

## COMPOSITIONAL HETEROGENEITY OF FINE-GRAINED RIMS IN THE SEMARKONA (LL3) CHONDRITE

Satoshi MATSUNAMI, Hiroshi NISHIMURA and Hideo TAKESHI

*Department of Geosciences, Faculty of Science, Naruto University of Education,  
Takashima, Naruto 772*

**Abstract:** The fine-grained opaque matrix and chondrule rims in the Semarkona (LL3) chondrite have been investigated in detail with the scanning electron microscope. The chemical analyses were made by the SEM-EDS technique.

Although the rims have similarities in texture and composition to the matrix, they show wider variabilities in chemical composition in comparison with the matrix in Semarkona. Based on both mode of occurrence and Al/Si ratio, the fine-grained opaque rims in Semarkona are classified into three types: type I, type IIa and type IIb. Type-I rims commonly occur as chondrule-rimming materials, having high Al/Si ratios. Type-I rims are composed mostly of smectite, showing a wider variation of the FeO and Al<sub>2</sub>O<sub>3</sub> contents than that of the matrix. Type-IIa rims occur as magnetite-bearing chondrule rims, characterized by their low Al/Si ratios. They are composed of mixtures of smectite, fayalitic material and its alteration products. Metal-sulfide-magnetite aggregates have opaque rims (type IIb) with the lowest Al/Si ratios. The SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and FeO contents of type-IIb rims suggest that they consist mainly of fayalitic material and its alteration products. In composition, it is suggested that 'fayalitic' material and its alteration products in types-IIa and IIb rims correspond to one of the non-refractory, SiO<sub>2</sub>-, FeO-rich components of precursor materials of the chondrules in Semarkona. The 'fayalitic' material might have formed through intensive fractional condensation of forsterite in the cooling nebula gas.

### 1. Introduction

The compositional and petrologic studies of opaque matrix and chondrule rims in type-3 ordinary chondrites have been conducted by many investigators with the use of electron microscopy and electron-microprobe analyses (ASHWORTH, 1977; ALLEN *et al.*, 1980; KING and KING, 1981; HUSS *et al.*, 1981; IKEDA *et al.*, 1981; NAGAHARA, 1984; SCOTT *et al.*, 1984; MATSUNAMI, 1984; ALEXANDER, 1987; ALEXANDER *et al.*, 1989a). In particular, the Semarkona (LL3) chondrite has attracted much attention because it is considered to be the least metamorphosed one. HUSS *et al.* (1981) were the first to provide a characterization of the opaque silicate matrix in Semarkona. NAGAHARA (1984) investigated the mineral constituents in Semarkona matrix by the SEM-EDS technique and showed that Semarkona matrix is composed mainly of low-FeO olivine, low-Ca pyroxene and uncharacterized FeO-rich silicate phase. Recently, HUTCHISON *et al.* (1987) have showed that some of the fine-grained FeO-rich silicates in Semarkona are composed of smectite by a transmission electron microscope (TEM). This indicates that the Semarkona chondrite has suffered aqueous alteration.

Although the major chemical compositions of matrices and chondrule rims in unequilibrated ordinary chondrites (UOCs) have been published, comparative study of chemical compositions between matrices and rims is particularly scarce. MATSUNAMI (1984) made a comparison of compositional data of matrix with those of chondrule rims in eight UOCs. Recently, ALEXANDER *et al.* (1989a) also have examined fine-grained matrix and rims in some primitive UOCs. In order to clarify their relationship to chondrules, we need more detailed data on compositional heterogeneity of fine-grained matrix and chondrule rims in UOCs.

In this paper we present a petrological study on mode of occurrence and chemical compositions of fine-grained matrix and rims in the Semarkona (LL3) chondrite, which has the lowest thermoluminescence (TL) sensitivities (SEARS *et al.*, 1980). We discuss their compositional heterogeneities and the implications for the formation process of chondrules, matrix and rims in UOCs.

## 2. Samples and Analytical Procedure

The Semarkona (LL3.0) chondrite specimen was chosen for measurement of opaque, fine-grained matrix and rims. Since Semarkona is highly unequilibrated, it has been considered to be the most pristine ordinary chondrite available for comparative studies among chondrules, matrix and rims. In this study, the matrix is defined as fine-grained material located between chondrules and other inclusions (fine-grained lithic fragments and metal-sulfide aggregates) that apparently does not form a coating on them (MATSUNAMI, 1984; SCOTT *et al.*, 1988; ALEXANDER *et al.*, 1989a). The rims around chondrules and metal-sulfide aggregates are defined as fine-grained materials adhering to them. The rims are recognized as petrologically distinct from the matrix in UOCs (ASHWORTH, 1977; MATSUNAMI, 1984; ALEXANDER *et al.*, 1989a).

One small chip, provided by Dr. B. MASON of the Smithsonian Institution (Spec. No. USNM 1805), was mounted in epoxy, sectioned and polished for optical and SEM observations and X-ray microanalysis. First, polished thin sections were studied microscopically under transmitted and reflected light. After the microscopic study, textures of matrix and rim were studied in detail. For the purpose the textures of matrix and rim were investigated by scanning electron microscopy (SEM) and X-ray energy-dispersive spectroscopy (EDS) to identify individual matrix constituents and to select areas for analysis of bulk composition of matrix and rims. The SEM-EDS analysis was made using a LINK SYSTEM Model 860 energy-dispersive spectrometer, equipped to a SEM, JEOL-T200 of the National Science Museum. The accelerating voltage was 15 kV and the specimen current was  $3 \times 10^{-9}$  A. Counting time was 100 s for each analysis. Synthetic metals were used as standards. Correction was made by the ZAF method (STATHAM, 1980). Precision and detection limits of analyses with similar EDS system were discussed by DUNHAM and WILKINSON (1978) and MORI and KANEHIRA (1984). They showed that the accuracy and precision of energy-dispersive analysis (EDA) were comparable to those of wavelength-dispersive analysis (WDA). Scanning of electron beam on  $\{(10-30) \mu\text{m}\}^2$  area was used to determine abundances of 13 elements (Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, K, P, Ni and S). Analyses were made on at least 3-12 different locations on each rim of Semarkona. Bulk compositions of

seven chondrules in Semarkona were also analyzed by scanning electron beam on larger areas to compare their compositions with those of their rims. Two to five analyses were made on each chondrule. Number and size of the scanning areas were dependent on size and texture of the chondrule. The size was ranging from 100  $\mu\text{m}$  to 300  $\mu\text{m}$  in diameter. The empirical correction method for WDA of polyphase samples with a broad beam was discussed by IKEDA (1980). However, the correction was not made because it is not clear that the correction method is applicable to the SEM-EDS technique in this study.

