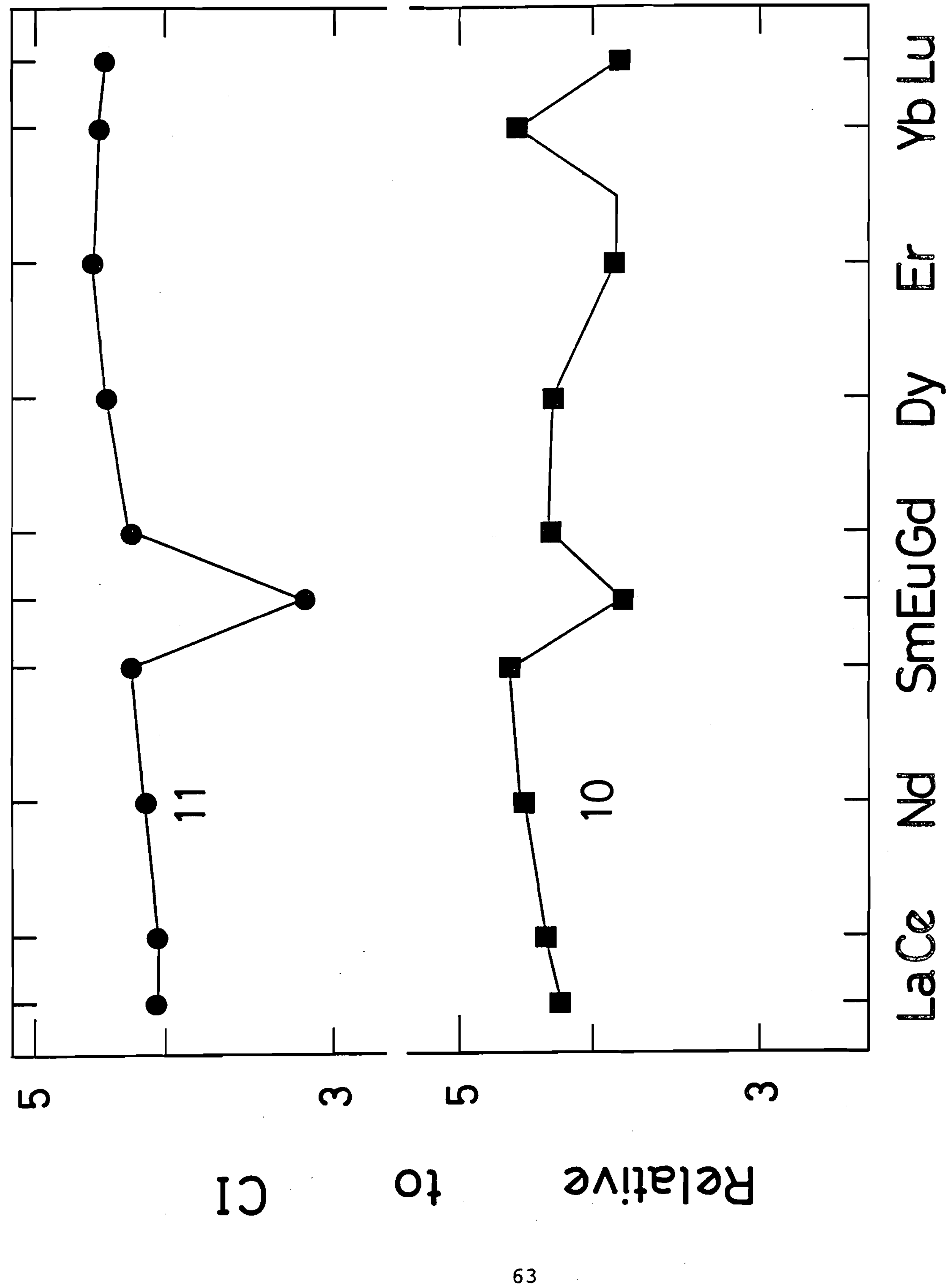


Fig.19

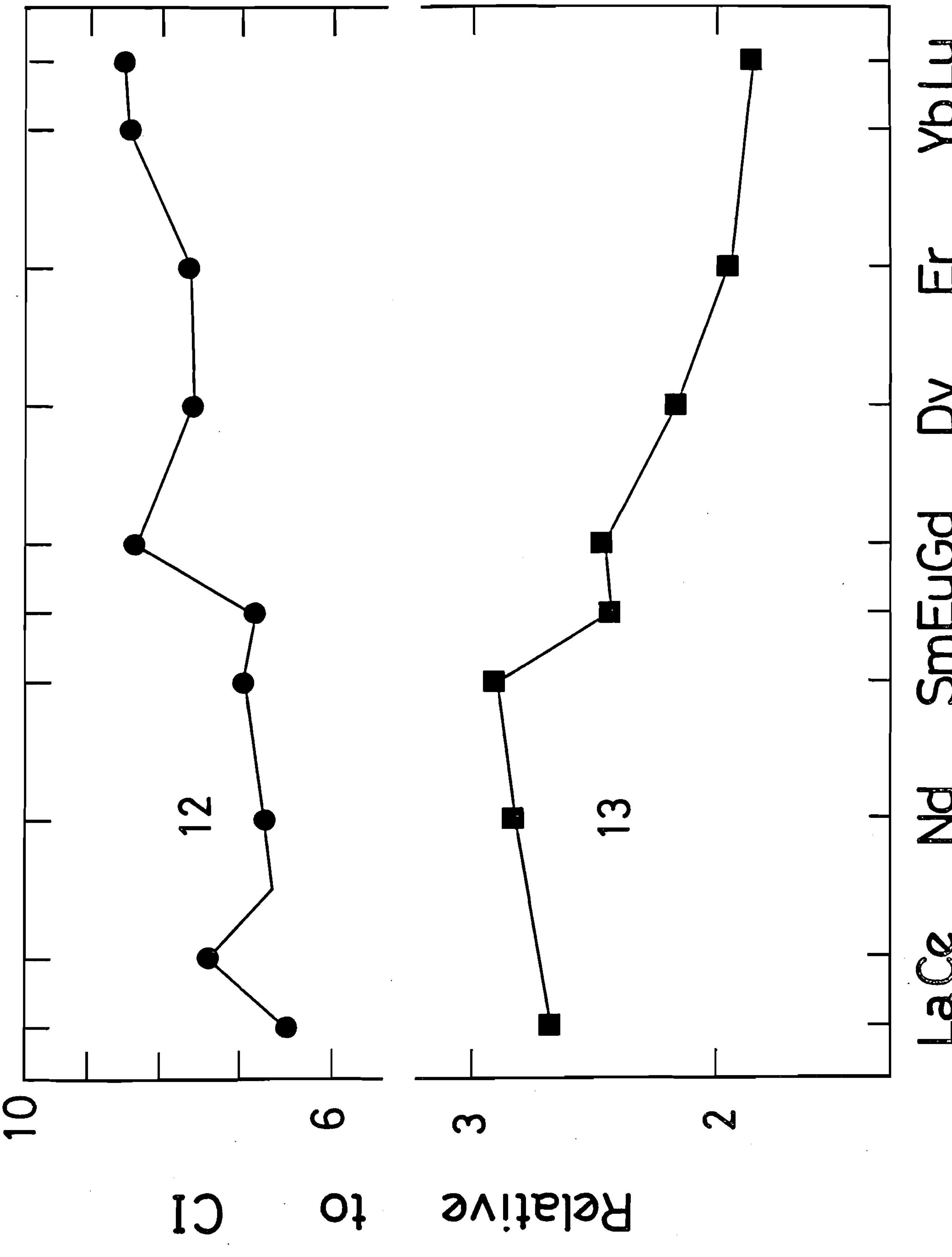


Fig. 20

Figure 21.

CI-normalized REE patterns for Allende olivine-rich chondrules 14, 15 and 16.

Figure 22.

CI-normalized REE patterns for Allende olivine-rich chondrules 17 and 19.

Figure 23.

CI-normalized REE pattern for Allende olivine-rich chondrule 18. Repeated analyses of two different portions of the chondrule, sample 18-1 and 18-2, show different REE abundances.

Figure 24.

CI-normalized REE patterns for Allende olivine-rich chondrules 20 and 21.

Figure 25.

CI-normalized REE patterns for Allende olivine-rich chondrules 22, 23, 24 and 25.

