Opaque Minerals in LL3.0-6 Chondrites I: Mineralogy of Ti-oxides and $^{53}$Mn-$^{53}$Cr Systematics of Ilmenite

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Abstract We conducted a systematic study of oxide minerals in LL3.0-6 chondrites, and found ilmenite, rutile, perovskite and an unknown Al-Ti-Zr-oxide. Ilmenite is low in abundance, but is present in the chondrules and matrix of all the samples that we studied. The MnO content of ilmenite in LL3.0-3.3 is lower than that in LL3.5-6. The low concentration of MnO in the former is due to crystallization from chondrules melts at high temperatures. On the other hand, ilmenite composition in LL3.5-6 reflects thermal metamorphism. Therefore, ilmenite is indicative of petrologic type. We also made the first measurements of the $^{53}$Mn-$^{53}$Cr systematics of ilmenite in ordinary chondrites. The age for ilmenite in Y790256 (LL6) is determined to be about 2 Ma older than angrites. This may represent the metamorphic age of the LL chondrites.

Key words: chondrite, ilmenite, Mn-Cr isotopes

1 Introduction

Ordinary chondrites consist mainly of silicate minerals, Fe-Ni metal and troilite. These chondrites also contain minor amounts of oxide minerals, such as spinel group minerals and ilmenite. In comparison with other minerals in ordinary chondrites, these oxides have not been intensively studied. However, they are important because their mineral chemistry reflects chemical groups (e.g. Bunch et al., 1967). In addition, we expected that these oxide minerals would be more sensitive to metamorphic conditions than the silicates because of their relatively high diffusion rates.

Therefore, we conducted a systematic study of oxide minerals in LL chondrites. Here we report the results of our petrologic, mineralogic and Mn-Cr isotopic study of Ti-oxides in LL3.0-6 chondrites. There are few previous studies of Ti-oxides in ordinary chondrites (e.g. Snetsinger and Keil, 1969; Krot et al., 1993). We found four kinds of Ti-oxide minerals. Their occurrences vary widely, and we show that ilmenite is an especially sensitive indicator of petrologic subtype. Our preliminary results were reported in Kimura et al. (2003).

Mn-Cr systematics, the decay of $^{53}$Mn to $^{53}$Cr ($t_{1/2} = 3.7$ Ma), has been recently utilized for dating carbonates (Endrëß et al., 1996), chondrules (Nyquist et al., 2001) and olivine (Hutchcheon et al., 1998; Sugiura, 2003; Tomiyama and Misawa, 2004) in chondrites. We made the first Mn-Cr isotopic measurements of ilmenite in ordinary chondrites. Our goal is to decipher the chronological evolution of the LL chondrite parent body.

2 Samples and Experimental Methods

We investigated polished thin sections of ten LL chondrites selected from the meteorite collections of the National Institute of Polar Research and the American Museum of Natural History, and Boxian (LL3.9) from the Guangzhou Institute of Geochemistry.

The back-scattered electron (BSE) imaging and mineral analyses were obtained using the JEOL 733 electron-probe microanalyzer (EPMA) at Ibaraki University. We conducted quantitative mineral analyses at 15 kV and a sample current of 30 nA, and corrected the X-ray overlaps of K$\beta$ on K$\alpha$ lines of some successive elements with a deconvolution program. The Bence-Albee matrix correction methods were used. We also measured the bulk compositions of some ilmenite-bearing chondrules with broad beam EPMA, and corrected the data using the method of Ikeda (1980).

The Cr isotopic compositions and Mn/Cr ratios were measured by secondary ion mass spectrometry (SIMS) using the Cameca-6f at University of Tokyo. The primary
O^− beam was ~30 micrometer in diameter and the primary ion current was 2 nA for ALH77304 and Yamato 790256. A smaller beam was used for the analysis of Wells because of the small size of the ilmenite. We measured 53Cr and 54Cr with an EM whereas Mn was measured with a Faraday cup. Measurement time durations of these ions per cycle were 1 s, 4 s and 0.5 s, respectively, and 100–140 cycles of measurements were made.

3 Occurrence of Ti-oxides

3.1 Petrography

Table 1 is a list of the eleven samples that we studied, two LL3.0, six LL3.1-3.9 and three LL4-6 chondrites. The shock degrees of these samples are S3 or less. All of these samples contain ilmenite. We also found rutile, perovskite and an unknown Al-Ti-Zr-oxide in the type 3.0-3.3 chondrites.

3.2 Ilmenite

Ilmenite is rarely reported in ordinary chondrites (e.g. Snetsinger and Keil, 1969). However, we found ilmenite in all of the samples studied here, and predict that ilmenite is present in all LL chondrites, though it is low in abundance. A few grains are encountered in each section.