### 3. Petrographical Description of Matrix and Chondrule Rims in Semarkona

The textural features and mode of occurrence of the fine-grained matrix and rims in Semarkona are briefly described below. Some typical occurrences of matrix and rims under microscope are shown in Figs. 1–3. Observed matrix occurrences are mostly opaque in thin sections (Fig. 1). Most of the opaque matrix of Semarkona show similar textures as those of matrices in other primitive UOCs and are found to consist predominantly of a porous aggregate of submicron-sized, subrounded to sub-angular silicate crystals (low-FeO olivine and low-Ca pyroxene), uncharacterized FeO-rich “possibly amorphous materials”, aggregates of very fine-grained ( $\sim 0.1 \mu\text{m}$  in diameter) materials, and minute grains of troilite, metallic Fe-Ni, magnetite, maghemite, spinel and calcite (HUSS *et al.*, 1981; NAGAHARA, 1984; MATSUNAMI, 1984; HUTCHISON *et al.*, 1987). Interstitial spaces between these grains are sometimes filled by loose aggregates of “possibly amorphous materials”, which appear to connect these fine-grained materials to each other as “glue” (HUSS *et al.*, 1981; MATSUNAMI, 1984). Recently, these “possibly amorphous materials” in matrix and rims of Semarkona have been examined in detail by analytical TEM and shown to be composed of smectite or ‘fayalitic’ material and its alteration products (HUTCHISON *et al.*, 1987; ALEXANDER *et al.*, 1989b). Chondrule mesostases in Semarkona are also shown to have been altered to phyllosilicates. Calcite grains have been found in Semarkona matrix (MATSUNAMI, 1984; NAGAHARA, 1984; HUTCHISON *et al.*, 1987). The smectite, maghemite and calcite in Semarkona matrix and rims would have formed during aqueous alteration of fine-grained matrix materials (HUTCHISON *et al.*, 1987; SCOTT *et al.*, 1988).

Most chondrules in Semarkona appear to have fine-grained opaque rims that are thick and clearly resolvable under an optical microscope or SEM. Figure 2 shows chondrule rims partially rimmed with opaque minerals and troilite-rich rims. Figure 3 illustrates opaque rim on a metal-sulfide-magnetite aggregate. Opaque rims around metallic aggregates are commonly present in UOCs. Similar rims around metallic objects were described by RAMBALDI and WASSON (1981, 1984) and SCOTT *et al.* (1984). These metallic objects are surrounded by a layer of rimming materials varying in width from 10 to 50  $\mu\text{m}$ . Attached to the outside of this layer are irregularly shaped grains of metal, sulfide and magnetite (Fig. 3).

Several chondrule rims show marked layered structures composed of two concentric layers (ALLEN *et al.*, 1980; ASHWORTH, 1977; MATSUNAMI, 1984). Two kinds of concentric layers are distinguished. In some cases, troilite is concentrated in the



Fig. 1. Transmitted-light photomicrograph of opaque matrix in Semarkona (LL3.0). Width 3.53 mm.

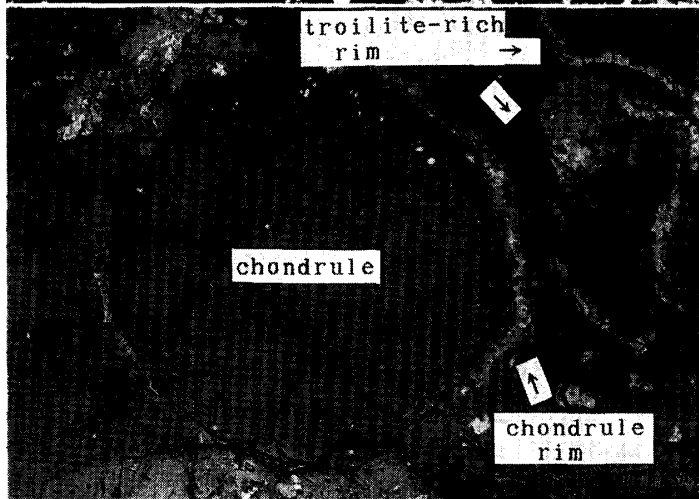


Fig. 2. Reflected-light photomicrograph of opaque rims surrounding chondrules in Semarkona, showing a chondrule rim (left: No. 21) and a troilite-rich rim (right: No. 20). Width 1.33 mm.

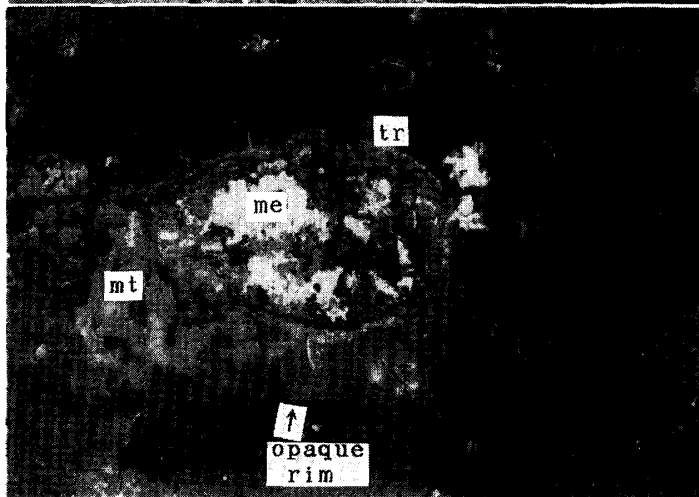


Fig. 3. Reflected-light photomicrograph of opaque rim around a metal-sulfide-magnetite aggregate in Semarkona (type IIb opaque rim: No. 9). me: metal; mt: magnetite; tr: troilite. Width 0.67 mm.