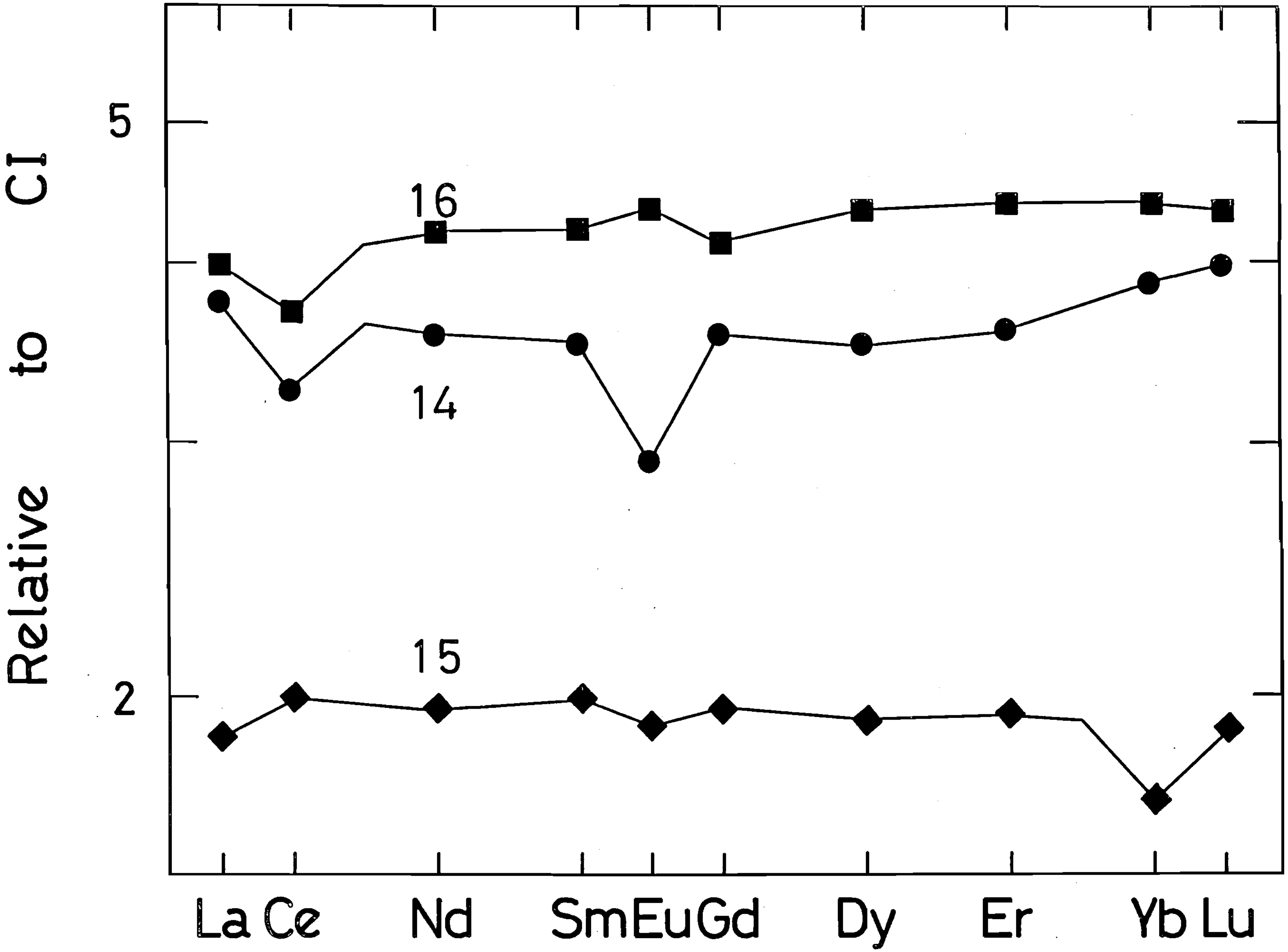


Fig. 21

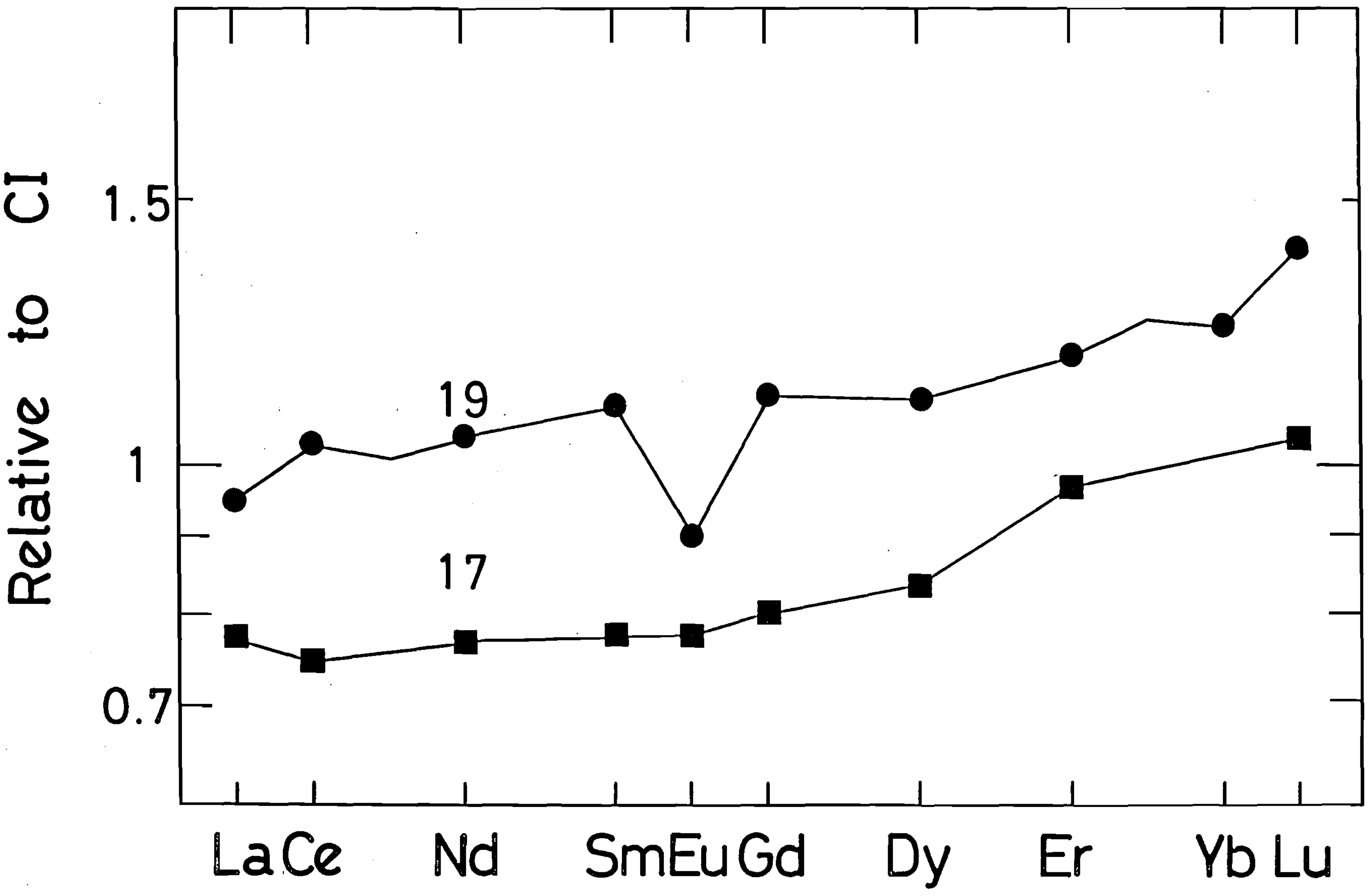


Fig. 22

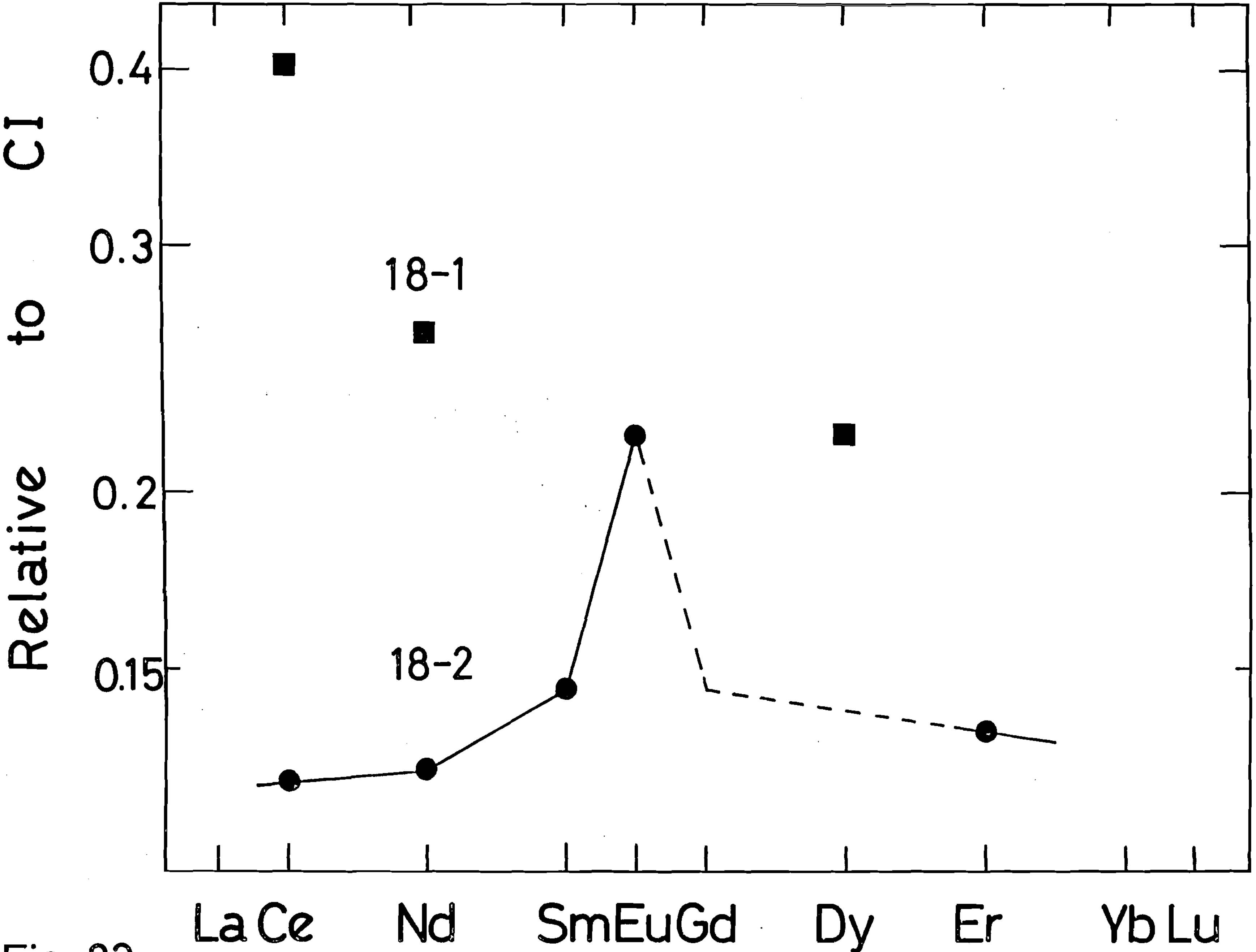


Fig. 23

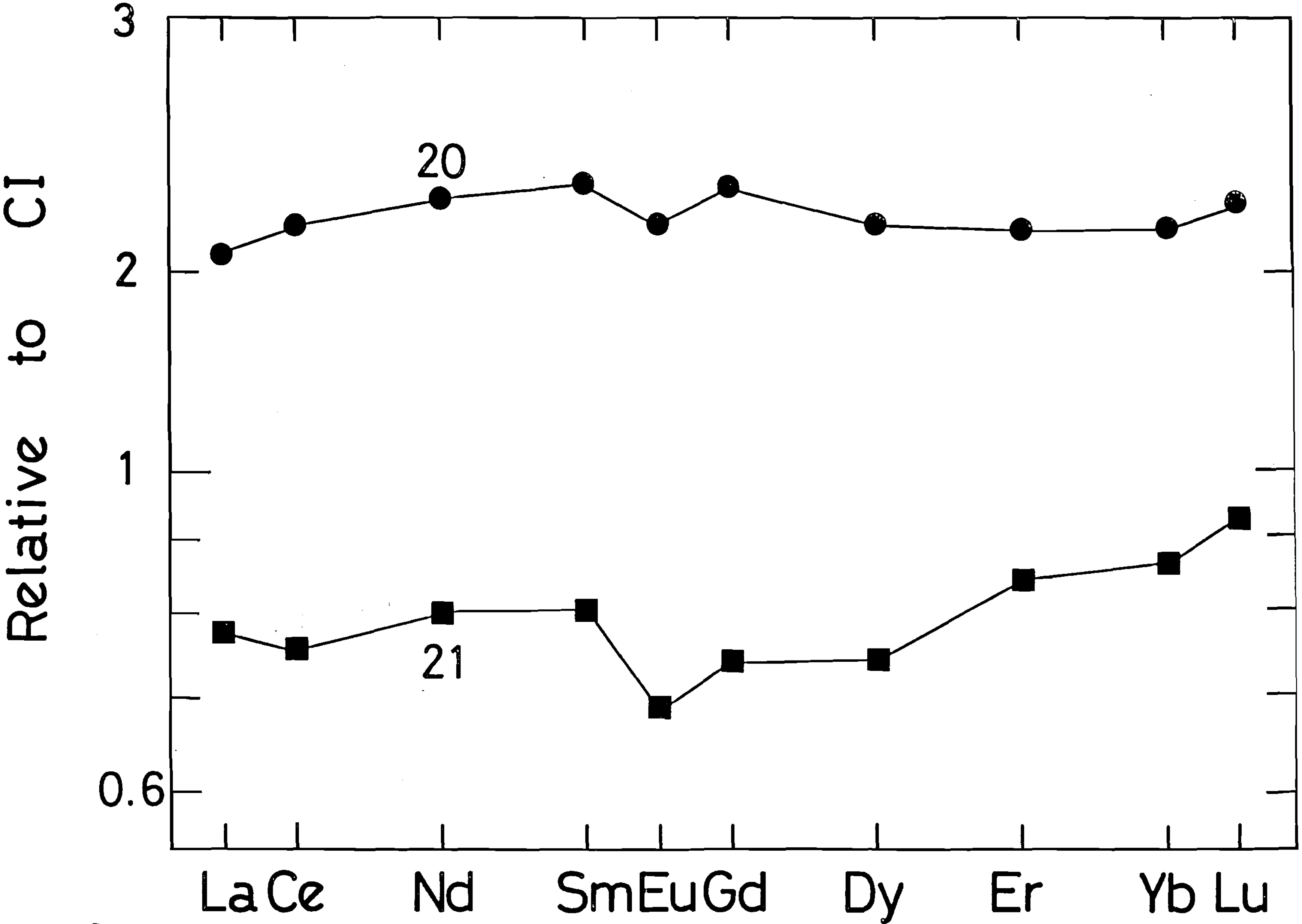


Fig. 24

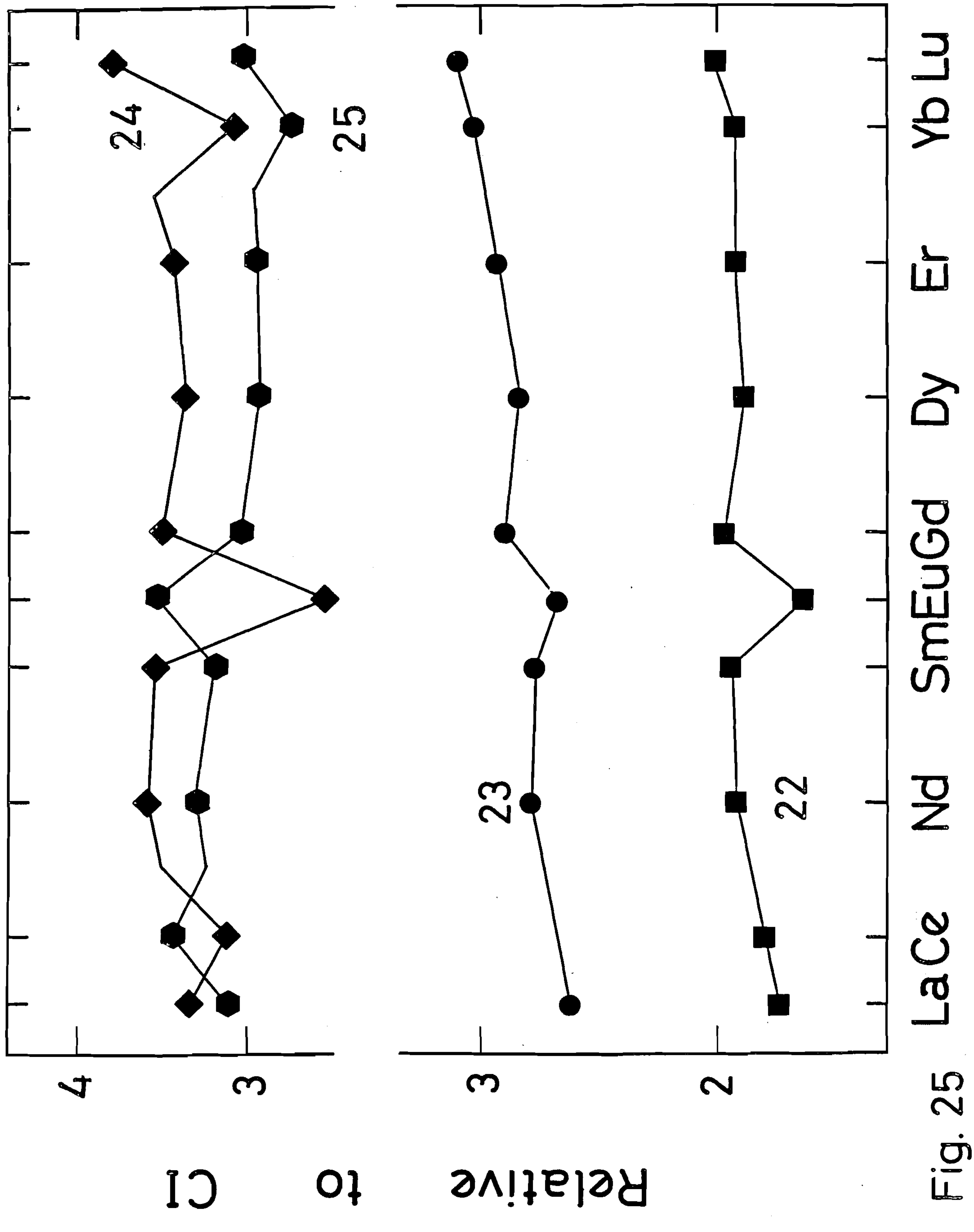


Fig. 25

Some significant features can be noted from the abundance patterns. First, chondrules show considerable variations in absolute REE abundance (0.15-10 x CI), even in the same textural type. The barred olivine and pyroxene-rich chondrules have higher REE abundances (2-10 x CI) compared with the olivine-rich chondrules (0.15-4 x CI). Second, Ce, Eu and Yb anomalies are clearly observed for many chondrules. Third, significantly large REE fractionations (e.g., light/heavy REE fractionation) in the general pattern are noted for many chondrules. These results are partly in agreement with the observation of refractory lithophiles in Allende chondrules by RUBIN and WASSON (1987b), but manifest substantially new trace element features.

Although many cases of Ce and Yb irregularities have been reported for bulk chondrites (MASUDA et al., 1973; NAKAMURA and MASUDA, 1973; NAKAMURA, 1974; EVENSEN et al., 1978) and the Allende Group II Ca,Al-rich inclusions (CAIs) (e.g., TANAKA and MASUDA, 1973; CONARD et al., 1975), well-documented Ce and Yb anomalies have rarely been found for chondrules, except a few cases of Ce anomalies: a giant-olivine chondrule from Allende (TANAKA et al., 1975) and two chondrules from the Parnallee (LL3) chondrite (HAMILTON et al., 1979). Thus, presence of these anomalies in chondrules have not been well-established in the previous studies. In our results, however, Ce, Eu and Yb anomalies are clearly identified in many chondrules. Most chondrules (~80 %) analyzed show negative Eu anomalies and both negative and positive anomalies of Ce and Yb are found in the same population. The magnitude of the Ce anomaly is, in general, smaller than those of Eu and Yb.

In addition, there seems "Gd or Dy anomaly (or Er and Lu anomalies)" in a few patterns. For example, it appears that most chondrules show smoothly fractionated (concave downward) patterns for heavy REE (except for Yb in some cases), but data points of Gd (or possibly Er and Lu) for 2 of the 25 Allende chondrules (chondrule 2 and 10) deviate significantly from the smooth curves. On the other hand, chondrule 12 seems to exhibit an apparent positive Gd anomaly if a linear REE abundance pattern is drawn. This pattern could be interpreted as a mineral effect similar to that of Type B3 CAIs (WARK *et al.*, 1987). The origin of positive anomalies at both Ce and Gd, however, remains unclear. It is suggested that the apparent Gd anomaly is a result of artifact due to misleading drawing procedures of REE abundance patterns.

It was suggested that the REE fractionation between gas and solid is not a smooth function of ionic radius but varies in an extremely irregular pattern with Eu and Yb anomalies, and predicted that the tendency for parallel behavior of the La-Sm, and Gd-Lu sub series (BOYNTON, 1975). From all these considerations, it would appear that apparent anomalies of Gd are not "anomalous" but they are the light/heavy REE "discontinuities".

In Fig. 26, the magnitude of the anomaly for Eu or Yb, taken as indicators of light/heavy REE fractionation, are plotted against La/Lu ratios. It is found that chondrules enriched in heavy REE relative to light REE show negative Yb anomalies, but that those appreciably depleted in heavy REE show positive Yb anomalies. Thus, it is suggested that the Yb anomalies were produced by the same or related processes which generate the light/heavy REE fractionations. It is shown that the Eu anomalies are predominantly negative. Since there is no correlation among Eu anomaly, chondrule texture or chemical composition, we rule out the redox effect and the contribution of feldspar on the the origin of the Eu anomaly. It is most probable that the most volatile REE, Eu, was partitioned off the other REE during high temperature processes.

<u>Figure</u> <u>26</u>.

Plots of CI-normalized Eu/Eu^* and Yb/Yb^* *vs*. La/Lu ratio for Allende chondrules (* denotes interpolated values). The chondrules enriched in light REE relative to heavy REE have positive Yb anomalies. Majority of chondrules have negative Eu anomalies.