Figure 1 shows the textural setting of ilmenite, which usually occurs in subhedral to anhedral form in chondrules, associated with silicate phenocrysts, spinel group minerals and Fe-Ni metal (Fig. 1a). Ilmenite also occurs as isolated grains in the matrix (Fig. 1b). Ilmenite grains are 5–40 μm in size, in spite of their textural setting and the petrologic type of chondrite in which they are found. However, ALH77304 (LL3.7) contains a coarse-grained, isolated ilmenite grain, 200 × 150 μm in size (Fig. 1b).

Some ilmenite grains contain a small amount of chromite inclusions (Fig. 1b), which generally occur in close association with rutile (Fig. 1c). However, the ilmenite studied here does not contain rutile lamella, like that reported in lunar rocks (e.g. El Goreisy, 1976) and mesosiderite (Kimura et al., 1991).

3.3 Rutile

Rutile is a fairly rare mineral in chondrites (e.g. Buseck and Keil, 1966). However, we found that Semarkona (LL3.0), Y74660 (LL3.0), Krymka (LL3.1) and Wells (LL3.3) contain rutile, which always shows the anhedral form, and is tiny, less than 5 μm in size. The rutile always occurs in close association with ilmenite, and the rutile-ilmenite assemblage appears to be a breakdown texture (Fig. 1c).

3.4 Perovskite

Y790448 (LL3.2) contains a large chordule, 2.5 × 3 mm in size (Fig. 1d). This chordule shows barred texture in the center, and is porphyritic on the margin. It consists mainly of olivine (Fo76 in average), with low-Ca pyroxene (En64Fs36Wo12), high-Ca pyroxene (En38Fs62Wo22) and plagioclase (An68Ab12). Minor spinel and ilmenite are also present.

This chordule also contains five grains of perovskite (Fig. 1e). They are fine-grained, 3–9 μm in size. Perovskite is reported from refractory inclusions in ordinary chondrites (Bischoff and Keil, 1984; Kimura et al., 2002). However, this is the first discovery of perovskite in chondrule in an ordinary chondrite.

3.5 Al-Ti-Zr-oxide

In one chondrule in Semarkona (LL3.0), we found an unknown Al-Ti-Zr-oxide, 8 μm in size, among the low-Ca pyroxene phenocrysts (Fig. 1f). This grain seems to be homogeneous and does not contain any inclusions or lamella.

4 Mineral Compositions of the Ti-oxides

4.1 Ilmenite

Table 2 shows the selected analytical data of the oxide minerals in LL chondrites. In spite of the variety of textural
Fig. 1 (a) Backscattered electron (BSE) image of a porphyritic chondrule in Semarkona (LL3.0), consisting of olivine (Oli), high-Ca pyroxene (Hpx) and glass mesostasis (Gla). An ilmenite (Ilm) grain is enclosed in olivine phenocrysts. Width 170 μm; (b) BSE image of a coarse-grained isolated ilmenite, containing chromite inclusions (Chr) in ALH77304 (LL3.7). Width 210 μm; (c) BSE image of an intimate intergrowth of ilmenite and rutile (Rut) in a porphyritic chondrule in Wells (LL3.3). Width 35 μm; (d) BSE image of a large perovskite-bearing chondrule in Y790448 (LL3.2), 2.5 x 3 mm in size, showing barred texture in the center and is porphyritic on the margin. Although this chondrule consists mainly of olivine, Mg-Al-rich spinel is included (Spi); (e) A part of Fig. 1d. A perovskite (Per) grain is encountered with olivine, plagioclase (Pla) and spinel. Width 50 μm; (f) BSE image of an unknown Al-Ti-Zr oxide grain enclosed in low-Ca pyroxene (Lpx) in a porphyritic chondrule in Semarkona. Width 50 μm.
settings, the composition of ilmenite is generally not correlated with its occurrence within a single chondrite. However, the MnO content of the ilmenite depends on petrologic type; ilmenites in LL3.0-3.3, 3.5-3.9 and 4-6 chondrites contain 0.15%–0.57%, 0.78%–1.47% and 0.81%–2.63% MnO, respectively. The MnO contents of ilmenites in LL3.0-3.3 are evidently lower than those in LL3.5-6 (Fig. 2). Our data for ilmenite in LL4-6 chondrites are consistent with those (1.1%–3.8% MnO) of Snetsinger and Keil (1969).

The MgO content of the ilmenite varies widely: 0.97%–14.6% in LL3.0-3.3, 1.78%–3.09% in LL3.5-3.9 and 1.63%–2.70% in LL4-6 chondrites. However, ilmenite in some of the low petrologic type LL chondrites, Semarkona (LL3.0), Krymka (LL3.1) and Wells (LL3.3), has the highest MgO content (up to 14.6%). The MgO contents of the ilmenites in LL3.5-6 are relatively low and uniform, which agrees with previous work (1.6%–2.5% MgO by Snetsinger and Keil, 1969).