outermost parts of the rim, and silicate grains are predominant in the inner part. These structures are common in chondrule rims of Semarkona. Another kind of concentric layers is characterized by the presence of inner silicate-rich layer and outer metal-magnetite-bearing layer, which are easily distinguished by the different modal compositions of opaque minerals. Figure 4 shows an example of layered structure of

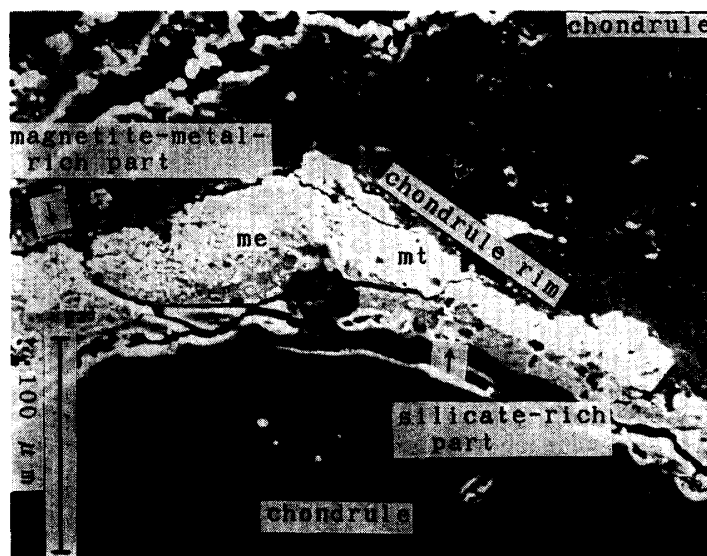


Fig. 4. SEM photograph of a layered structure of a chondrule rim (No. 21: type IIa) in Semarkona, characterized by inner silicate-rich layer and outer magnetite-FeNi-rich layer. me: metallic Fe-Ni; mt: magnetite.

a chondrule rim, characterized by the inner silicate-rich part and the outer metal-magnetite-rich part.

#### 4. Compositional Heterogeneity of Fine-grained Rims in Semarkona

General characteristics of major element chemistry of matrix and rims in Semarkona have already been reported by MATSUNAMI (1984). Here, we describe the compositional heterogeneity of fine-grained rims in Semarkona.

##### 4.1. A classification of fine-grained rims in Semarkona

Thirty thick and clearly resolvable chondrule rims in Semarkona were selected to analyze the compositions. In addition, 4 opaque rims around metal-sulfide-magnetite aggregates (Fig. 3) were included. Compositions of these 34 rims obtained by the SEM-EDS analysis are listed in Table I. Generally they resemble the S-poor rims described by ALLEN *et al.* (1980) and KING and KING (1981). Most chondrule rims and matrix are not systematically different in composition from the matrix occurrences analyzed by HUSS *et al.* (1981), SCOTT *et al.* (1984), MATSUNAMI (1984) and ALEXANDER *et al.* (1989a). Means of 3–12 analyses on each rim failed to show any correlation with textural type of chondrule.

Fine-grained rims are classified into the following three types: type I, type IIa and type IIb. These types are defined by a combination of mode of occurrence and Al/Si ratios. Figure 5 shows the distribution of Si-normalized, sample/CI ratio of Al, having two distinct peaks with different marked ranges of the  $(Al/Si)_{CI}$  ratio. Type I is characterized by  $(Al/Si)_{CI}$  ratios higher than 0.5. The ratios of type-I rims range from 0.88 to 2.77. Type-IIa and type-IIb rims have  $(Al/Si)_{CI}$  ratios lower than 0.5. The ratios of type-IIa rims range from 0.38 to 0.42. Type-IIa rims are usually accompanied with small amounts of Fe-Ni metals, troilite and magnetite (*e.g.*, No. 21 in Fig. 4). Sulfides in type-IIa rims frequently exhibit typical textures due to aqueous alteration (ALEXANDER *et al.*, 1989b). Chondrule rims of type IIa (Nos. 1, 17, and

Table 1. Compositions of 30 chondrule rims and 4 opaque rims rimming aggregate of metallic Fe-Ni, troilite and magnetite, in Semarkona (LL3) chondrite, obtained by SEM-EDS analysis.

type	type I																	
rim No.	2	3	4	5	7	10	12	13	14	16	19	20	22	23	24	25	28	29
N <sup>1</sup>	3	3	3	3	3	3	3	3	4	3	4	4	3	3	3	3	3	4
SiO <sub>2</sub>	36.3	35.7	36.9	39.4	40.0	36.2	35.3	34.1	36.8	33.8	36.6	38.1	37.5	40.4	35.9	36.0	35.2	47.8
TiO <sub>2</sub>	.10	—	.15	—	.13	.10	—	.19	—	.11	.13	.11	.11	—	.15	.14	—	.13
Al <sub>2</sub> O <sub>3</sub>	4.93	6.08	4.59	6.17	5.89	3.17	4.57	3.28	3.52	2.15	3.36	4.59	4.53	4.75	5.38	4.25	5.53	3.18
Cr <sub>2</sub> O <sub>3</sub>	.38	.21	.32	.42	.30	.27	.24	.30	.36	.49	.41	.50	.35	.33	.27	.36	.23	.75
FeO*	25.5	26.3	25.6	25.6	26.2	30.6	31.7	26.0	31.4	27.6	24.9	25.1	29.2	29.8	33.2	28.7	28.4	19.0
MnO	.25	.20	.21	.27	.25	.24	.25	.19	.18	.20	.18	.29	.25	.14	.32	.25	.18	.82
MgO	12.5	10.8	12.1	14.8	15.6	10.7	8.76	10.8	11.3	11.4	12.6	15.2	10.6	11.7	6.53	11.0	10.1	23.1
CaO	.71	.67	.76	.59	.76	.58	.38	.55	.59	.66	1.35	1.50	.78	1.36	.69	1.16	1.32	1.56
Na <sub>2</sub> O	1.55	2.56	2.10	3.13	2.56	1.97	2.61	2.20	2.17	1.84	2.20	1.42	2.38	1.93	2.70	1.65	2.63	1.28
K <sub>2</sub> O	.47	.69	.61	.75	.77	.53	.70	.50	.50	.36	.44	.50	.67	.64	.59	.57	.70	.34
P <sub>2</sub> O <sub>5</sub>	— <sup>2</sup>	.14	.12	—	.34	.25	—	.11	—	.18	.54	.13	—	—	.13	.40	.45	—
Ni	1.14	.68	1.06	1.13	.84	.67	.98	.66	.95	.84	.90	1.28	1.05	.82	.36	.76	1.06	—
S	1.49	.91	1.18	1.22	1.12	1.72	1.52	1.46	1.72	1.67	1.38	2.70	1.34	1.06	.68	1.37	1.72	—
Total	85.3	84.9	85.7	93.5	94.8	87.0	87.0	80.3	89.5	81.3	85.0	91.4	88.8	92.9	86.9	86.6	87.5	98.0