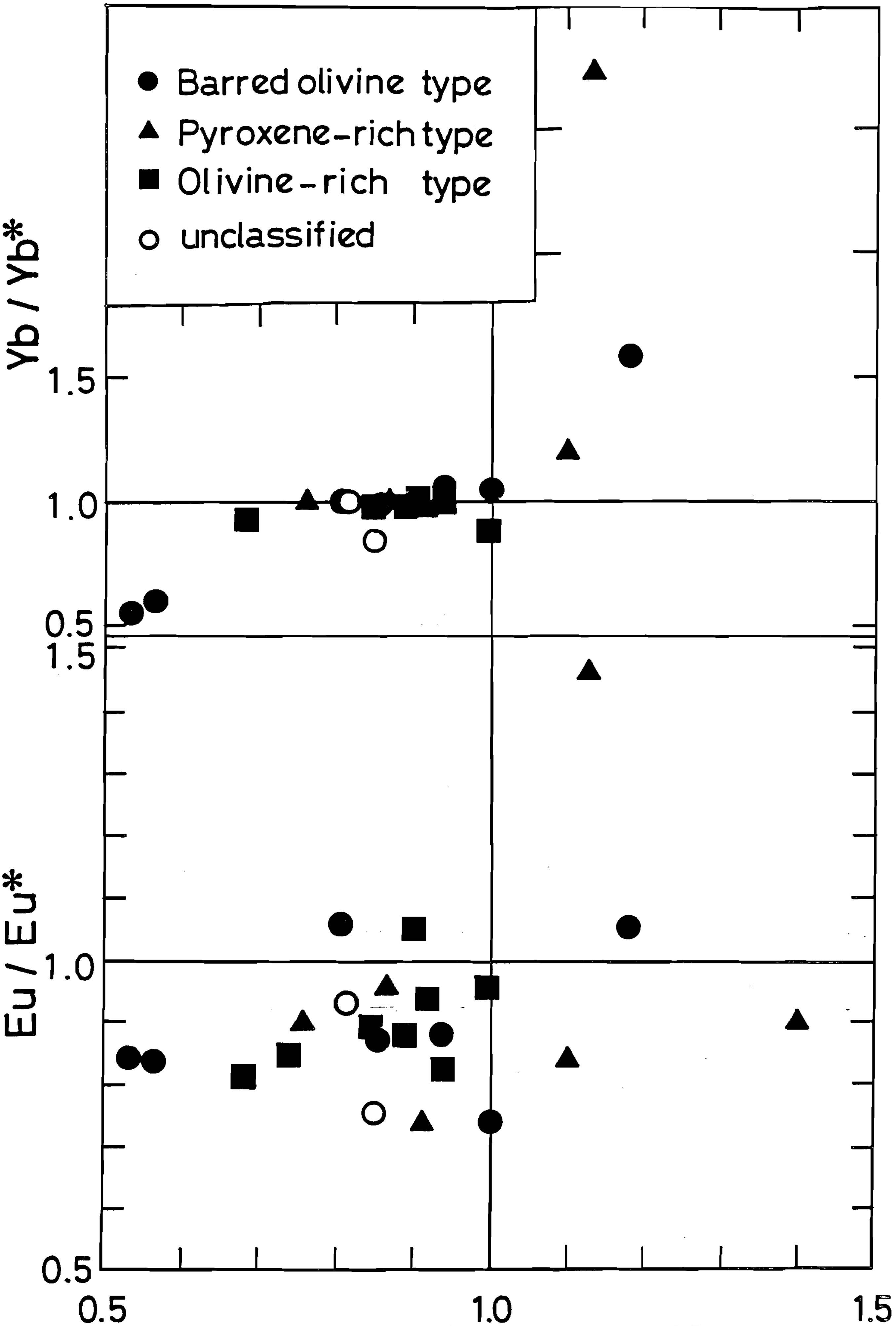
● Barred olivine type
▲ Pyroxene-rich type
■ Olivine-rich type
○ unclassified
Yb / Yb*
1.5
1.0
0.5
Eu / Eu*
1.5
1.0
0.5
0.5
1.0
1.5
La / Lu relative to CI

Fig. 26

Distinctive REE fractionations are observed for some chondrules. Two BO chondrules (1 and 2) show a heavier REE enriched pattern with large negative anomalies of Eu and Yb. The pattern seems to be composed of two parts; from light to middle REE the pattern is substantially flat but heavier REE (Er and Lu) show a sudden enrichment. This may be a new REE pattern not previously reported for chondrules or even for CAIs, but could be better understood if it were a mixture between an ultra-refractory component and an unfractionated component as mentioned later. The REE patterns for one BO, two PP and one RP chondrules (4, 9, 10 and 13) are characterized by depletion of heavy REE together with the presence of positive Yb anomalies, although Yb data on chondrule 13 was not obtained. The degree of light to heavy REE fractionations are different among chondrules. The PP chondrule 9 exhibits a surprisingly anomalous REE pattern with a smooth increase from La to Eu and an abrupt decrease at Gd and in heavy REE, and with superimposed large positive (60 %) Ce and (170 %) Yb anomalies. The REE pattern with positive Ce and Yb anomalies is complement of the pattern with negative Ce and Yb anomalies in the Murchison ultra-refractory inclusions (e.g., BOYNTON et al., 1980). The abundance pattern of the PP chondrule 12 exhibits a discontinuity at Gd and a depletion of light REE with the positive Ce anomaly.

In the volatility diagrams (Figs. 9-10) fractionation patterns of REE in many chondrules appear to be smooth but not monotonic. For Allende chondrules 1, 2 and 24, they are rather in contrast to the abundance patterns of the REE plotted against atomic number (Figs. 14-25) which sometimes show large anomalies of Eu and Yb. Thus, it is suggested that the REE fractionations of chondrules were partly controlled by elemental volatilities during high temperature processes such as condensation and/or vaporization. In the dome-shaped, moderately refractory REE-enriched pattern, which typically observed in Group II CAIs, La is severely depleted relative to the neighboring REE. This may be due to the assignment of La which is less refractory than Nd and Sm.

IV. FELIX RESULTS

1. Petrography

Petrographic descriptions of the Felix chondrules and CAI analyzed for trace elements are presented in Table 13.

All chondrules show porphyritic texture with mainly olivine and/or pyroxene (*i.e.*, PO, POP, and PP). Sulfide and metallic Fe,Ni form discrete rims around the chondrules.

Coarse-grained CAI #2 may be assigned to Type B1 (WORK and LOVERING, 1977) from its texture, constituent mineral assemblage and chemical composition.

Table 13.

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 Al,Ti-rich pyroxene.
#3	Microporphyritic texture with low-, and high-Ca pyroxene ($Wo_{1.4-6}$ $En_{98-88.5}Fs_{0.5-5.5}$, $Wo_{33}En_{67}$), olivine (Fa_{3-7}), abundant metallic Fe,Ni and Fe-sulfide.
#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} , $Wo_{44}En_{56}$).
#8	Porphyritic texture with low-Ca pyroxene ($Wo_{0.3}En_{98.7}Fs_{1}$) with fine-grained dendritic Si,Al-rich mesostasis. A small low-Fe porphyritic olivine (Fa_{4-9}) chondrule is contained. Iron-sulfide formes discrete rims around chondrule.
#30	Porphyritic texture with euhedral olivine ($Fa_{0.8-3}$) in glassy mesostasis. Minor metallic Fe, Ni and sulfide.

2. Mineral chemistry

The results of electron microprobe analyses of olivines are shown in Fig. 27. Olivines in each chondrule are Mg-rich, with a large proportion in the range of Fa_{0-10}. Some olivines in chondrules #4 and #5, which are poikilitically enclosed by twinned clinoenstatite, are more fayalitic ($\sim Fa_{25}$). These fayalitic olivines may be interpreted as relicts of chondrule precursor materials that were incompletely melted during chondrule formation (e.g., NAGAHARA, 1981).

The results of electron microprobe analyses of pyroxenes are shown in Fig. 28. The pyroxene is Mg-rich, in the range of Fs_{0-5}.

Figure 27.

Compositions of olivines in Felix chondrules. Most analyses fall the range of Fa_{0-10} .

Figure 28.

Compositions of pyroxenes in Felix chondrules. All analyses fall the range of Fs_{0-5} .

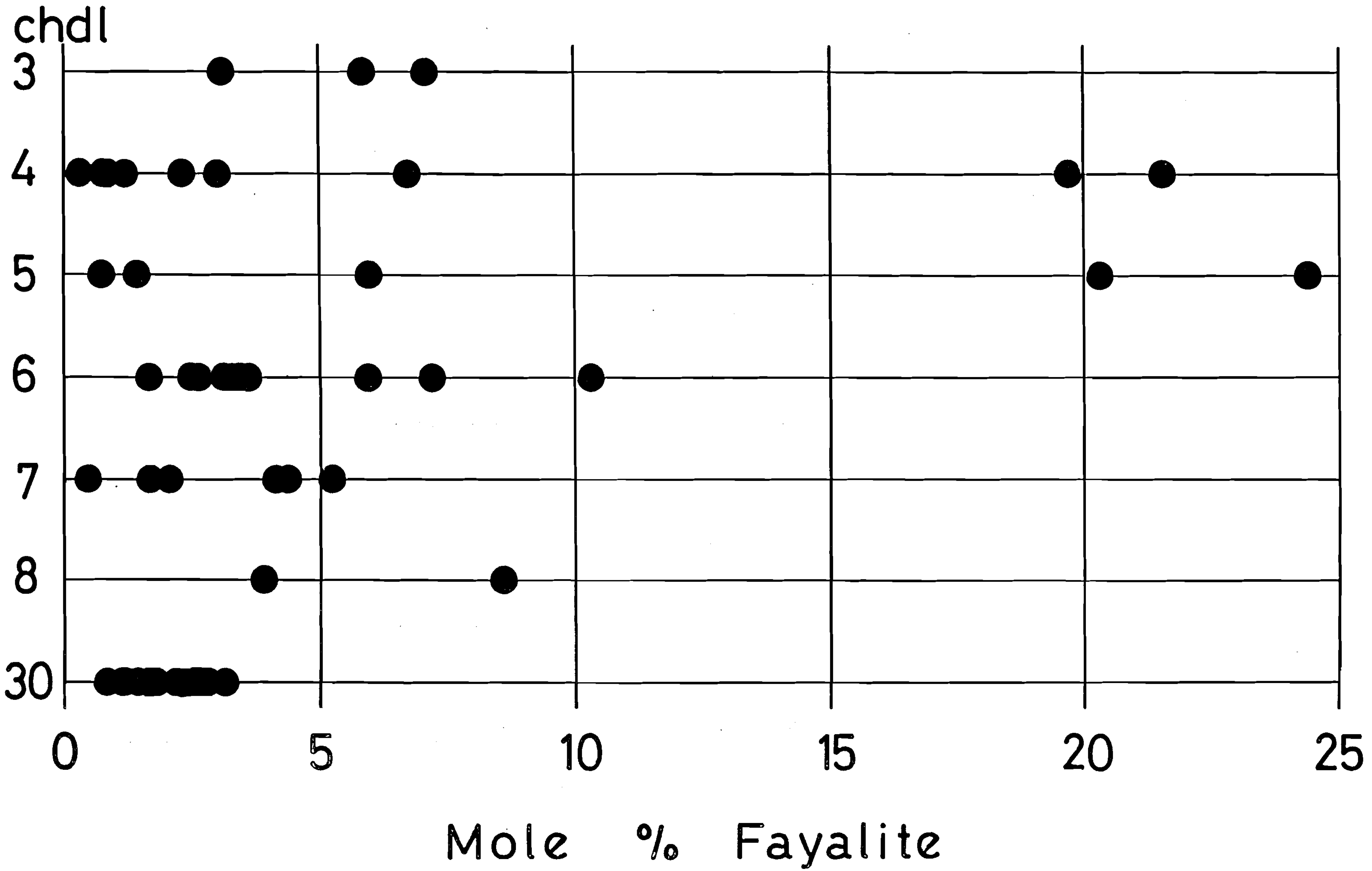
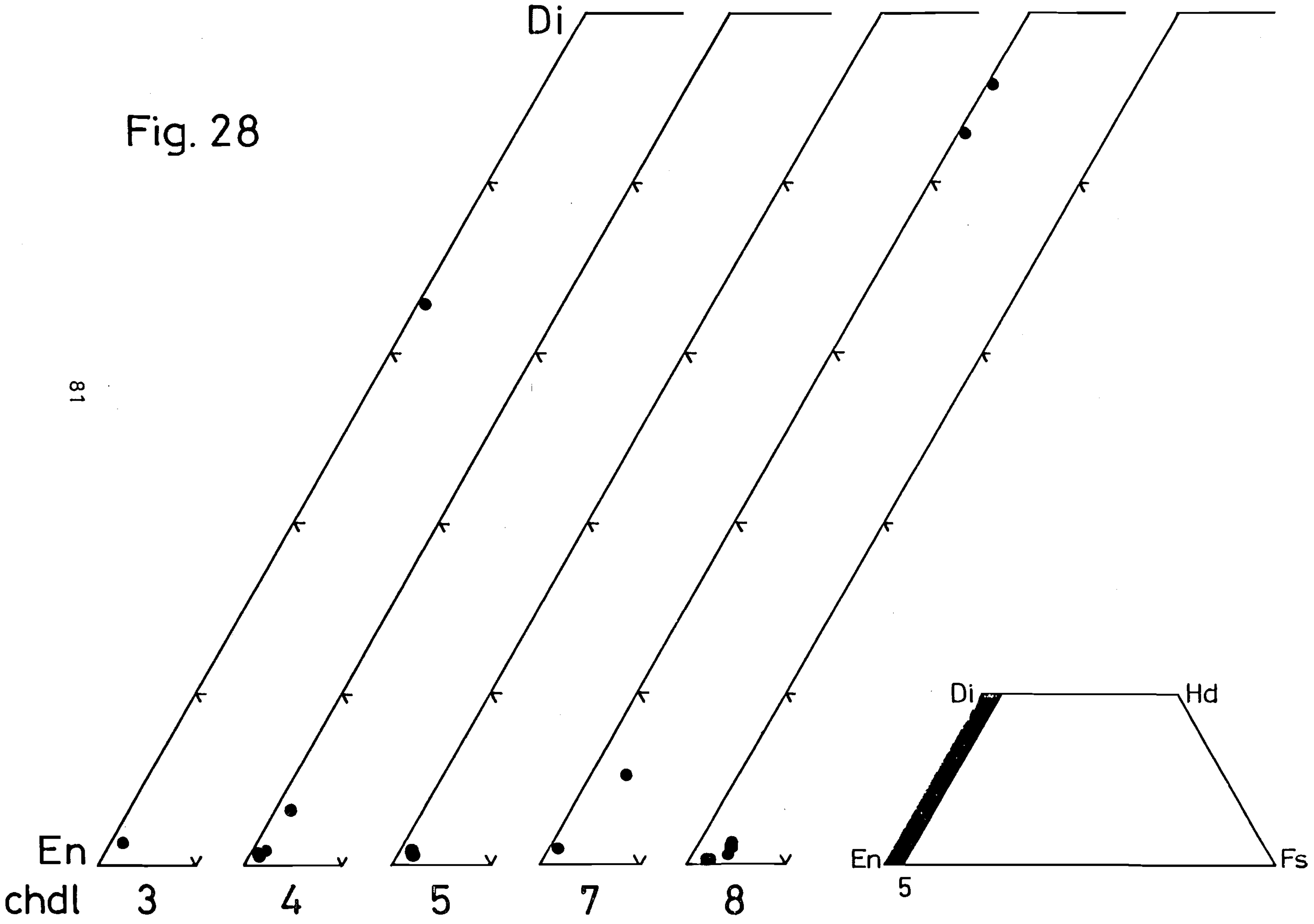


Fig. 27

Fig. 28



3. Bulk chemical composition

The results of EPMA defocused beam analyses for chondrules and CAI are listed in Tables 14 and 15. The results of MSID analyses for the chondrules, CAI and fine-grained fraction of the "bulk Felix chondrite" are given in Table 16.

The CI-normalized elemental abundances of constituent components are shown in Fig. 29.

Table 14.

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

chdl	#3	#4	#5	#6	#7	#8	#30
SiO_2	43.85	45.35	49.44	45.16	43.82	47.44	41.48
Al_2O_3	7.27	6.95	2.87	4.93	2.00	14.42	3.11
FeO	7.35	4.51	4.44	5.49	1.94	5.39	4.72
MnO	0.07	0.09	0.09	0.18	0.06	0.41	0.05
MgO	32.29	35.30	36.99	37.99	47.27	13.65	43.26
CaO	5.85	3.67	1.81	3.12	1.99	8.05	2.10
Na_2O	0.32	0.47	0.08	0.07	0.03	2.73	0.97
Cr_2O_3	0.55	0.67	0.82	0.86	0.38	1.10	0.53
Total	97.55	97.01	96.54	97.80	97.49	93.19	96.22

Table 15.

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 16.

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

	#2	#3	#4	#5	#6	#7	#8	#30	bulk**
sample wt. (µg)	850	849	1175	>1056*	569	1228	713	472	1.1 (g)
dissolved wt. (µg)	545	408	674	555	334	493	365	181	11.974 (mg)
Mg(%)	5.80	14.3	8.59	12.6	21.8	20.1	7.13	24.1	n.d.
Ca(%)	20.7	4.72	2.14	2.00	2.07	1.59	4.21	2.99	n.d.
K	44.5	1020	659	503	363	222	1830	461	n.d.
Rb	0.173	3.25	2.12	1.83	1.31	0.870	7.02	1.80	n.d.
Sr	155	74.0	42.8	36.4	42.5	25.8	88.7	9.52	n.d.
Ba	16.4	9.42	4.81	4.86	12.3	5.06	13.5	8.18	n.d.
La	4.33	0.688	0.728	n.d.	0.746	0.347	1.70	0.511	0.434
Ce	11.0	2.37	1.96	1.83	1.96	0.950	6.76	1.35	1.31
Nd	8.89	1.30	1.45	1.05	n.d.	0.688	3.76	1.02	0.797
Sm	3.03	0.457	0.464	0.356	n.d.	0.227	1.74	0.334	0.255
Eu	1.09	0.210	0.119	0.107	n.d.	0.0921	0.199	0.150	0.0948
Gd	3.89	0.514	0.624	0.467	n.d.	0.301	0.414	0.440	0.337
Dy	4.80	0.587	0.735	0.483	n.d.	0.365	0.379	0.552	0.421
Er	3.08	0.383	0.467	0.313	n.d.	0.246	0.142	0.359	0.276
Yb	1.96	0.668	0.426	0.318	n.d.	0.250	0.374	0.371	0.281
Lu	0.527	0.0608	0.0714	0.0528	0.0701	0.0392	0.0191	0.0565	0.0447

* Sample #5 is fragment of chondrule.