The contents of the other elements are low: <0.3% Al₂O₃, <0.4% Cr₂O₃ and <0.3% V₂O₅ in all the samples. Only some ilmenite grains in Semarkona chondrules contain 1.1%–1.4% Cr₂O₃, and they do not contain chromite lamella or inclusions that are resolvable at the scale of the BSE imaging. We did not detect Zr and Nb in the ilmenites we studied.

### 4.2 Rutile

Because all of the rutile grains we studied are tiny and are closely associated with ilmenite, we could not obtain good analytical data for them. However, high apparent TiO₂ contents (>92%) suggest that these grains are TiO₂. TiO₂ occurs as three polymorphs, rutile, anatase and brookite. Kimura et al. (2002) identified rutile in an H3 chondrite by the laser micro Raman spectroscopy. Although we did not use Raman spectroscopy for these tiny grains in the LL3 chondrites, we refer to them as rutile.

Although Nb-bearing rutile was reported in irons (El Goresy, 1971) and winonaites (Kimura et al., 1992), the rutile in the LL3 chondrites does not contain detectable Nb.

### 4.3 Perovskite

Perovskite in Y790448 is small in size, and the total of our (weight percent) microprobe analyses of the perovskite is about 96% (Table 2).
Nevertheless, the chemical formula is Ca_{0.85}Ti_{0.05}O_3 on average, and the grains are nearly stoichiometric CaTiO_3 in composition.

4.4 Ti-Al-Zr-oxide

An Al-Ti-Zr-oxide in Semarkona chondrule contains 3.2%–3.6% SiO_2, 48.1%–49.0% TiO_2, 35.1%–35.4% Al_2O_3, 0.2%–0.3% FeO, 0.2%–0.3% MnO, 3.0%–3.1% MgO and 8.0%–8.2% ZrO_2. The content of CaO is lower than 0.1%. Other elements we measured, Cr, V, Zn, Na, Ni, Nb, Ga, Y, Sc, Ge, Nd, Sr and Ba, were not detected. The chemical formula is (Ti_{1.8}Mg_{0.2}Zr_{0.2})_2(Al_{1.5}Si_{0.1})_2O_9, assuming that all of the Ti is 4+, or (Al_{1.43}Si_{0.08}Ti_{1.32}Mg_{0.13})_2(Fe_{0.10}Zr_{0.45})_1O_9 in case that Ti is partly 3+.

Such a phase has never been reported from any ordinary chondrite. However, ALH85085 (CH) contains an unknown Al-Ti-Zr-phase (Weisberg et al., 1988), although its composition was not reported and it is not yet known if the mineral observed here is similar to the phase in ALH85085.

5 Chondrule Compositions

We measured the bulk compositions of some ilmenite-bearing chondrules (Table 3). Ilmenite-bearing chondrules do not seem to be enriched in TiO_2 (0.1%–0.3%), in comparison with other chondrules (0.1%–0.4% after Kimura et al., 2003). These chondrules have a wide range of FeO and MgO contents, 8.1%–18.9% and 24.6%–38.4%, respectively. Table 3 also shows the average composition of phenocrysts in these chondrules, ranging from Fa_{11} to Fa_{34}. Therefore, all these ilmenite-bearing chondrules are classified as Type II.

A perovskite-bearing chondrule in Y790448 contains 0.1% TiO_2 and 3.1% Al_2O_3, which are within the ranges of the other chondrules, respectively (Table 3).

6 Mn-Cr isotope data

Table 4 gives the results of Mn-Cr systematics. The Mn/Cr relative sensitivity factor [RSF = (Mn/^{54}Cr)/(Mn/Cr)], which is needed for estimating Mn/Cr ratios, is not established for ilmenite. An ilmenite grain in ALH77304 contains chromite inclusions (Fig.1b). Since the Cr concentrations in the ilmenite were high near the chromite grains, SIMS measurements were made on spots far away from the chromites, where Mn/Cr atomic ratios were 30–56. For these spots the $^{55}$Mn/$^{54}$Cr ion ratio was 31.97±3.23. Therefore, the RSF is estimated to be ~0.6. An ilmenite in Y790256 contains a very small amount of Cr and the Mn/Cr atomic ratio was ~1.54. The $^{55}$Mn/$^{54}$Cr ion ratio was 220. Hence the RSF is estimated to be ~1.2. In the case of Wells, ilmenite grains were small, and a large fraction of the Cr signal of SIMS came from the surrounding minerals. Therefore, the RSF cannot be estimated. Until better data of RSF for ilmenite are obtained, we assume that the RSF is 1.