type	type I										type IIa			type IIb			
rim No.	33	39	43	44	52	63	65	66	68	1	17	21	9	15	54	73	
N <sup>1</sup>	3	3	3	3	4	3	3	3	3	12	7	6	3	3	3	3	
SiO <sub>2</sub>	34.7	32.0	34.6	36.3	35.6	35.8	36.7	35.0	32.8	32.9	32.7	25.5	30.4	26.0	25.3	25.2	
TiO <sub>2</sub>	.43	—	.28	—	.12	—	—	.11	—	—	—	—	—	—	—	—	
Al <sub>2</sub> O <sub>3</sub>	6.94	2.98	4.43	5.37	3.92	4.29	4.71	2.55	2.38	1.00	.89	.69	.80	.47	.46	.41	
Cr <sub>2</sub> O <sub>3</sub>	.54	.22	.26	.31	.18	.34	.28	.25	.30	.18	.21	.29	.25	.17	.12	—	
FeO*	36.0	33.8	24.6	30.7	33.6	26.6	26.4	38.6	41.2	47.3	42.0	58.3	50.4	63.4	67.2	61.9	
MnO	.31	.25	.26	.30	.27	.23	.18	.19	.13	.13	.15	.12	.26	—	.16	.14	
MgO	3.96	10.6	12.3	8.65	9.20	11.3	12.1	8.38	8.94	7.30	6.77	6.38	6.60	5.11	5.33	3.94	
CaO	1.32	.78	1.14	.82	.92	1.49	.85	.58	.71	.55	.49	.49	.45	.35	.37	.40	
Na <sub>2</sub> O	2.96	2.25	1.98	3.03	2.29	2.86	2.63	1.91	1.75	1.13	1.94	.80	.98	.23	.15	.15	
K <sub>2</sub> O	.63	.40	.49	.69	.44	.55	.62	.38	.23	.20	.28	.11	.22	—	—	—	
P <sub>2</sub> O <sub>5</sub>	— <sup>2</sup>	—	.43	—	.14	.57	—	—	—	—	—	—	.14	—	—	—	
Ni	—	.60	.71	.62	.65	.88	.84	1.31	1.11	1.51	.53	.79	.95	.70	.69	.92	
S	.99	1.79	1.02	1.04	.99	1.39	1.22	1.71	1.74	1.58	1.70	1.65	1.43	1.59	1.49	1.78	
Total	88.8	85.7	82.5	87.8	88.3	86.3	86.5	91.1	91.3	93.8	87.7	95.1	92.9	98.0	101.3	94.8	

<sup>1</sup>: number of analyses, <sup>2</sup>: not detected, \*: total Fe as FeO.

Fig. 5. Histogram showing a variation of (Al/Si) ratios of opaque rims in Semarkona. The data are normalized to C1 chondrite composition (ANDERS and EBIHARA, 1982). Opaque rims in Semarkona are classified into three types (type I, IIa and IIb) with a combination of (Al/Si) ratio and mode of occurrence.

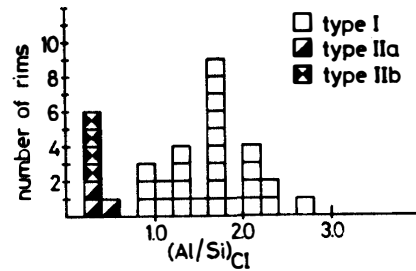
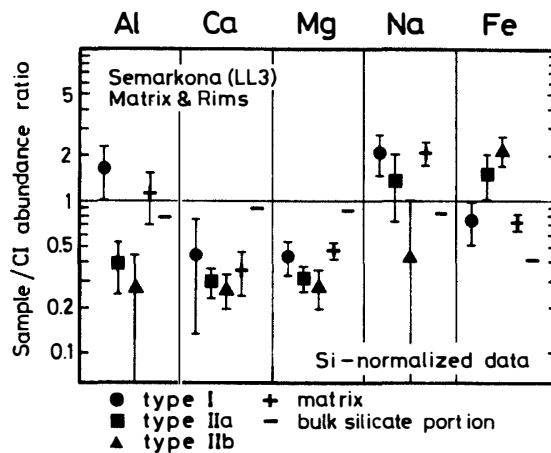


Table 2. Average compositions of matrix and rims in the Semarkona (LL3) chondrite, obtained by SEM-EDS analysis.