** Fine-grained (<50 µm) fraction produced by freeze-thaw processing.

n.d. = not determined.

Figure 29 .

CI-normalized abundances of lithophile elements for Felix chondrules and CAI. Plots are the same manner as in Fig. 9.

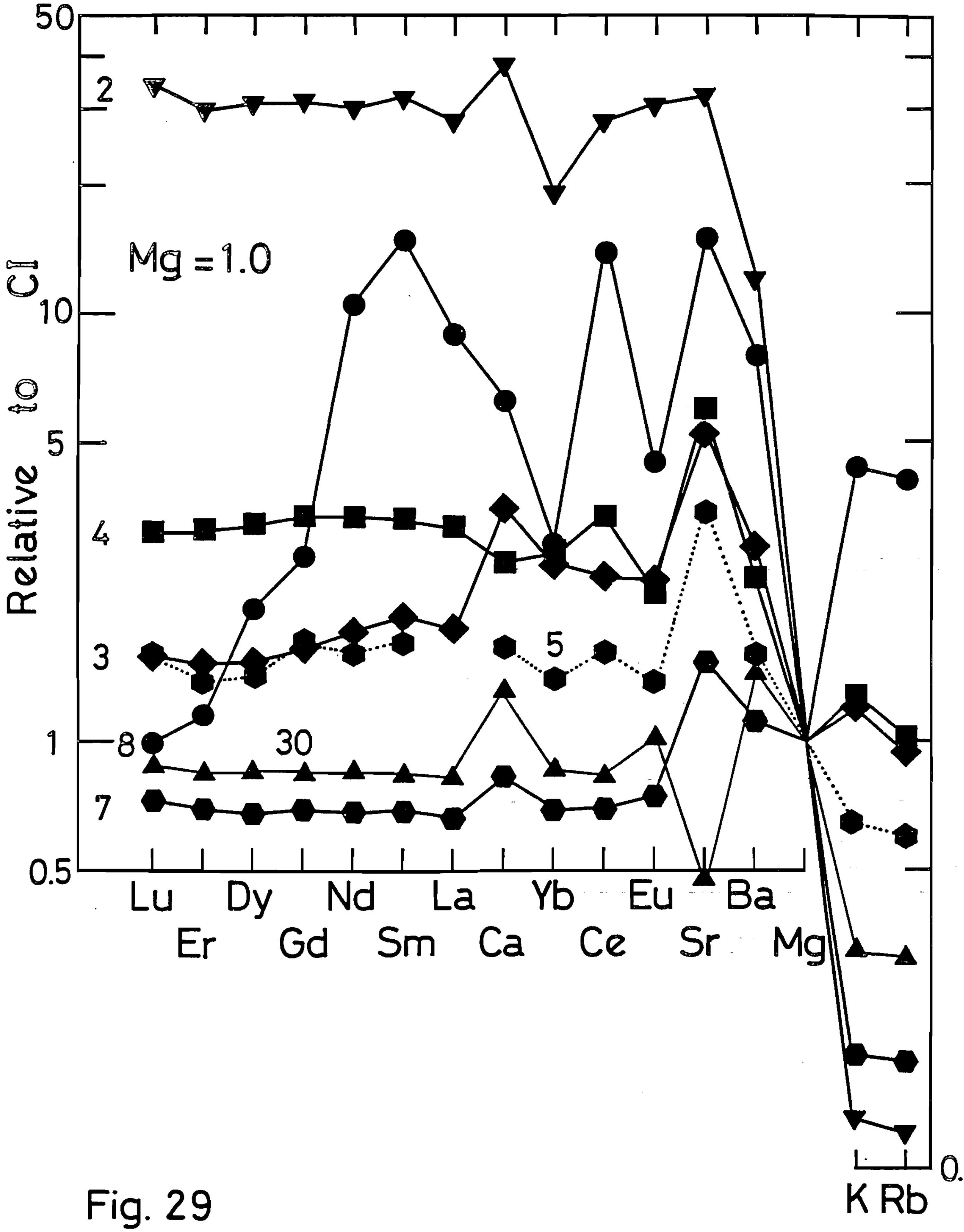

50
10
5
1
0.5
0.1
Relative to CI
Mg = 1.0
2
4
3
8
30
5
7
Lu
Er
Dy
Gd
Nd
Sm
La
Ca
Yb
Ce
Eu
Sr
Ba
Mg
K
Rb

Fig. 29

3-1. Major element

The bulk chemical compositions of the chondrules and CAI are plotted SiO_2-$CaO+Al_2O_3$-MgO diagram (Fig. 30). The major element compositions of the Felix chondrules are almost within the range of those of ferromagnesian chondrules analyzed by SIMON and HAGGERTY (1980) and MCSWEEN *et al.* (1983) except for that of chondrule #8.

Figure 30.

Bulk compositions of chondrules and CAI in Felix. Data for Mg,Fe-rich chondrules are from MCSWEEN (1977b), and for Ca,Al-rich chondrules are from BISCHOFF and KEIL (1983).

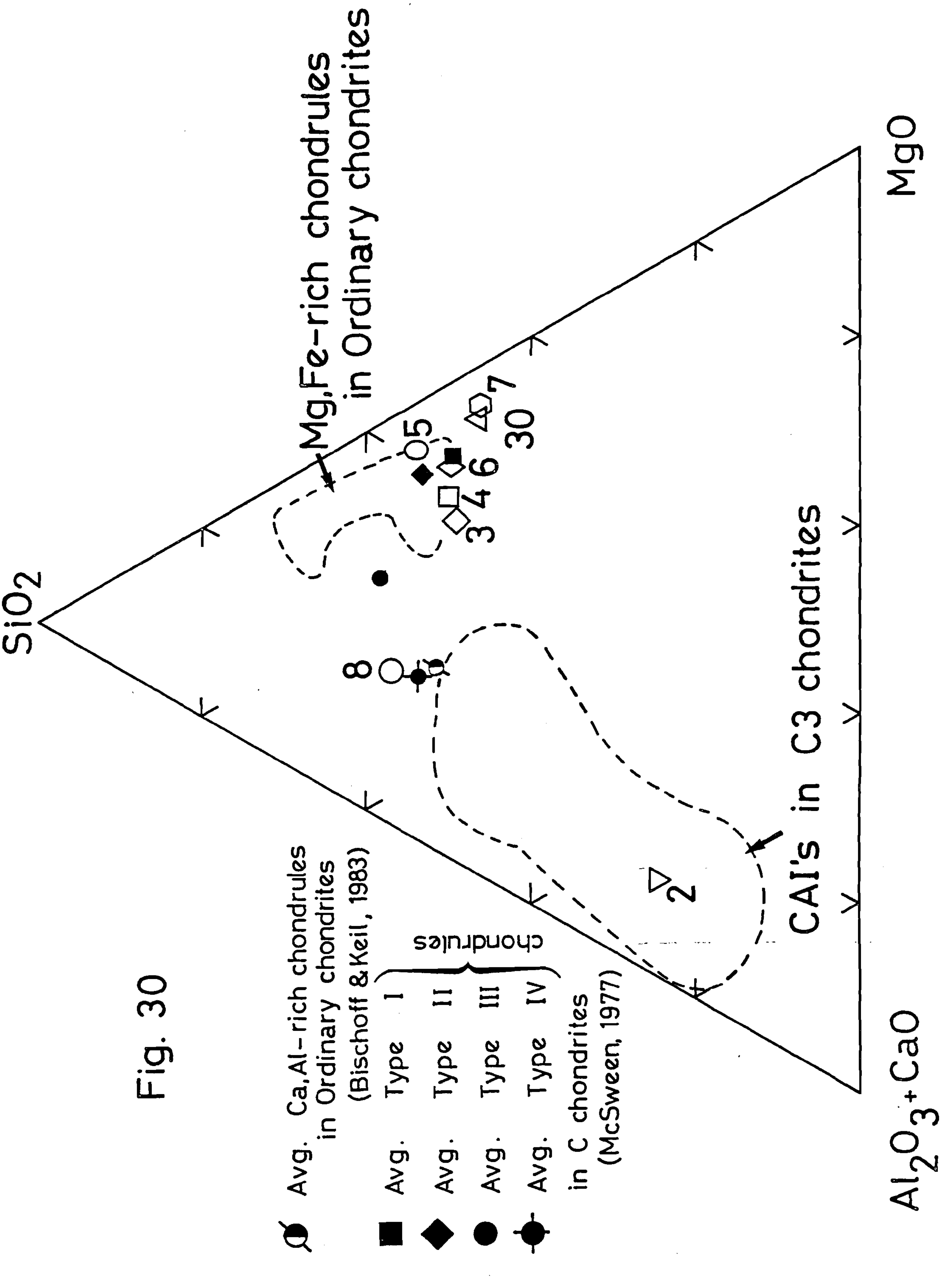

SiO2
MgO
Al2O3+CaO
Mg,Fe-rich chondrules in Ordinary chondrites
CAI's in C3 chondrites
2
3
4
5
6
7
8
30
Avg. Ca,Al-rich chondrules in Ordinary chondrites (Bischoff & Keil, 1983)
Avg. Type I
Avg. Type II
Avg. Type III
Avg. Type IV
chondrules
in C chondrites (McSween, 1977)

Fig. 30

The bulk chemical composition of chondrule #8 recalculated to 100 % are given in Table 17, along with those of McSween's type III (MCSWEEN et al., 1983) and Wark's CA chondrules (WARK, 1987) for comparison. It appears that chondrule #8 is poor in Fe and richer in Al than those of type III, and transitional in composition from type III to type IV or CA chondrules. WARK (1987) suggested that plagioclase-rich inclusions in carbonaceous chondrites are of two types: Ti,Al-rich group and Ti,Al-poor group. The latter is labeled "CA (for Ca-Al-rich) chondrules". According to this classification, samples 3510 (CLARKE et al., 1970; MASON and TAYLOR, 1982), RC-11 (WLOTZKA and PALME, 1982) and 2LN (KURAT and KRACHER, 1980) are of CA chondrules.

Table 17.

Comparison of bulk chemical compositions of Al,Ca-rich chondrules from Felix (CO3) with average of Type III chondrules and range of Ca,Al-rich chondrules in carbonaceous chondrites (values in wt % for SEM-EDS and EPMA analysis).

	Felix chondrules #3*	#8*	Average of** Type III (McSween et al.,1983)	Range of CA chdl (Wark,1987)
SiO_2	45.0	52.5	52.4(4.1)	40-53
TiO_2	n.d.	0.3	0.28(.17)	0.2-0.8
Al_2O_3	7.5	13.8	7.65(4.93)	11-23
Cr_2O_3	0.6	0.8	0.54(.24)	
FeO	7.5	2.8	7.45(3.77)	
MnO	0.1	0.3	0.24(.17)	
MgO	33.1	18.9	23.0(9.1)	9-22
CaO	6.0	6.5	7.26(3.80)	7-16
Na_2O	0.3	3.8	1.81(1.50)	
K_2O	n.d.	0.2	0.08(.11)	

* Excluded opaque minerals (recalculated to 100 %).
n.d. = not determined.
** Numbers in parentheses represent one standard deviation.

3-2. Alkalis and alkaline earths

As shown in Fig. 29, abundances of alkalis in the Felix chondrules vary from 0.4 to 1.2 x CI but alkalis in CAI #2 are strongly depleted ($\sim$0.08 x CI).

Rbidium is plotted against K for the Felix chondrules along with that for chondrules from Allende (Fig. 31). As is the case of Allende, K/Rb ratio is close to that of CI's.

Figure 31.

Relationship between CI-normalized Rb/Mg *vs*. K/Mg in individual chondrules from Felix (solid symbols). Open symbols represent Allende chondrules.

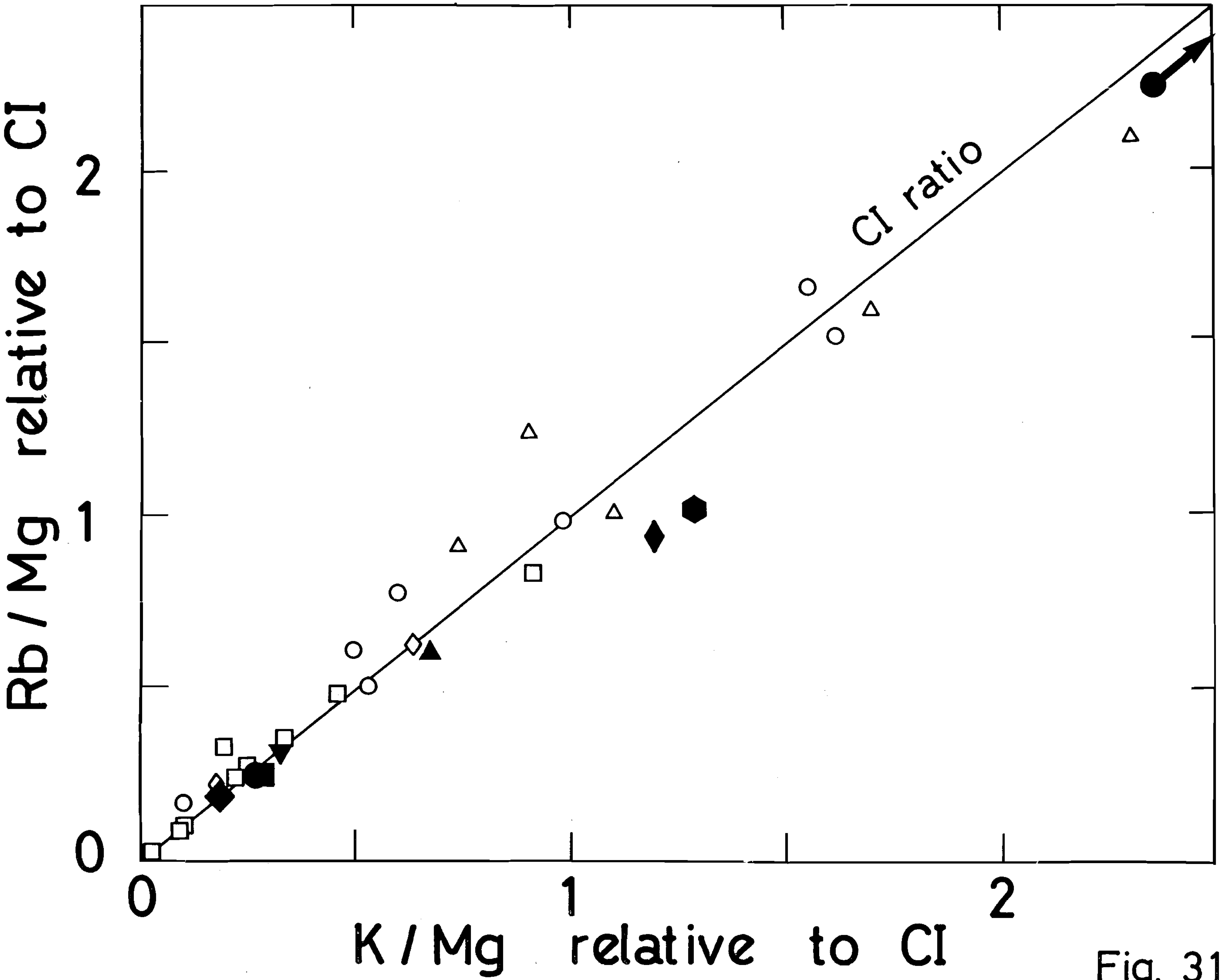


Fig. 31

Abundances of alkaline earths in the Felix chondrules vary from 1.2 to 5.4 x CI. In Figs. 32 and 33, plots of Ca _vs_. Sm, Sr _vs_. Sm and Ba _vs_. Sm for the Felix chondrules are shown along with those for Allende. Refractory lithophiles, Ca, Sr and Ba are positively correlated with REE. 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, 1987a).

Figure 32.

Plots of K/Mg _vs_. Sm/Mg and Ca/Mg _vs_. Sm/Mg for Felix chondrules. Open symbols denote Allende chondrules.

Figure 33.

Plots of Ba/Mg _vs_. Sm/Mg and Sr/Mg _vs_. Sm/Mg for Felix chondrules. Open symbols denote Allende chondrules.

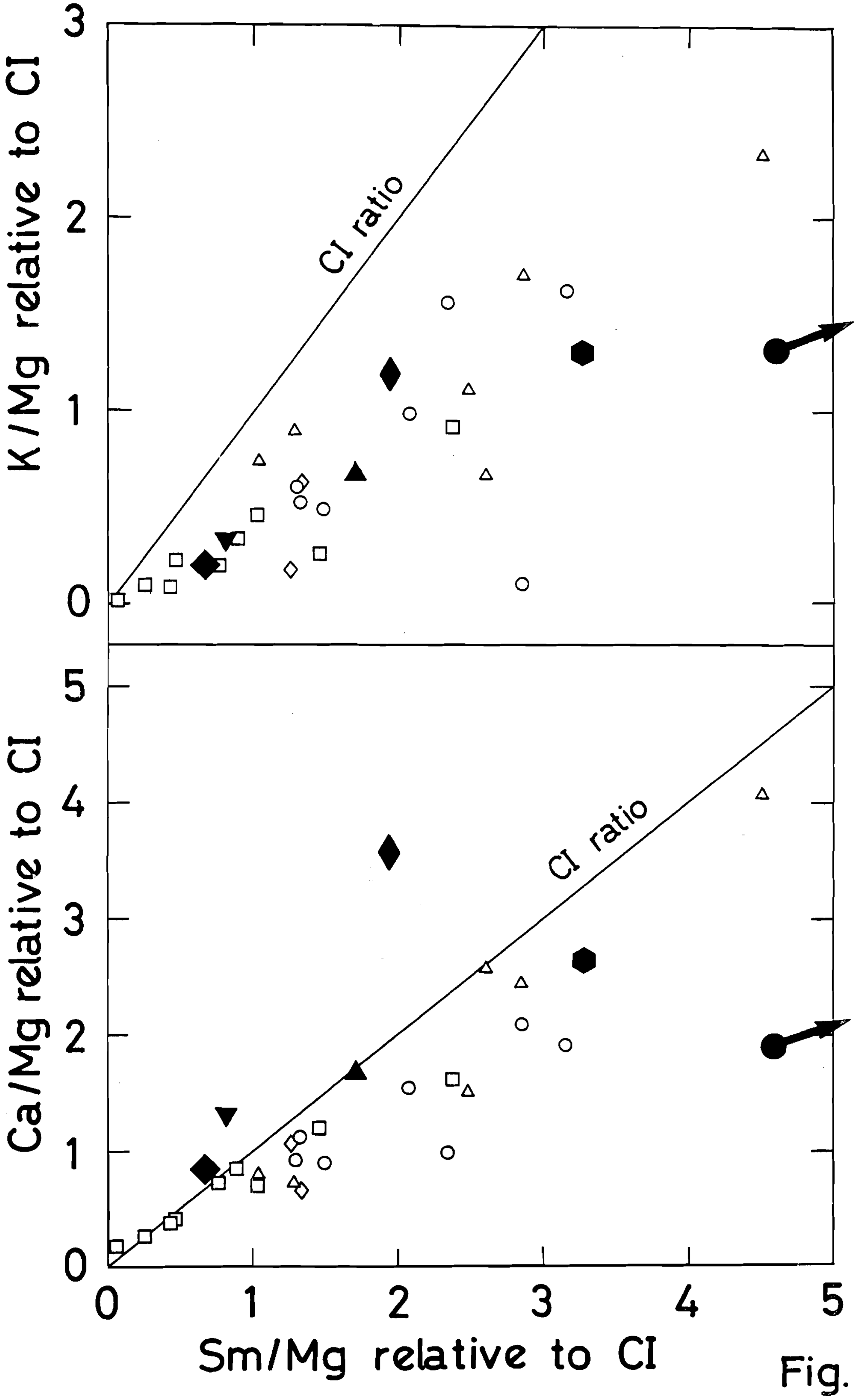
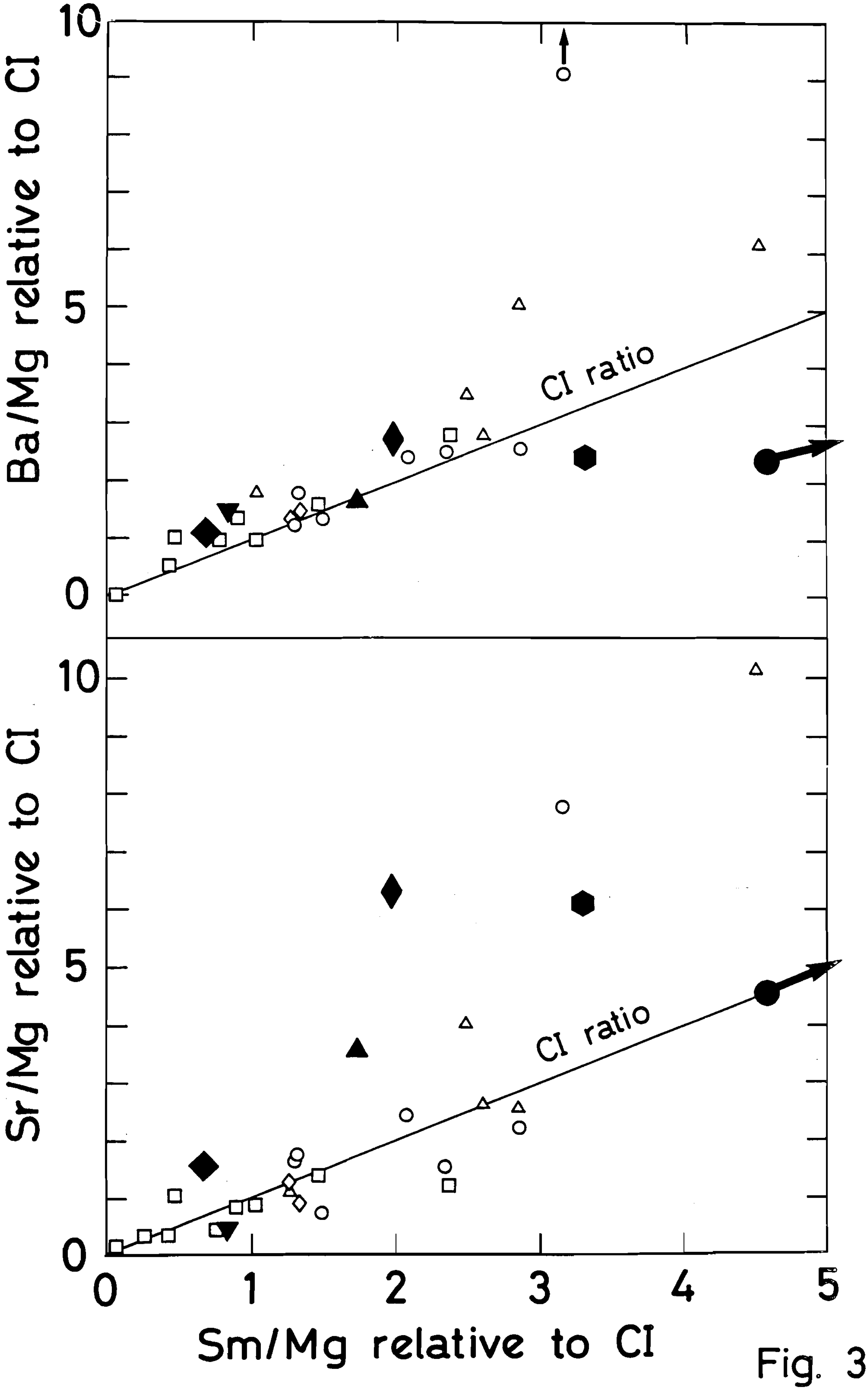

K/Mg relative to CI
Ca/Mg relative to CI
Sm/Mg relative to CI
CI ratio
CI ratio
0
1
2
3
4
5
0
1
2
3
0
1
2
3
4
5

Fig. 32



Ba/Mg relative to CI
Sr/Mg relative to CI
Sm/Mg relative to CI
CI ratio
CI ratio
0
5
10
0
5
10
0
1
2
3
4
5

Fig. 33

3-3. Rare earths

In Figs. 34-37, CI-normalized REE abundance patterns for the "bulk Felix chondrite", chondrules and CAI are shown.

The REE abundance of "bulk chondrite" is 1.6-1.7 x 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.

Figure 34.

CI-normalized REE pattern for a 'fine-grained fraction' of "bulk Felix chondrite". Open symbols represent INAA data from KALLEMEYN and WASSON (1981).

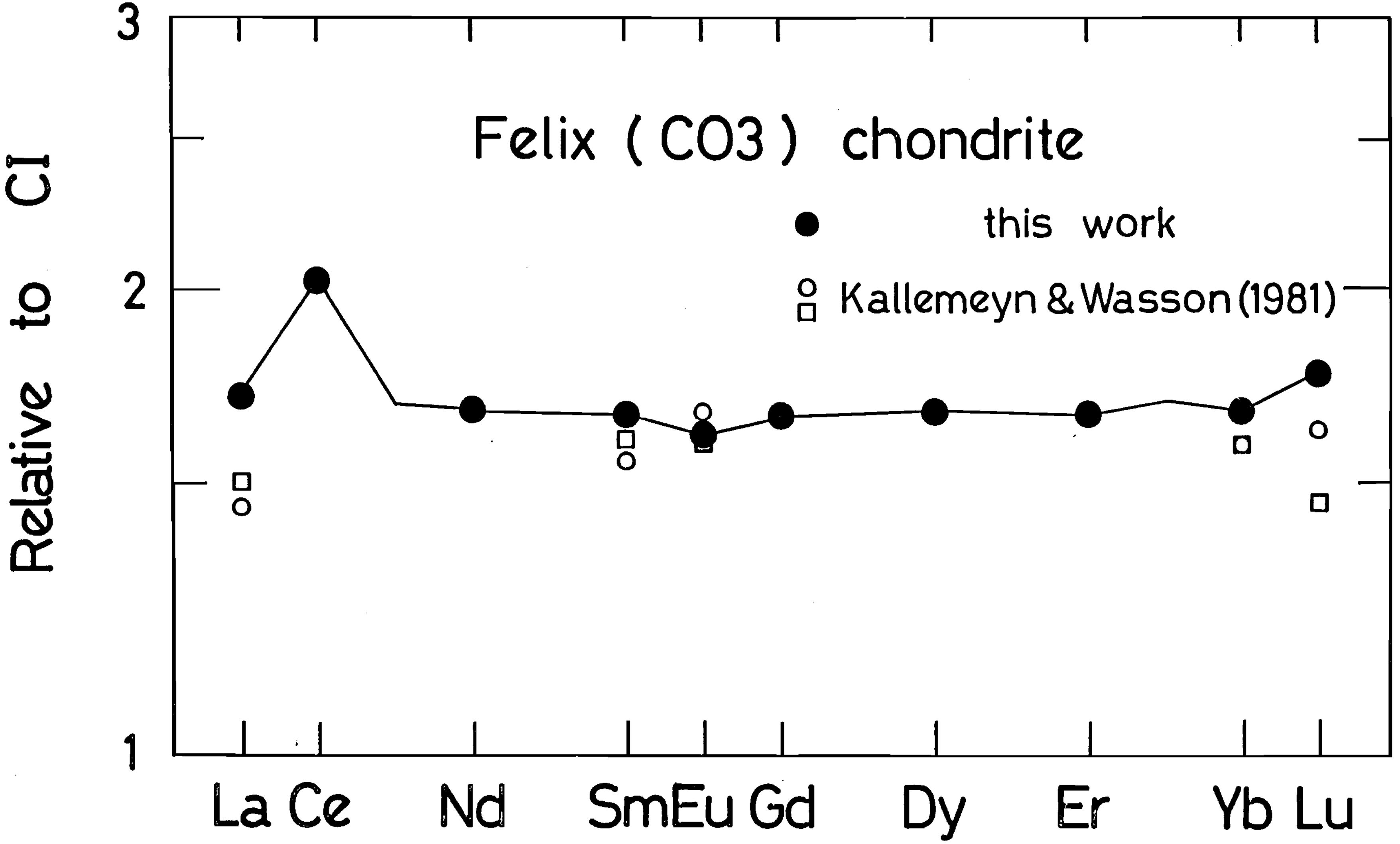

Felix (CO3) chondrite
● this work
○ □ Kallemeyn & Wasson (1981)
Relative to CI
3
2
1
La
Ce
Nd
Sm
Eu
Gd
Dy
Er
Yb
Lu

Fig. 34

The rare earth abundances in individual chondrules (#4, #5, #6, #7 and #30) are 1.5-4 x 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. The CI chondrite normalized REE patterns of these chondrules are almost flat.

Figure 35.

CI-normalized REE patterns of ferromagnesian chondrules #4, #5, #6, #7, and #30 from Felix. The TEE patterns are drawn by he same manner described in Allende chondrules. In Felíx chondrules, data points which deviate more than 3 % from the fitting line are regarded as "anomalous".