N <sup>1</sup>	chondrule rim				opaque rim		matrix	
	type I		type IIa		type IIb			
	86	25	12	49	mean	$\sigma$	mean	$\sigma$
SiO <sub>2</sub>	36.6	4.0	31.1	4.3	26.7	3.4	33.1	1.8
TiO <sub>2</sub>	.12	.13	— <sup>2</sup>	—	—	—	—	—
Al <sub>2</sub> O <sub>3</sub>	4.31	1.68	.89	.44	.54	.47	2.65	1.00
Cr <sub>2</sub> O <sub>3</sub>	.35	.18	.21	.12	.15	.10	.33	.15
FeO*	29.0	6.4	48.5	9.21	60.7	8.4	25.8	3.4
MnO	.26	.17	.13	.09	.16	.11	.21	.10
MgO	11.5	3.9	6.93	1.59	5.25	1.81	11.1	1.6
CaO	.93	.65	.52	.12	.40	.11	.66	.20
Na <sub>2</sub> O	2.22	.67	1.28	.66	.38	.61	2.01	.33
K <sub>2</sub> O	.54	.19	.20	.11	—	—	.39	.13
P <sub>2</sub> O <sub>5</sub>	.16	.32	—	—	—	—	—	—
Ni	.81	.45	1.06	.61	.81	.42	.87	.22
S	1.34	.76	1.63	.41	1.57	.33	1.41	.39
Total	88.1	6.0	92.5	4.4	96.6	3.8	78.5	4.6
X <sub>Fe</sub> <sup>3</sup>	.59	.11	.80	.06	.87	.06	.57	.05

<sup>1</sup>: number of analyses, <sup>2</sup>: not detected, <sup>3</sup>: Fe/(Mg+Fe), \*: total Fe as FeO.

Fig. 6. Variations in compositions of 5 elements (Al, Ca, Mg, Na and Fe) between three types of rims and matrix in Semarkona. Bars represent  $\pm 1\sigma$ . The data are normalized to C1 chondrite composition (ANDERS and EBIHARA, 1982). Data for whole rock silicate portion of Semarkona (JAROSEWICH, 1966) are also shown.



21) are relatively minor compared to the other 27 type-I chondrule rims in Semarkona. Type-IIb rims are fine-grained rims around metal-sulfide-magnetite aggregates (Fig. 3). They have the lowest values of (Al/Si)<sub>C1</sub> ratios, ranging from 0.23 to 0.36.

Table 2 lists the average compositions of type I, type IIa and type IIb opaque rims. Mean composition of matrix is also listed. Figure 6 shows abundance patterns of 5 elements (Al, Ca, Mg, Na and Fe) for matrix and three types of rims in Semarkona. For comparison, the chemical composition of the whole rock silicate portion analyses of Semarkona (JAROSEWICH, 1966) is plotted in this diagram. Type-I chondrule rims and matrix are relatively enriched in Al and Na compared to other elements. Type IIa rims are relatively enriched in Na and Fe. They are characterized by enrichment of non-refractory elements (Si, Na and Fe) relative to refractory lithophile elements such as Al, Ca and Mg. Type-IIb opaque rims are commonly richer in Fe but poorer in Al, Ca and Mg than matrix and other occurrences of rims in Semarkona.

#### 4.2. Heterogeneity in the FeO and Al<sub>2</sub>O<sub>3</sub> contents of matrix and rims

In Semarkona, most opaque rims show a wide variation in composition, but some of individual rims are relatively homogeneous. This is illustrated in FeO vs. Al<sub>2</sub>O<sub>3</sub> variation diagram (Fig. 7). In this figure, data of selected 18 rims (14 type-I rims, 3 type-IIa rims and 1 type-IIb rim) are shown. The compositional data and field of matrix are also illustrated. Some type-I chondrule rims show relatively narrow variations on the FeO-Al<sub>2</sub>O<sub>3</sub> diagram. A few type-I rims plot within the compositional field of matrix and some type-I rims and types-IIa and IIb rims plot outside the field. SCOTT *et al.* (1984) described the inverse correlations of FeO and Al<sub>2</sub>O<sub>3</sub> in matrices of several type-3 ordinary chondrites. In Semarkona, the FeO contents are clearly uncorrelated with the Al<sub>2</sub>O<sub>3</sub> contents in the cases of type-I chondrule rims. However, type-IIa rims show an inverse correlation of FeO with Al<sub>2</sub>O<sub>3</sub>. From these compositional features, it is shown that opaque rims mostly show wider variabilities than matrix in

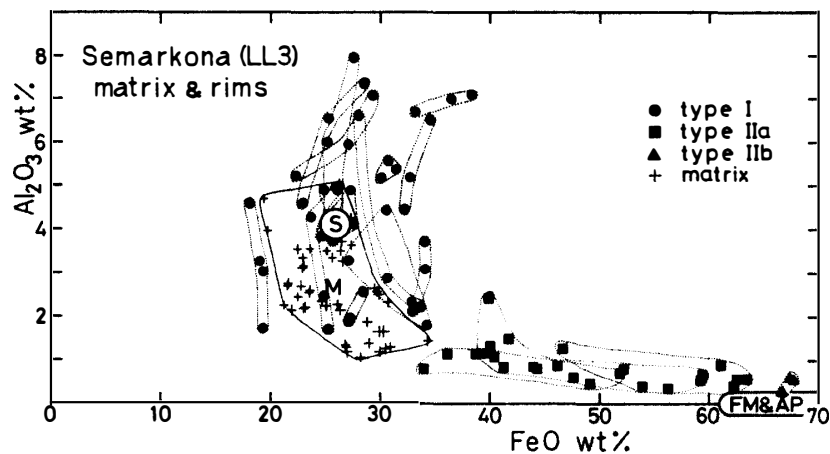


Fig. 7. Compositions of three types of rims and matrix in Semarkona, plotted on a FeO-Al<sub>2</sub>O<sub>3</sub> diagram. FeO includes Fe in Fe-Ni metals and sulfides. Dotted curves represent the compositional ranges of selected 18 rims (type I: Nos. 3, 4, 5, 7, 10, 14, 16, 19, 24, 29, 33, 39, 44, 63; type IIa: Nos. 1, 17, 21; type IIb: No. 54). Solid curve represents compositional range of opaque matrix. "M" denotes mean composition of opaque matrix (Table 2). "S" represents mean composition of Semarkona smectite (ALEXANDER *et al.*, 1989b), on the basis of total oxide wt % = 76.3% (= that of mean composition of opaque silicate matrix, this work). "FM&AP" denotes compositional range of 'fayalitic' material and its alteration products in Semarkona (ALEXANDER *et al.*, 1989b).