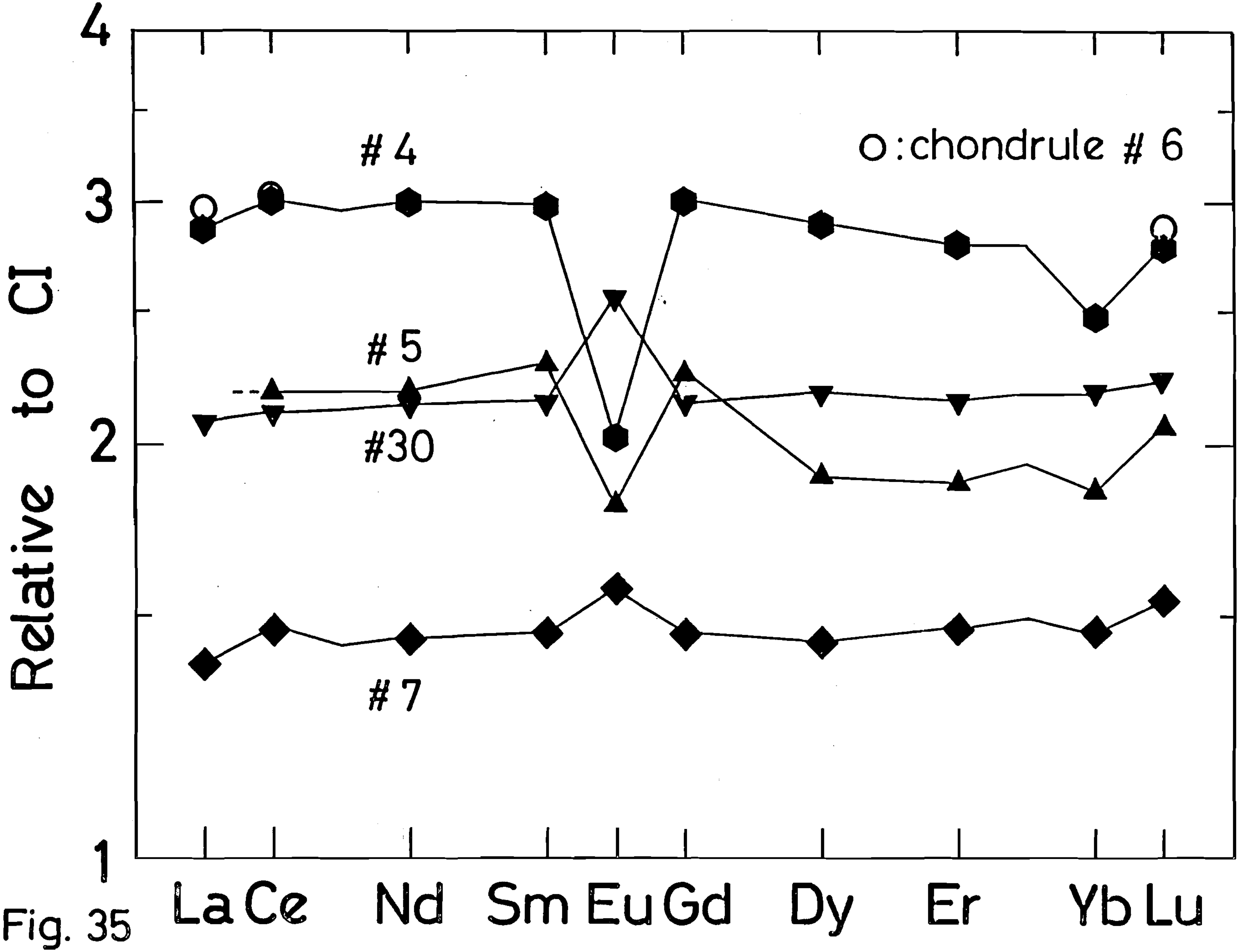

4
3
2
1
Relative to CI
La
Ce
Nd
Sm
Eu
Gd
Dy
Er
Yb
Lu
4
5
#30
7
o : chondrule # 6

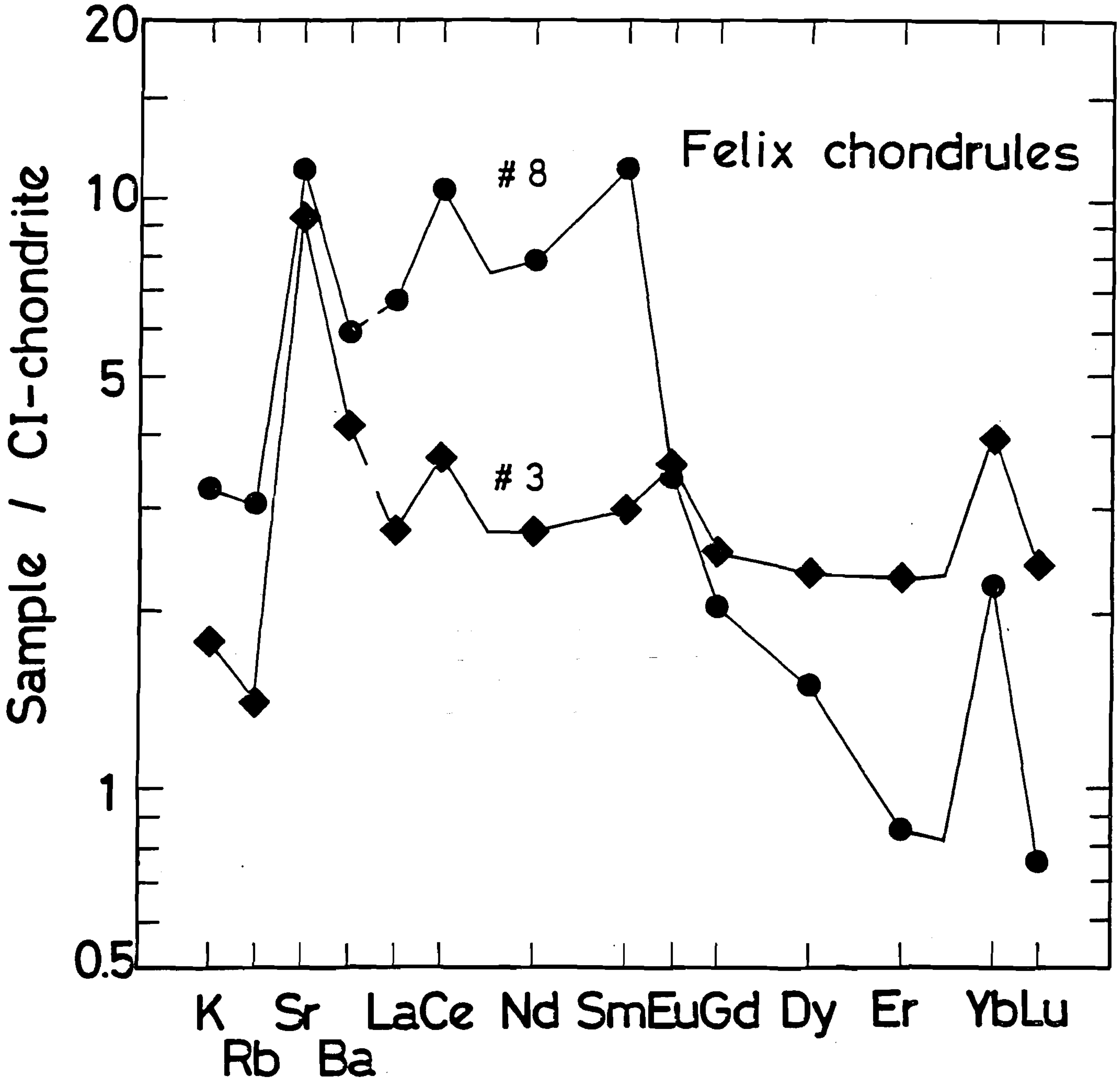
Fig. 35

Two Al- and Ca-rich (Al_2O_3>7 wt %, CaO>5 wt %) chondrules show unique REE patterns. Chondrule #8 exhibits the most highly fractionated REE pattern not previous reported on chondrules, characterized by light REE enrichment relative to heavy REE together with a rapid decline in abundance from Eu to Lu with positive Ce and Yb anomalies. Chondrule #3 shows positive anomalies of relatively volatile REE (i.e., Ce, Eu and Yb). These large positive Ce anomalies (40-50 %) substantiate the REE pattern for the "bulk chondrite".

Figure 36.

CI-normalized trace element abundance patterns of Al,Ca-rich chondrules #3 and #8 from Felix.

Fig. 36


Felix chondrules
8
3
Sample / CI-chondrite
20
10
5
1
0.5
K
Rb
Sr
Ba
LaCe
Nd
SmEuGd
Dy
Er
YbLu

Calcium,Al-rich inclusion #2 shows a nearly flat REE pattern with an enrichment factor of 17-21 x CI and a large negative Yb anomaly.

Figure 37.

CI-normalized REE pattern of coarse-grained Type B1 Ca,Al-rich inclusion #2 from Felix.

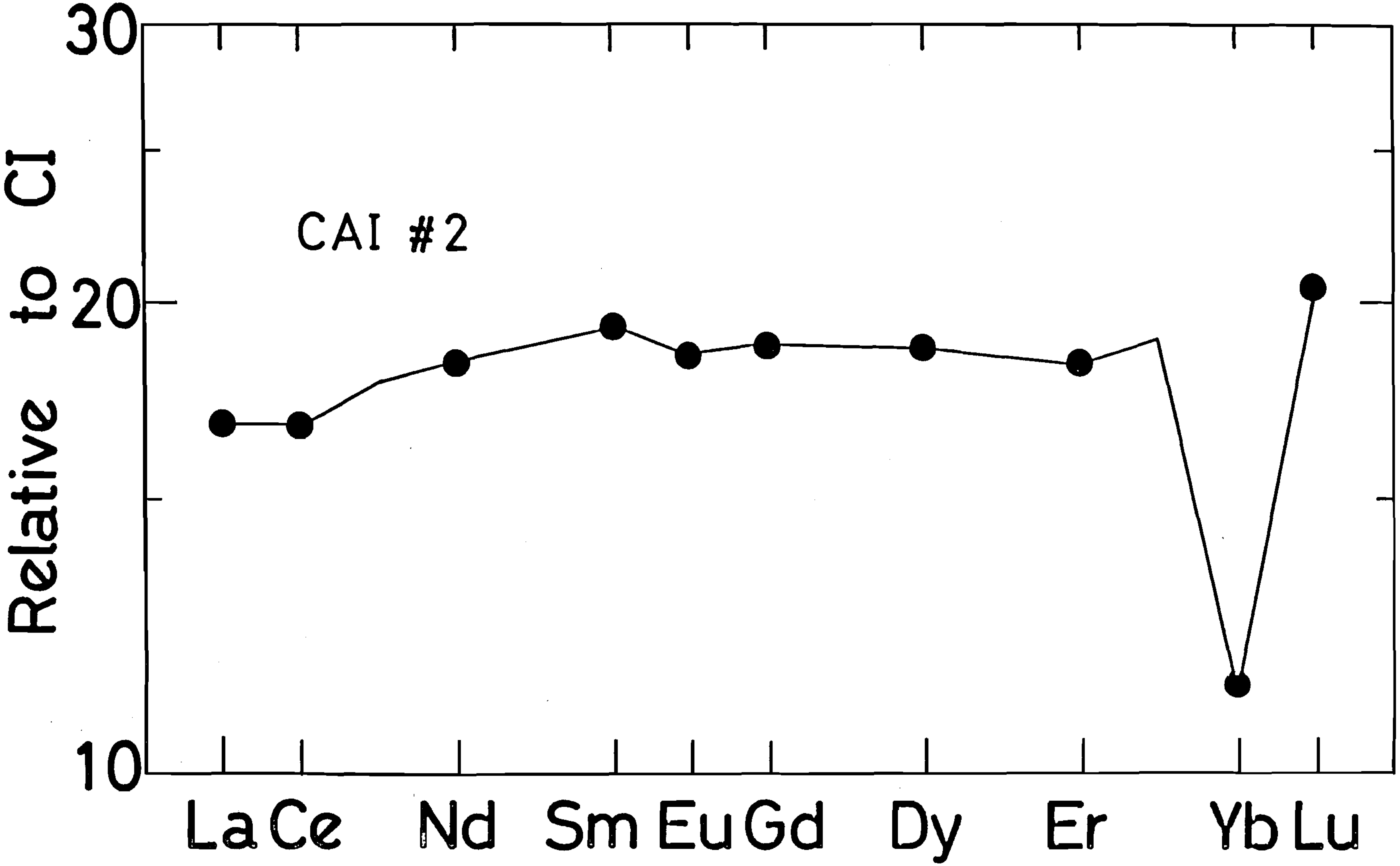


Fig. 37

V. DISCUSSION

1. Moderately volatile elements fractionation

Since K and Rb are among the most mobile lithophile elements during high temperature events which might have produced "droplets" of silicate melts, alkaline elements fractionation may constrain on the chondrule melting processes. Thermodynamic data (BREWER, 1953) show that vaporization temperatures of K_2O and Rb_2O at total pressure of 10^{-3} atm are 1150 ± 50 °C and 1100 ± 70 °C, respectively. FEGLEY and LEWIS (1980) carried out equilibrium calculations for volatile element in a solar composition system over a wide range of temperatures and pressures and showed that K is 50 % condensed at about 747 °C and completely condensed at 679 °C.

Dynamic crystallization experiments reproduced the texture of chondrules with cooling rates of 5-8000 °C/hr and melting temperature of 1200-1600 °C (TSUCHIYAMA and NAGAHARA, 1981; TSUCHIYAMA et al., 1980a,b; PLANNER and KEIL, 1982; HEWINS, 1983, 1988; HEWINS et al., 1981; LOFGREN and RUSSELL, 1986). Assuming liquidus temperature of 1500 °C and cooling rate of 1000 °C/hr, chondrules must have been above condensation temperatures of alkalis (∼1000 °C) at least for 30 minutes. Heating experiments of the long duration above 1000 °C for lunar basalts (GIBSON and HUBBARD, 1972), chondritic meteorites (GOODING and MUENOW, 1976, 1977) and synthetic basaltic materials (KREUTZBERGER et al., 1986) indicated that large elemental fractionations occur among alkalis. In addition, vaporization experiments for chondritic materials (NOTSU et al., 1978; HASHIMOTO et al., 1979) also indicated that alkaline elements evaporate in the early stage of the vaporization sequence.

However, the volatile element contents in chondrules are not so depleted compared with those in CI-chondrites. WILKENING et al. (1984) showed that the lithophilic volatile element Zn is not depleted severely in Chainpur (LL) chondrules. TSUCHIYAMA et al. (1981) showed that the rate of volatilization of Na from silicate melt spheres is the rate-controlling process, and suggested that chondrules experienced an instant heating followed by an immediate cooling. HEWINS (1988) suggested that 1000 °C/hr is a good estimate of the average cooling rate of 'classic' olivine-rich chondrules, and argued that this cooling rate is not high enough to allow Na to be retained by chondrules in hot nebular gases under reducing conditions. Based on thermal diffusion calculations, FUJII and MIYAMOTO (1983) suggested that the duration of each heating event should be less than 0.01 second for chondrules.

As noted in the previous sections, Allende and Felix chondrules show considerable abundance variations of alkalis, but have a constant K/Rb ratio close to that of CI's. This is clearly illustrated for Allende chondrules in Fig. 38. The most straightforward interpretation for the constant K/Rb ratio (close to CI's) observed for the Allende and Felix chondrules is that vaporization loss of alkalis accompanied by K/Rb fractionation was not significant during the melting event. In addition, the lack of any correlation between alkali abundance and chondrule mass observed in Felix chondrules can also be considered to support the interpretation that alkali loss from chondrules was minor. It implies that the precursor materials had the CI K/Rb ratio. On the other hand, in view of rapid cooling (> 1000 ^{o}C/hr) for barred olivine chondrules, it is suggested that the melting-vaporization process for some chondrules was kinetically controlled, yielding no substantial fractionation of the alkalis, even if vaporization of alkalis was significant. It cannot be ruled out that the lower abundances of alkalis and the constant K/Rb ratio for some olivine-rich chondrules (Fig. 11) resulted from vaporization loss during chondrule melting. Unfortunately, further implications may not be properly evaluated because almost no experimental data on the kinetic behavior of the alkaline elements are available at present.

Figure 38.

Plot of CI-normalized K/Rb ratio vs. K content for Allende chondrules. In spite of textural and major chemical differences, chondrules have a constant K/Rb ratio which does not deviate significantly from the CI K/Rb ratio.

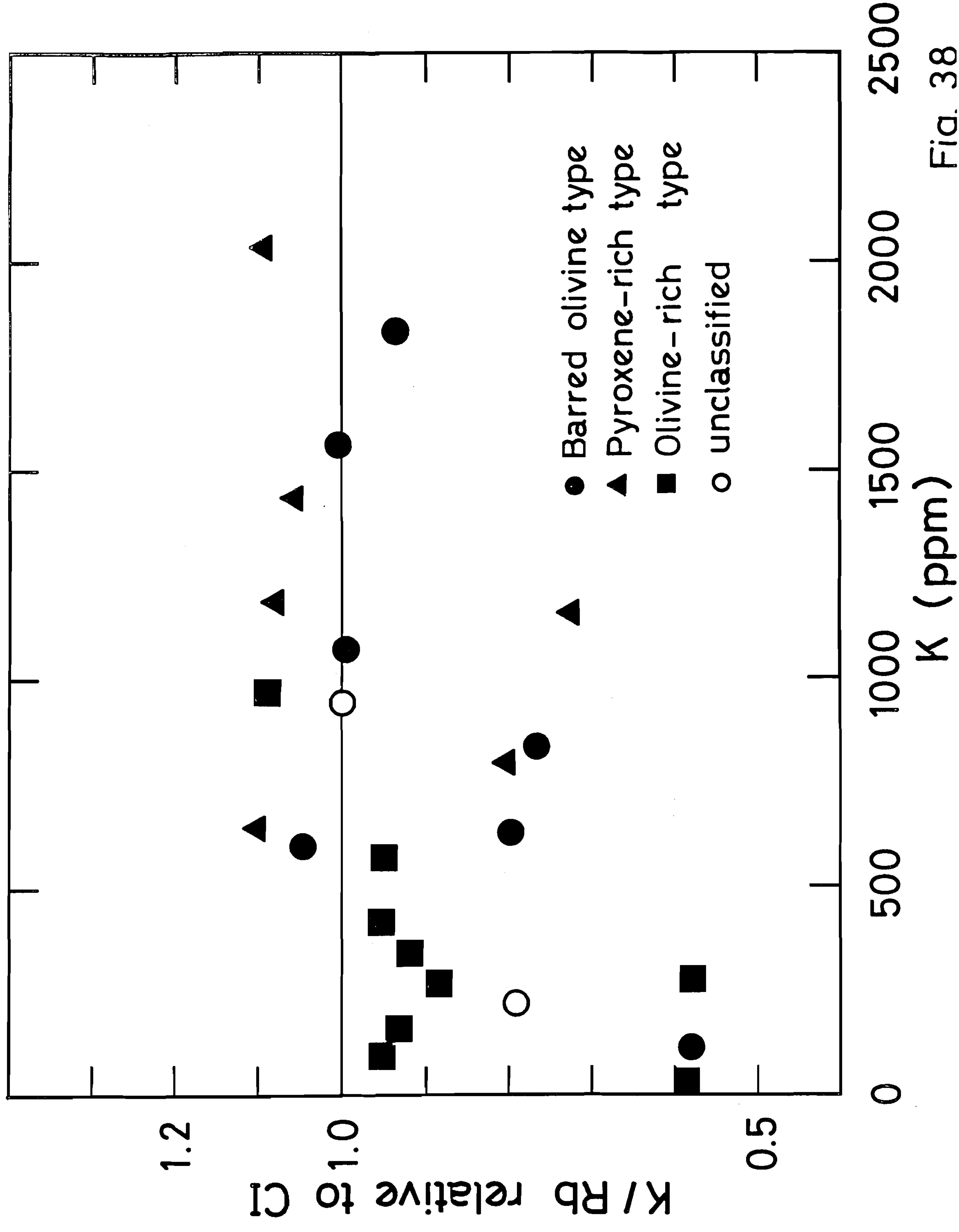

K / Rb relative to CI
1.2
1.0
0.5
K (ppm)
0
500
1000
1500
2000
2500
● Barred olivine type
▲ Pyroxene-rich type
■ Olivine-rich type
○ unclassified

Fig. 38

In any case, considering the simple regularity of the alkali abundances in every textural type of the chondrules examined in this work, we suggest that the K/Rb ratio close to the CI's, together with large abundance variations, were produced prior to the chondrule melting events, during formation and/or accretion of chondrule precursor materials. From the above discussion, it is suggested that the much more refractory lithophiles, REE, Ba, Sr, Mg and Ca did not experience appreciable vaporization loss in the chondrule melting event.