Semarkona.

#### 4.3. Correlation between chondrule composition and rim composition in Semarkona

Bulk compositions of 7 pairs of chondrule and its opaque rim in Semarkona are compared. Compositions of the selected chondrules are listed in Table 3. Chondrule compositions are in general much poorer in FeO than compositions of associated rims, as is normally found in type-3 chondrites (GROSSMAN and WASSON, 1983; SCOTT and TAYLOR, 1983). Concentrations of refractory lithophile elements such as Al, Ca and

Table 3. Compositions of seven chondrules, obtained by SEM-EDS analysis.

chondrule No.	1	2	3	7	17	19	21
$N^1$	4	4	2	5	4	4	5
SiO <sub>2</sub>	46.3	47.2	45.8	49.6	45.0	46.0	43.3
TiO <sub>2</sub>	.16	.22	.19	—	.13	.19	.18
Al <sub>2</sub> O <sub>3</sub>	4.54	5.46	2.42	2.22	3.85	3.07	5.21
Cr <sub>2</sub> O <sub>3</sub>	.65	.49	.65	.70	.66	.58	.44
FeO*	8.76	13.9	9.97	18.9	3.37	13.0	2.83
MnO	— <sup>2</sup>	.42	.50	.57	.24	.45	—
MgO	31.7	26.8	28.0	22.2	39.7	23.7	42.5
CaO	3.22	3.58	2.31	1.71	2.59	1.95	3.35
Na <sub>2</sub> O	.23	.29	.77	1.40	.75	1.96	.57
K <sub>2</sub> O	—	—	.20	.13	—	.18	—
P <sub>2</sub> O <sub>5</sub>	—	.12	.20	—	—	.16	—
Ni	.31	—	.21	.18	—	.16	—
S	—	—	.17	1.11	—	—	—
Total	95.9	98.5	91.4	98.7	96.3	91.4	98.4

<sup>1</sup>: number of analyses, <sup>2</sup>: not detected, \*: total Fe as FeO.

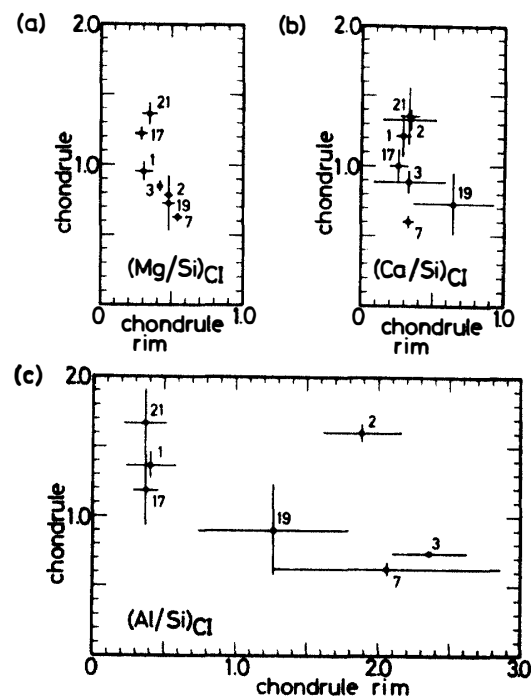


Fig. 8. Plot showing mean and  $\pm 1\sigma$  of (a) Mg/Si, (b) Ca/Si and (c) Al/Si ratios in seven chondrules and their rims of Semarkona (type I: Nos. 2, 3, 7, 19: type IIa: Nos. 1, 17, 21). The data are normalized to CI chondrite composition (ANDERS and EBHARA, 1982).

Mg normalized to Si in rims and chondrules are uncorrelated (Fig. 8). No significant correlations were observed.

## 5. Discussion

### 5.1. Effects of aqueous alteration to compositional heterogeneity of matrix and rims in Semarkona

As already suggested by many investigators, textures of chondrule rims in primitive type-3 ordinary chondrites indicate that coating materials would have adhered to chondrules prior to accretion (ALLEN *et al.*, 1980; KING and KING, 1981). Especially, layered structures of rims may be indicators for processes prior to parent body formation (METZLER and BISCHOFF, 1989). However, it is revealed that Semarkona would have suffered aqueous alteration. Therefore, we must evaluate effects of aqueous alteration on compositional heterogeneity of rims in Semarkona because some elements (Ca, Na and Fe) might have been redistributed in matrix and rims during aqueous alteration (ALEXANDER *et al.*, 1989b).

HUTCHISON *et al.* (1987) have demonstrated that fine-grained FeO-rich silicate materials in Semarkona are composed of smectite. ALEXANDER *et al.* (1989b) have also described the occurrence of 'fayalitic' material and its alteration products in matrix and rims in Semarkona. Table 4 lists representative analyses of silicate portions of opaque matrix and mean compositions of smectite and 'fayalitic' material and its alteration products (FMAP). Mean composition of type-IIb rims is also listed. Comparison of composition of Semarkona smectite with that of matrix indicates that the matrix is composed mostly of smectite. Composition of type IIb rims also resembles that of FMAP. In particular the SiO<sub>2</sub> and FeO contents are quite similar to those of FMAP, suggesting that type-IIb rims are mainly composed of FMAP. As already shown by MATSUNAMI (1984), compositional variations within the matrix and chondrule

Table 4. Comparison of mean compositions of opaque matrix, smectite and alteration products of 'fayalitic' material in Semarkona. Silicate recalculated to 100%.

	1	2	3	4	5	6	7
	opaque matrix	opaque matrix	opaque matrix	opaque matrix	Semarkona smectite	type IIb rims	APFM
SiO <sub>2</sub>	48.5	45.4	46.8	43.4	44.0	28.3	27.2
Al <sub>2</sub> O <sub>3</sub>	5.40	3.96	4.1	3.48	5.4	.57	0.0
Cr <sub>2</sub> O <sub>3</sub>	.31	.35	.4	.43		.16	
FeO	25.6	31.4	29.2	33.8	34.1	64.4	66.7
MnO	.18	.25	.3	.28		.17	
MgO	14.8	13.9	14.4	14.6	8.9	5.57	3.7
CaO	1.30	.88	.9	.87	.1	.42	.2
Na <sub>2</sub> O	2.80	3.06	3.2	2.64	6.1	.40	1.1
K <sub>2</sub> O	.78	.73	.8	.51	.9		.3

1: obtained by WDA, HUSS *et al.* (1981), 2: obtained by WDA, HUTCHISON *et al.* (1987), 3: obtained by WDA, ALEXANDER *et al.* (1989a), 4: obtained by SEM-EDS, this work, 5: Semarkona smectite, analyzed by ATEM (ALEXANDER *et al.*, 1989b), 6: mean composition of type IIb opaque rims (this work), obtained by SEM-EDS, 7: alteration products of 'fayalitic' material (APFM), obtained by ATEM (ALEXANDER *et al.*, 1989b).

rims can be explained by the variable mixing ratios of the Al-depleted component and the Al-enriched component. Semarkona smectite and FMAP are also plotted in Fig. 7. Smectite is plotted in the center of the field of compositions of matrix and type-I rims. This suggests that type-IIa rims are composed mostly of smectite having wider variabilities of FeO and Al<sub>2</sub>O<sub>3</sub> contents. From this figure, it is suggested that type-IIa rims are composed mostly of mixtures of variable mixing ratios of smectite and FMAP. The absence of the inverse correlation of FeO with Al<sub>2</sub>O<sub>3</sub> in type-I rims may be attributable to redistribution of Fe during aqueous alteration to mostly destroy original compositional features of matrix materials. It is reasonable that types-IIa and IIb rims may relatively preserve original chemical characteristics prior to alteration compared to type-I rims. This is because they show the inverse correlation of FeO with Al<sub>2</sub>O<sub>3</sub> and because of the incomplete conversion of 'fayalitic' material to alteration products in types-IIa and IIb rims (ALEXANDER *et al.*, 1989b). Types-IIa and IIb rims may have suffered weaker aqueous alteration than that of type-I rims and matrix. Another possibility is that 'fayalitic' material may be less easily affected by aqueous alteration compared to original materials of smectite.

### 5.2. Origin of compositional heterogeneity of matrix and rims in Semarkona

GROSSMAN and WASSON (1983) have found that chondrules of Semarkona show refractory element trends similar to those defined by the bulk compositions of ordinary and enstatite chondrites (KERRIDGE, 1979; LARIMER, 1979). They suggested that there are two major chondrule precursor components: a refractory, olivine-rich, FeO-free one and a non-refractory, SiO<sub>2</sub>-, FeO-rich one. They have considered that Semarkona chondrules would be essentially mixtures of these two components. MATSUNAMI (1984) suggested that the compositional trends of the Semarkona chondrules may be explained by the variable mixing ratios of "COMPONENT X" and the refractory component. The COMPONENT X is located on the lower extension of the "chondrule mixing line" (GROSSMAN and WASSON, 1983). COMPONENT X is SiO<sub>2</sub>-, FeO-rich, enriched in volatiles (Na, K) and poor in refractory lithophile elements (Mg, Al and Ca), suggesting that formation of COMPONENT X is important to understand refractory lithophile fractionation of chondritic meteorites (MATSUNAMI, 1984). In this study it is shown that types-IIa and IIb rims in Semarkona are highly enriched in the COMPONENT X (Fig. 6). Since types-IIa and IIb rims may contain 'fayalitic' material and its alteration products (FMAP), it is suggested that FMAP may correspond to one of the non-refractory components of Semarkona chondrules and major constituent of COMPONENT X of MATSUNAMI (1984).

The non-refractory nature of COMPONENT X and 'fayalitic' material in Semarkona may be a result of fractional condensation of forsterite from the cooling nebular gas, although ALEXANDER *et al.* (1989a) considered that the reaction of FeO with silica derived from chondrule mesostases is responsible for the formation of fayalitic olivine. NAGAHARA (1984) and NAGAHARA and KUSHIRO (1987) suggested that the silica saturation in the nebular gas due to forsterite fractionation is necessary to formation of Fe-rich olivine within the matrix. Micron-sized silica-rich objects in matrix and rims of Chainpur and Sharps chondrites have been described by MATSUNAMI *et al.* (1990). These silica-rich objects have thin rinds of Fe-rich olivine, indicating that they would

have played important roles in the formation of Fe-rich olivine in the matrix of UOCs, especially 'fayalitic' material in Semarkona. They may be direct evidences for suggestions of NAGAHARA (1984) and NAGAHARA and KUSHIRO (1987). COMPONENT X may be formed through intensive fractional condensation of refractory early condensates and forsterite. It is suggested that COMPONENT X is the final end-product of the fractional condensation processes in the cooling nebular gas.

In conclusion, the compositional heterogeneity of matrix and rims in Semarkona can be explained by variable mixing ratios of 'fayalitic' material and its alteration products (FMAP) and smectite widely varying in the FeO and Al<sub>2</sub>O<sub>3</sub> contents. Types-IIa and IIb rims contain abundant FMAP. The non-refractory component of Semarkona chondrules may be composed mainly of FMAP. The 'fayalitic' material might have formed through fractional condensation processes in the cooling solar nebula.

#### Acknowledgments

We thank Prof. I. KUSHIRO and Dr. H. NAGAHARA of the University of Tokyo for valuable suggestions, constructive discussions and encouragement during this work. The helpful reviews of two anonymous referees are also acknowledged. We also thank Drs. K. YOKOYAMA and Y. SAITO of the National Science Museum for permitting S. M. to use the SEM-EDS system. We are grateful to Dr. B. MASON of the Smithsonian Institution for providing Semarkona sample.