2. Rare earth element fractionation

Many Allende and Felix chondrules show light/heavy REE fractionations and anomalies of Ce, Eu and Yb. Since there are no correlations among Eu anomalies, absolute REE abundances, light/heavy REE fractionations or Ca contents of chondrules, and because the solid/liquid partitioning of elements cannot produce such REE fractionations (SCHNETZLER and PHILPOTTS, 1970), it seems likely that the origin of Ce, Eu and Yb and light/heavy REE fractionations did not result from solid/liquid partitioning of REE in the plagioclase- or clinopyroxene-bearing assemblages. As inferred from Figs. 9, 10 and 29, elemental volatilities may have played an important role in lithophile element fractionations. If this is true, the observed REE fractionations in Allende and Felix chondrules can be reasonably explained by gas/solid (or liquid) fractionation processes at high temperature in the nebula.

Similar but more pronounced anomalies and fractionations of REE have been reported for the Group II CAIs (TANAKA and MASUDA, 1973; MARTIN and MASON, 1974; L. GROSSMAN and GANAPATHY, 1976b; L. GROSSMAN *et al.*, 1979; CONARD, 1976; MASON and MARTIN, 1977; MASON and TAYLOR, 1982; NAGASAWA *et al.*, 1977), the ultra-refractory inclusions (*e.g.*, BOYNTON *et al.*, 1980), FUN inclusions C1 (CONARD *et al.*, 1975), HAL (DAVIS *et al.*, 1982) and EK 1-4-1 (NAGASAWA *et al.*, 1983).

According to the equilibrium condensation theory (BOYNTON, 1975; DAVIS and L. GROSSMAN, 1979; BOYNTON and CUNNINGHAM, 1981; DAVIS *et al.*, 1982), the heavy REE depleted pattern is explained as due to the presence of condensates which formed from the gas after removal of ultra-refractory elements. On the other hand, the heavy REE enriched pattern is thought to represent early condensates from a gas of solar composition or vaporization residues of dusts with the solar elemental composition.

The newly found REE fractionation for the BO chondrules (1 and 2) may also be explained as representing a kind of ultra-refractory component as inferred from the Group II CAI, FG13 (DAVIS and L. GROSSMAN, 1979). The less-pronounced fractionations and lower abundances of REE for chondrules, compared to CAIs, may be understood as the following. The REE-carriers in chondrules, formed from highly fractionated REE materials such as Group II or from ultra-refractory REE components. They were then diluted by unfractionated components to yield the observed REE abundances in chondrules. In this way, the majority of fractionated REE patterns found in chondrules appears to be explained in terms of equilibrium gas/solid fractionation processes similar to those of CAIs (DAVIS and L. GROSSMAN, 1979). Hence, it is considered that elemental volatilities played an important role in the fractionation processes.

The REE patterns of Allende PP chondrule 9 and Felix Al,Ca-rich PP chondrule #8 are different from the CA chondrule RC-11 (WLOTZKA and PALME, 1982), and quite remarkable when compared with those of Group II CAIs. First, light REE fractionation, that is, monotonic increase in abundance from La to Sm, is recognized. Second, positive Ce anomaly up to 50 % exists. Third, negative Eu anomaly, common in Group II CAIs, is not observed. As a result, the pattern appears to be a new type of Group II or possibly related to Group IIA termed by DAVIS and L. GROSSMAN (1979). Chondrite-normalized lithophile element abundance pattern of the Allende coarse-grained CAI A-2 analyzed by CONARD (1976) is similar to that of Allende chondrule 9 and Felix chondrule #8 (Fig. 39), except that alkaline element abundances are depleted in A-2 (CONARD, 1976; GRAY *et al.*, 1973) relative to that of chondrite. The mineralogy of A-2 (melilite + fassaite + anorthite + spinel; GRAY *et al.*, 1973) is, however, different from that of Allende chondrule 9 and Felix chondrule #8.

Figure 39.

Comparison between Felix chondrule #8 and Allende coarse-grained CAI, A-2 (CONARD, 1976). It appears that light REE abundance patterns of both samples are in good agreement each other. The heavier REE (*i.e.*, the most refractory REE, Er and Lu) are depleted in chondrule #8 compared with that of CAI A-2. The group II REE pattern such as chondrule #8 and CAI A-2 with slight negative Eu anomaly may be reflected the mixing of at least two REE-bearing components (*i.e.*, a fractionated REE component and a chondritic REE component).

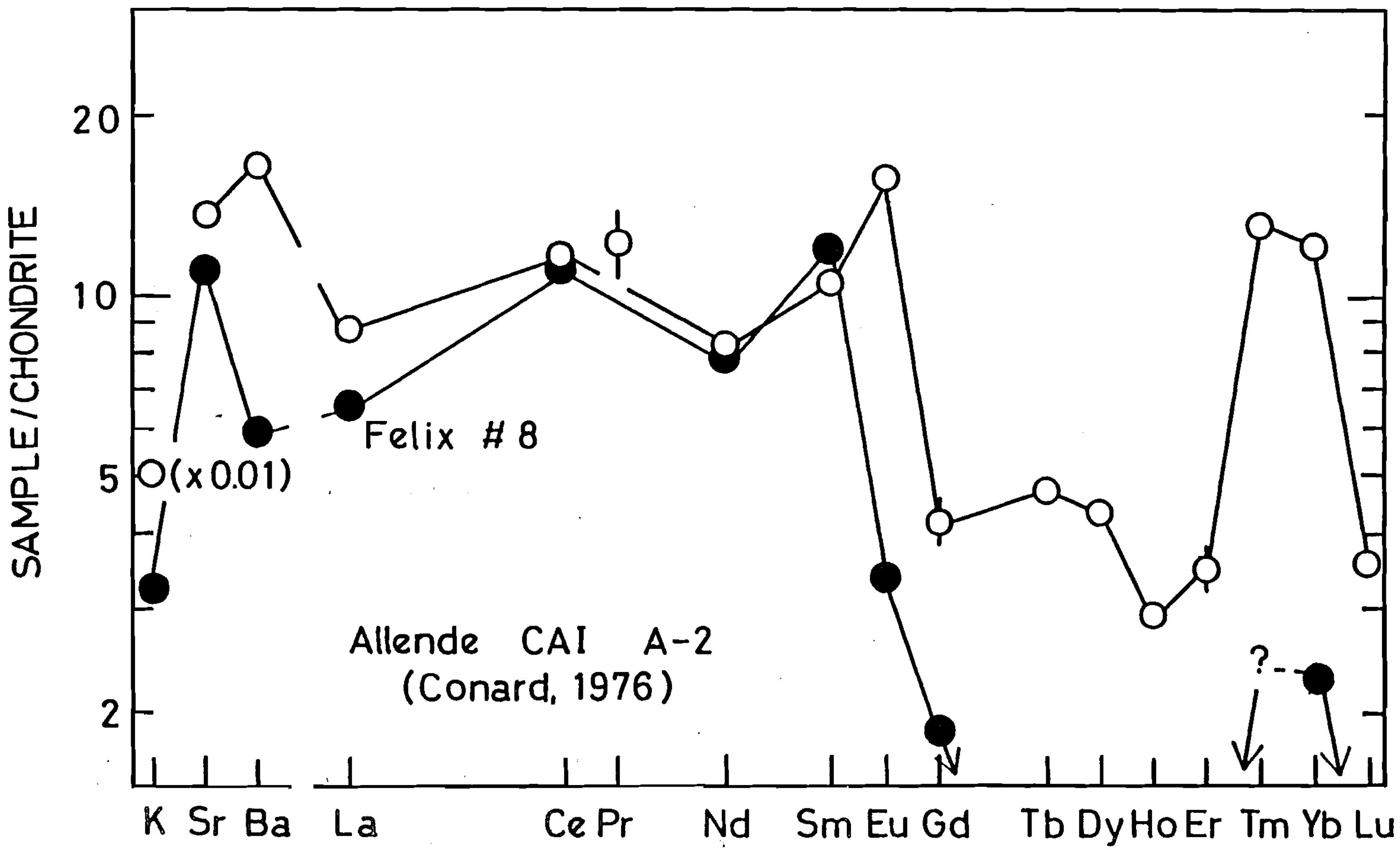

SAMPLE / CHONDRITE
20
10
5
2
K
Sr
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
○(x 0.01)
Felix # 8
Allende CAI A-2
(Conard, 1976)
?

Fig. 39

In addition to anomalies of both Ce and Yb, Felix chondrule #3 has positive Eu anomaly. Although light/heavy REE fractionation is not pronounced, it is suggested in terms of REE features that refractory precursor materials in chondrule #3 may be similar in composition to those of chondrule #8. The positive anomalies at Ce and Yb for chondrule #3 may be qualitatively explained by mixing between fractionated REE components such as precursors of chondrule #8 and chondritic components (Fig. 40). Alternatively, refractory precursors of chondrule #3 may have scavenged the later stage (*i.e.*, lower temperature) condensates enriched in relatively volatile REE (*i.e.*, Ce, Eu and Yb).

Figure 40.

Assuming that Felix chondrule #8 is composed of a mixture of refractory and chondritic components, we can obtain a refractory end member (*e.g.*, $REE_{\text{chondrule \#8}} = REE_{2.25 \text{ x CI-chondrite}} + REE_{\text{refractory end member}}$).

CI-normalized REE abundances in a Felix chondrule #3 compared to the abundance predicted to mixing model. Note the irregularity in the REE abundances in the chondrule and the depletion in the heavy REE as predicted for a mixing model(lower).

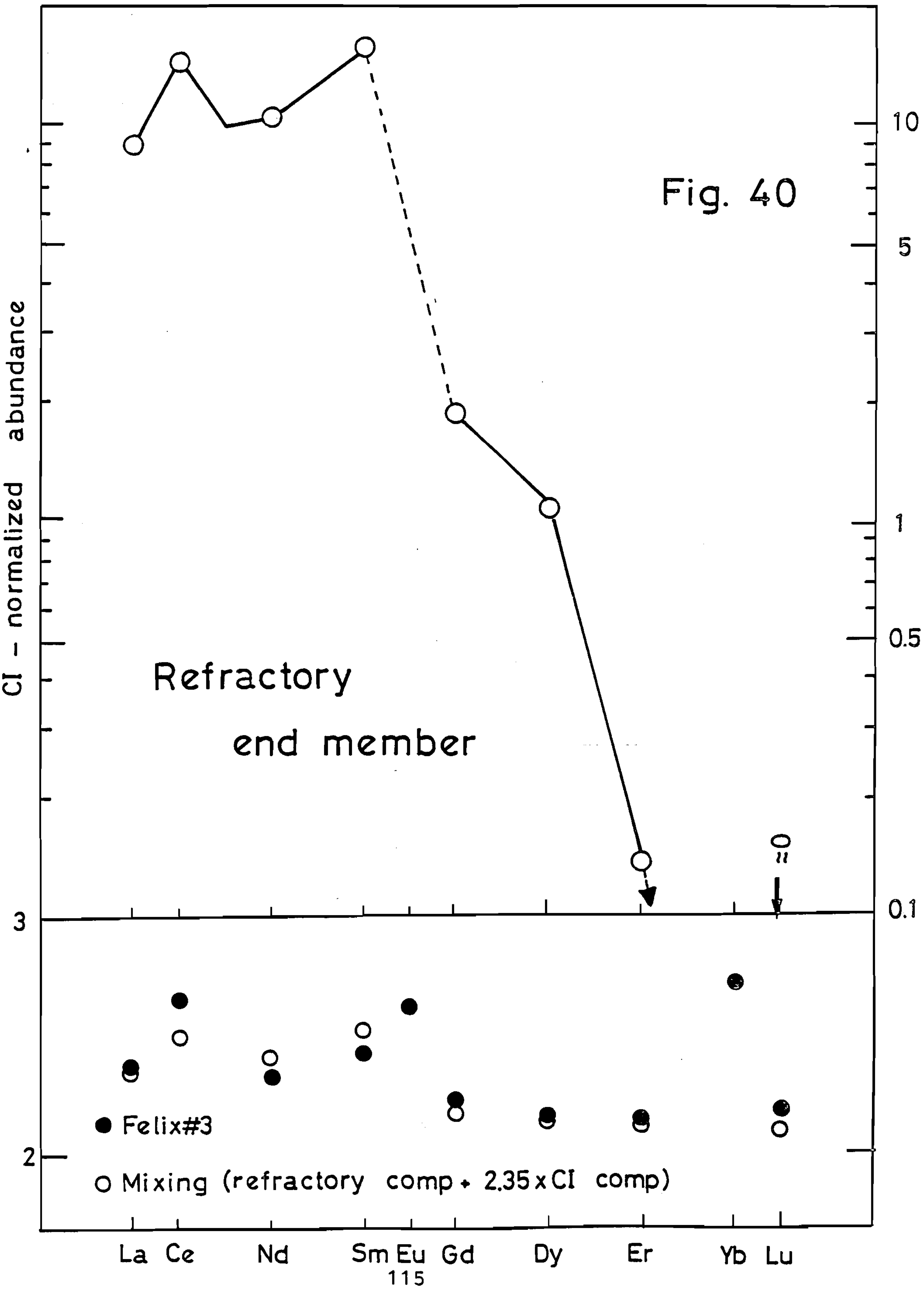


Fig. 40
CI - normalized abundance
10
5
1
0.5
0.1
Refractory end member
≈0
3
2
● Felix#3
○ Mixing (refractory comp + 2.35 x CI comp)
La
Ce
Nd
Sm
Eu
Gd
Dy
Er
Yb
Lu

According to thermodynamic equilibrium calculations, it is shown that the REE pattern of Group II CAIs was established when the REE were in the gas phase in equilibrium with an ultra-refractory component. The particular REE pattern of chondrule #8 may be explained by this model. However, the results of thermodynamic calculations did not show light REE fractionation and positive anomaly at Ce. The Group II REE pattern with slight Eu anomaly of chondrule #8 may be reflecting the mixing of at least two REE-bearing components (DAVIS and L. GROSSMAN, 1979). Alternatively, the REE pattern was reflecting a more complicated history or even a disequilibrium origin of the chondrule precursors. The isotopic data showed that the homogenization of the material in the solar system was not complete, and that the thermal history of the solar nebula may have been more complex (e.g., CLAYTON et al., 1974). On the analogy of evaporation/re-condensation history of CAIs (e.g., NIEDERER et al., 1985), refractory precursor materials of chondrules may have been recorded the same kinds of high-temperature fractionation processes. The light/heavy REE fractionated patterns with anomalies of both Ce and Yb were recently reported in hibonites (e.g., MUR-31) from CM2 Murchison (IRELAND et al., 1986) and CAIs (CL 7-1 and CL 9) from CV Mokoia (LIU et al., 1987). It is suggested that gas/solid fractionations, which were similar to CAIs, occurred in the nebula where the chondrule precursor was formed.

For these reasons, it is suggested that refractory precursor components of Allende chondrule 9 and Felix chondrules #3 and #8 were not formed from Si,Ca-rich melts produced during evaporation of primitive dust aggregates and separation from spinel-rich residues (KORNACKI and FEGLEY, 1984; BISCHOFF and KEIL, 1984) but from condensates during the gas/solid fractionation processes occurred either in the solar nebula (BOYNTON, 1975) or in the presolar environment (WOOD, 1981; FEGLEY and KORNACKI, 1984).

An increase of oxygen fugacity in the nebula makes Ce volatile (BOYNTON, 1978). Ytterbium exhibits the opposite effect and becomes more refractory like other heavier REE (BOYNTON and CUNNINGHAM, 1981; DAVIS et al., 1982). The presence of anomalies of both Ce and Yb in Allende chondrules 4, 9 and 24, and Felix chondrules #3 and #8 suggests, therefore, a complicated history of chondrule precursors. Alternatively, processes such as an instantaneous vaporization of dust particles, thereby generating local enhancement oxygen fugacity (i.e., a modest oxidizing condition), may be important for these specific REE fractionations. In any case, concerning to the Ce anomaly of chondrules, the canonical redox states of the nebula may not be acceptable.

The depletions of Mo, W, V, U, and Ce in CAIs (FEGLEY and PALME, 1985; BOYNTON and CUNNINGHAM, 1981; NAGASAWA and ONUMA, 1979), the occurrence of hibonites in a variety of color (IHINGER and STOLPER, 1986), and the high FeO contents in clinoenstatite (JOHNSON, 1986) indicate more oxidizing conditions than the expected for primitive solar nebula.

MCSWEEN et al. (1983) suggested that type II (i.e., FeO-rich) chondrules must have formed from more highly oxidized precursor materials than type I or III (*i.e.*, FeO-poor). Chondrules 7 and 22, which may be of type II in terms of the compositions of olivine and spinel, do not exhibit Ce anomalies. However, chondrules 14 and 16, which may not be of type II, exhibit weak negative Ce anomalies. Hence, the redox state estimated from the Fe^{2+} content in olivine and spinel appears to conflict with that from the degree of the Ce anomaly. Redox states indicators for chondrules may be understood as implying that Ce anomalies had been produced prior to the time when the Fe redox system was established in the chondrule precursors.

The REE pattern of CAI #2 may be classified as a Group III REE pattern (MARTIN and MASON, 1974) 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 at the temperature of 50 % oxide condensation, 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 reflects a complicated history or may be a disequilibrium origin of the inclusion precursor. WARK and LOVERING (1982a,b) suggested that Type B CAIs are residues from the heating and incomplete evaporation of interstellar dust during the accretion of the protosolar nebula. Similar Group III REE patterns having lower CI-normalized Yb abundances than that of Eu were observed in meteoritic hibonites, especially in CM2 Murchison (EKAMBARAM *et al.*, 1984, 1985; FAHEY *et al.*, 1987).

3. Refractory trace elements fractionation

The elemental correlations illustrated in Figs. 11-13 and 31-33, and REE fractionations observed for many Allende and Felix chondrules (Figs. 14-25, 35 and 36), are considered to be the results of accretion of different types of precursor materials. In view of positive correlations among these refractory elements as well as the moderately volatile elements K and Rb, it is suggested that at least one of the precursor components of the Allende chondrules was enriched in alkalis and refractory elements and had a constant K/Rb ratio close to that of CI's. These correlations show that the elemental distributions in the precursor materials had not been established by the fractional condensation sequence. There is a large difference (~600 C^o) in condensation temperatures between K and Sm (L. GROSSMAN and LARIMER, 1974). Such a trend could not be expected for nebular processes from thermodynamic considerations of gas/solid (or liquid) partitioning.

The most plausible hint could be that alkalis and REE are both large ion lithophile elements and have geochemical affinities for specific phases under some conditions. The close correlations of alkalis to refractory elements observed in CAIs are believed to be the result of the reaction of melilite with nebular gas enriched in alkalis (WARK, 1981; MACPHERSON et al., 1981; IKEDA, 1982). Drastic changes in the composition of the ambient gas may have occurred in the region of the nebula where precursor materials were formed efficiently. If dust grains enriched in refractory elements were removed into cooler nebular regions prior to the total condensation or evaporation of REE, they may have reacted with the alkali-rich gas, and feldspathoids may have formed as by-products of the alteration process (Fig. 41). Such a possibility might fit the turbulent proto-planetary cloud model of MORFILL (1983). In the same way, the positive correlations of Al-Na for some UOC chondrules (DODD, 1978; LUX *et al.*, 1981) and of REE-alkalis for Qingzhen (EH) and Ornans (CO) chondrules (J.N. GROSSMAN *et al.*, 1985; RUBIN and WASSON, 1987a) could be explainable.

Figure 41.

Schematic diagram of alkali-alteration processes for refractory precursors of chondrules.

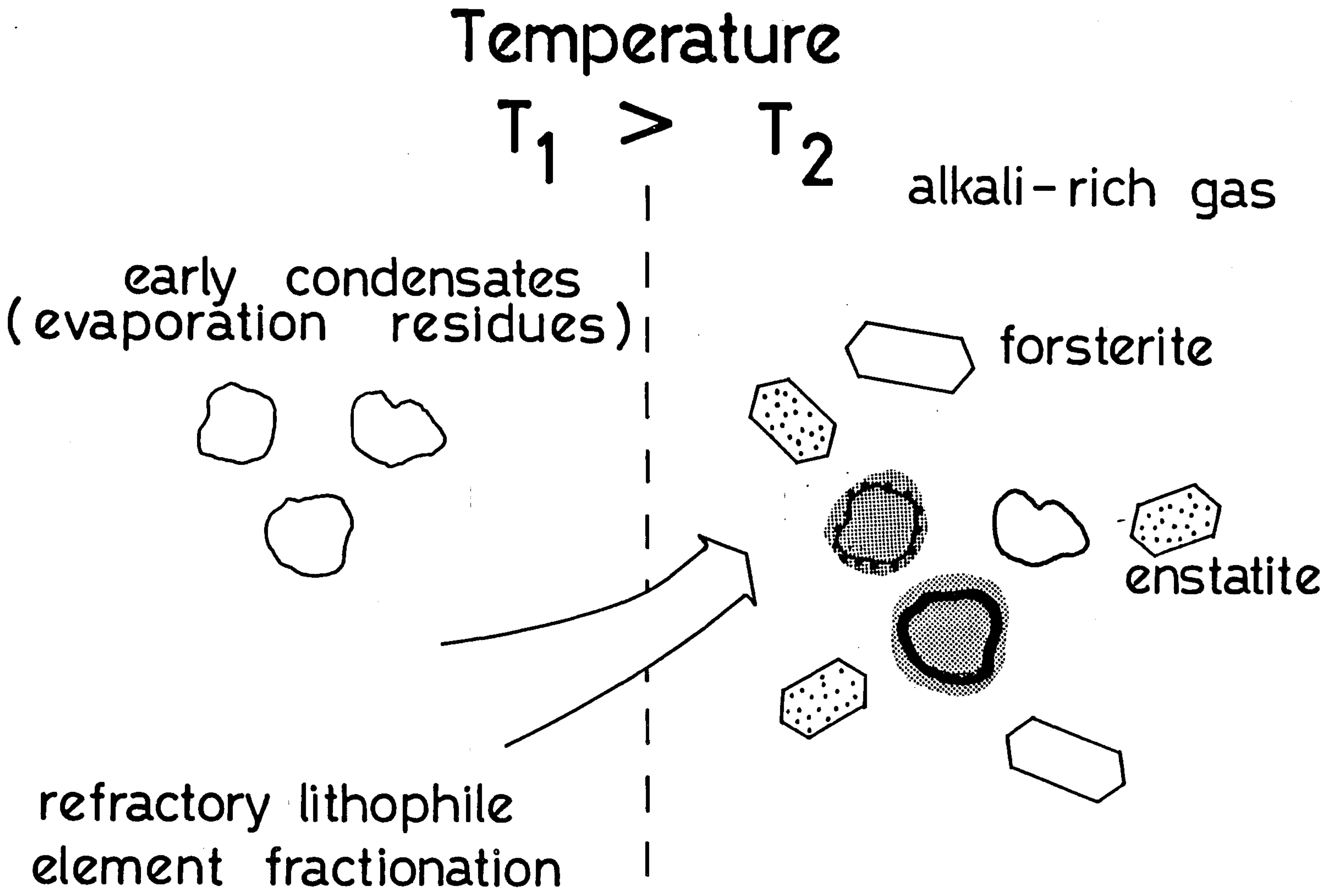

Temperature
$T_1 > T_2$
alkali-rich gas
early condensates
(evaporation residues)
forsterite
enstatite
refractory lithophile
element fractionation

Fig. 41

The Allende barred olivine chondrules show a systematic depletion of Ca relative to REE of similar volatility. One of the possible explanation of the depletion is that Ca evaporated from the refractory precursors along with the increase of its volatility at temperature < 727 °C (HASHIMOTO and WOOD, 1986). Strong enrichments of Sr and Ba in some Allende and Felix chondrules (*e.g.*, 7, 12, #3 and #8) suggests that their precursor might be scavenged to the specific phases enriched in Sr and/or Ba such as discovered in Allende (TANAKA *et al.*, 1976; TANAKA and OKUMURA, 1977) and in a CAI from Essebi (CM2) (EL GORESY *et al.*, 1984). In any case, further studies are necessary to confirm this explanation.

A problem then arises whether the precursor materials of chondrules are the same as those for CAIs or not. In this connection, it is pointed out that the Sm *vs*. Ca diagram for the Allende CAIs (Fig. 42) does not show a clear trend like that for the chondrules (Fig. 12). It is suggested, therefore, that REE-carriers in chondrules were not contributed by a specific type of CAI but that similar REE fractionation processes prevailed during formation of precursors of chondrules. This is consistent with the results of oxygen isotopic studies which indicate that Allende chondrules have a distinctly different trend of oxygen isotopic composition from that of CAIs' (CLAYTON *et al.*, 1983, 1987a,b).

Figure 42.

Plot of Sm vs. Ca for Ca,Al-rich inclusions from the Allende chondrite. Data are from MASON and MARTIN (1977) and MASON and TAYLOR (1982). In spite of the positive correlation for chondrules, the data points for CAIs are scattered, indicating that specific types of CAIs did not contribute to the REE carriers in Allende chondrules.

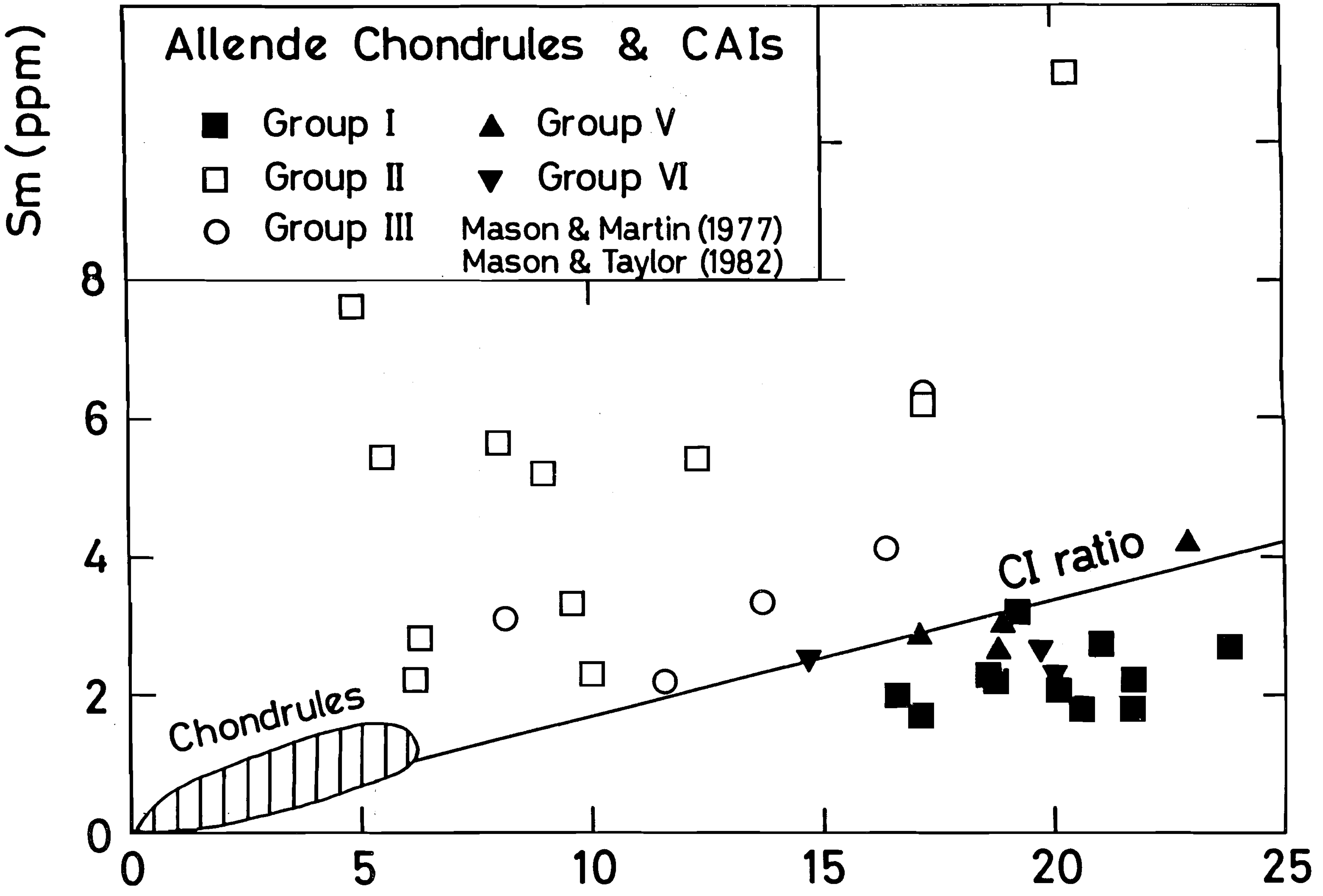

Allende Chondrules & CAIs
■ Group I
□ Group II
○ Group III
▲ Group V
▼ Group VI
Mason & Martin (1977)
Mason & Taylor (1982)
Sm (ppm)
8
6
4
2
0
0
5
10
15
20
25
Ca (%)
CI ratio
Chondrules

Fig. 42

As already mentioned, heavy REE enrichment relative to light REE is dominant in Allende chondrules. In addition, negative Eu anomalies are predominant. Positive Ce and Yb anomalies, on the other hand, appear to be compensated by those of negative ones. If the REE composition was identical to that of CI-chondrites in the Allende chondrule formation location, refractory lithophile precursors of Allende chondrules must have lost some degree of Eu and light REE (i.e., moderately refractory REE) during their formation. Mass balance constraints would then require that REE component of lost material had positive Eu and/or light REE enrichment relative to heavy REE. The matrix and Group II CAIs appear to be the most plausible candidates for the complementary components.

Matrix materials may have been formed from later stage nebular products and expected to have the missing REE components. Detailed REE features of the Allende matrix, however, have not been established. Group II CAIs, which are depleted in the most refractory REE (e.g., Lu and Er) relative to light REE, could be one of the candidates for light REE carriers.

It is suggested that refractory precursors of Allende chondrules were related to this type of CAIs. It is possible that a very large fraction of the ultra-refractory component have been scavenged by Allende chondrule precursors from the nebular region, where Group II CAIs were formed. This also explains in part why the ultra-refractory inclusions have been mainly identified in CM and CO chondrites (e.g., BOYNTON et al., 1980; PALME et al., 1982; EKAMBARAM et al., 1984,1985; EL GORESY et al., 1984) but rarely in CV Allende.

It is suggested that CV and CO chondrules have formed in a region of the nebula where the refractory lithophile precursors above mentioned were accreted. These chondrules must have been generated by transient heating (WASSON _et_ _al_., 1982; WOOD, 1984) in a cool gas, and instantaneous vaporization of dust and ice may have been generate oxidizing conditions and thus volatile loss from the chondrule melt may have been reduced.

VI. CONCLUSIONS

(1) The abundances of K and Rb in Allende and Felix chondrules show large variations among the chondrules. In spite of the textural and major chemical differences of chondrules, the K/Rb ratio of chondrules are quite uniform and close to that of the CI ratio, indicating that K/Rb fractionation did not occur during chondrule-formation melting events and/or vaporization loss of alkalis was not significant, and that one of the precursor components was enriched in alkalis and had the CI K/Rb ratio.

(2) The REE abundances are fractionated among individual chondrules. Particularly the barred olivine and pyroxene-rich chondrules often show light/heavy REE fractionations and/or definitely large anomalies of Ce, Eu and Yb, indicating that gas-solid (or liquid) processes yielding REE fractionations took place during the formation of refractory precursors, and that these fractionation processes were ubiquitous in the region of the nebula where CO and CV chondrule precursors formed.

(3) Positive correlations are found among REE, Ca, Sr, Ba, K and Rb for the chondrules. They are interpreted in terms of mixing of different types of precursor materials; chondrules rich in refractory element sampled more efficiently alkali-bearing refractory lithophile precursors.

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