#### References

- ALEXANDER, C. M. O. (1987): The rims and matrices of unequilibrated ordinary chondrites; Origin, metamorphism and alteration. Ph. D Thesis, University of Essex.
- ALEXANDER, C. M. O., HUTCHISON, R. and BARBER, D. J. (1989a): Origin of chondrule rims and interchondrule matrices in unequilibrated ordinary chondrites. *Earth Planet. Sci. Lett.*, **95**, 187–207.
- ALEXANDER, C. M. O., BARBER, D. J. and HUTCHISON, R. (1989b): The microstructure of Semarkona and Bishunpur. *Geochim. Cosmochim. Acta*, **53**, 3045–3057.
- ALLEN, J. S., NOZETTE, S. and WILKENING, L. L. (1980): A study of chondrule rims and chondrule irradiation records in unequilibrated ordinary chondrites. *Geochim. Cosmochim. Acta*, **44**, 1161–1175.
- ANDERS, E. and EBIHARA, M. (1982): Solar-system abundances of the elements. *Geochim. Cosmochim. Acta*, **46**, 2363–2380.
- ASHWORTH, J. R. (1977): Matrix textures in unequilibrated ordinary chondrites. *Earth Planet. Sci. Lett.*, **35**, 25–34.
- DUNHAM, A. C. and WILKINSON, F. C. F. (1978): Accuracy, precision and detection limits of energy-dispersive electron-microprobe analyses of silicates. *X-Ray Spectrom.*, **9**, 8–12.
- GROSSMAN, J. N. and WASSON, J. T. (1983): Refractory precursor components of Semarkona chondrules and the fractionation of refractory elements among chondrites. *Geochim. Cosmochim. Acta*, **47**, 759–771.
- HUSS, G. R., KEIL, K. and TAYLOR, G. J. (1981): The matrices of unequilibrated ordinary chondrites; Implications for the origin and history of chondrites. *Geochim. Cosmochim. Acta*, **45**, 33–51.
- HUTCHISON, R., ALEXANDER, C. M. O. and BARBER, D. J. (1987): The Semarkona meteorite; First

- recorded occurrence of smectite in an ordinary chondrite, and its implications. *Geochim. Cosmochim. Acta*, **51**, 1875–1882.
- IKEDA, Y. (1980): Petrology of Allan Hills-764 chondrite (LL3). *Mem. Natl Inst. Polar Res., Spec. Issue*, **17**, 50–82.
- IKEDA, Y., KIMURA, M., MORI, H. and TAKEDA, H. (1981): Chemical compositions of matrices of unequilibrated ordinary chondrites. *Mem. Natl Inst. Polar Res., Spec. Issue*, **20**, 124–144.
- JAROSEWICH, E. (1966): Chemical analysis of ten stony meteorites. *Geochim. Cosmochim. Acta*, **30**, 1261–1266.
- KERRIDGE, J. F. (1979): Fractionation of refractory lithophile elements among chondritic meteorites. *Proc. Lunar Planet. Sci. Conf.*, 10th, 989–996.
- KING, T. V. V. and KING, E. A. (1981): Accretionary dark rims in unequilibrated chondrites. *Icarus*, **48**, 460–472.
- LARIMER, J. W. (1979): The condensation and fractionation of refractory lithophile elements. *Icarus*, **40**, 446–454.
- MATSUNAMI, S. (1984): The chemical compositions and textures of matrices and chondrule rims of eight unequilibrated ordinary chondrites; A preliminary report. *Mem. Natl Inst. Polar Res., Spec. Issue*, **35**, 126–148.
- MATSUNAMI, S., NISHIMURA, H. and TAKESHI, H. (1990): The chemical compositions and textures of matrices and chondrule rims of unequilibrated ordinary chondrites—II; Their constituents and the implications for the formation of matrix olivine. *Proc. NIPR Symp. Antarct. Meteorites*, **3**, 147–180.
- METZLER, K. and BISCHOFF, A. (1989): Accretionary dust mantles in CM chondrites as indicators for processes prior to parent body formation. *Lunar and Planetary Science XX*. Houston, Lunar Planet. Inst., 689–690.
- MORI, T. and KANEHIRA, K. (1984): X-ray energy spectrometry for electron probe analysis. *J. Geol. Soc. Jpn.*, **90**, 271–285.
- NAGAHARA, H. (1984): Matrices of type 3 ordinary chondrites—Primitive nebular records. *Geochim. Cosmochim. Acta*, **48**, 2581–2595.
- NAGAHARA, H. and KUSHIRO, I. (1987): Origin of iron-rich olivine in the matrices of type 3 ordinary chondrites; An experimental study. *Earth Planet. Sci. Lett.*, **85**, 537–547.
- RAMBALDI, E. R. and WASSON, J. T. (1981): Metal and associated phases in Bishunpur, a highly unequilibrated ordinary chondrite. *Geochim. Cosmochim. Acta*, **45**, 1001–1015.
- RAMBALDI, E. R. and WASSON, J. T. (1984): Metal and associated phases in Krymka and Chainpur; Nebular formational processes. *Geochim. Cosmochim. Acta*, **48**, 1885–1897.
- SCOTT, E. R. D. and TAYLOR, G. (1983): Chondrules and other components in C, O, and E chondrites; Similarities in their properties and origins. *Proc. Lunar Planet. Sci. Conf.*, 14th, Part 1, B275–B286 (*J. Geophys. Res.*, **88**, Suppl.).
- SCOTT, E. R. D., RUBIN, A. E., TAYLOR, G. J. and KEIL, K. (1984): Matrix material in type 3 chondrites—Occurrence, heterogeneity and relationship with chondrules. *Geochim. Cosmochim. Acta*, **48**, 1741–1757.
- SCOTT, E. R. D., BARBER, D. J., ALEXANDER, C. M. O., HUTCHISON, R. and PECK, J. A. (1988): Primitive material surviving in chondrites; Matrix. *Meteorites and the Early Solar System*, ed. by J. F. KERRIDGE and M. S. MATTHEWS. Tucson, Univ. Arizona Press, 718–745.
- SEARS, D. W., GROSSMAN, J. N., MELCHER, C. L., ROSS, L. M. and MILLS, A. A. (1980): Measuring metamorphic history of unequilibrated ordinary chondrites. *Nature*, **287**, 791–795.
- STATHAM, P. J. (1980): X-ray microanalysis with Si (Li) detectors. *J. Microsc.*, **123**, 1–23.

*(Received September 19, 1989; Revised manuscript received April 9, 1990)*