Figure 3 shows all of our results, including those for the terrestrial ilmenite. It is assumed that the initial $^{55}$Cr/$^{54}$Cr ratio for chondrules is equal to the terrestrial Cr ratio. Therefore, the terrestrial ilmenite data are plotted on the y-axis. All the Cr isotope compositions for the chondritic ilmenite are normal within 2 sigma errors. Note the error shown in the figure is 1 sigma.
ilmenite are normal within 2 sigma errors.

7 Discussion

7.1 Formation of ilmenite

The chemical composition of ilmenite depends on petrologic type; ilmenite in LL3.0-3.3 has lower MnO contents than that in LL3.5-6. The ilmenite mainly occurs in chondrules in LL3.0-3.3. Haggerty (1976) indicated that ilmenite crystallized at high temperatures contains lower MnO contents. It is, therefore, probable that low-MnO ilmenites in LL3.0-3.3 primarily crystallized from chondrule melts at high temperatures, although we cannot quantitatively determine the temperatures in the absence of a geothermometer. Some isolated ilmenite grains in LL3.0-3.3 are also poor in MnO, like those in chondrules in these chondrites. The isolated ilmenite may have been derived from chondrule breakage.

Ilmenite in LL3.0-3.3 shows a wide range of Mg contents. Figure 4 shows the composition of ilmenite and host chondrule. The Mg/Fe ratio of the ilmenite seems to be weakly correlated with the Mg/Fe ratio of the chondrule. Ilmenite in these chondrules preserves its primordial composition, which in part is due to the chondrule bulk chemistry. At any rate, ilmenite is encountered only in type II chondrules in LL3.0-3.3 chondrites studied here, which may suggest that ilmenite crystallized only in such FeO-rich chondrules.

On the other hand, ilmenite grains in LL3.5-6 have uniform Mg/Fe ratios. This is due to the secondary diffusion of Fe and Mg during parent body metamorphism, and the ilmenite compositions in these LL chondrites are distinct from those in equilibrated H and L chondrites (Fig.

![Plot of atomic Mg/Fe ratio of ilmenite versus host chondrule in LL3.0-3.3 chondrites. It is noted that ilmenite composition is weakly correlated with host chondrule composition.](image-url)

Table 3. The bulk compositions of ilmenite and petrocks-bearing chondrules, and the average compositions of pheno-cryst in LL3.0-3.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chondrule</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>FeO/FeO+MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Krymka</td>
<td>T1</td>
<td>18.9</td>
<td>0.53</td>
<td>2.08</td>
<td>0.53</td>
<td>40.52</td>
<td>0.07</td>
<td>0.28</td>
<td>0.07</td>
</tr>
<tr>
<td>Krymka</td>
<td>T3</td>
<td>18.9</td>
<td>0.53</td>
<td>2.08</td>
<td>0.53</td>
<td>40.52</td>
<td>0.07</td>
<td>0.28</td>
<td>0.07</td>
</tr>
<tr>
<td>Semarkona</td>
<td>T1</td>
<td>18.9</td>
<td>0.53</td>
<td>2.08</td>
<td>0.53</td>
<td>40.52</td>
<td>0.07</td>
<td>0.28</td>
<td>0.07</td>
</tr>
<tr>
<td>Wells</td>
<td>T7</td>
<td>18.9</td>
<td>0.53</td>
<td>2.08</td>
<td>0.53</td>
<td>40.52</td>
<td>0.07</td>
<td>0.28</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Note: * T3 = ilmenite, Per = petrocks; b.d. below detection limits (30), 0.06 for K2O and TiO2, 0.10 for Na2O, and 0.14 for CaO, MgO, SiO2, and FeO.

Fig. 4. Plot of atomic Mg/Fe ratio of ilmenite versus host chondrule in LL3.0-3.3 chondrites. It is noted that ilmenite composition is weakly correlated with host chondrule composition.
Ilmenite in LL3.5-6 chondrites also has uniform MnO contents, which are higher than those in LL3.0-3.3. In LL3.5-6 chondrites, MnO may have been partitioned into ilmenite from the surrounding silicate phases during metamorphism.

We conclude that ilmenite composition can be used to distinguish petrologic type, especially lower subtypes, in ordinary chondrites. Ilmenite, together with spinel group minerals (e.g., Kimura et al., 2003), is useful in identifying the least equilibrated ordinary chondrites.

Only ilmenite in Semarkona (LL3.0) contains ≈1% Cr₂O₃ as mentioned above. Some ilmenite that crystallized at high temperatures may contain small amounts of Cr₂O₃, although the solubility limit of Cr₂O₃ of ilmenite has not yet been determined experimentally. It is probable that chromite later exsolved from the Cr-bearing ilmenite during metamorphism at lower temperatures. Chromite inclusions in an ilmenite grain in ALH77304 (LL3.7) may be explained by such secondary processes.

### Table 4 Mn-Cr systematics in ilmenite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Occurrence</th>
<th>δ⁰⁶Cr (permil)</th>
<th>Error (1σ permil)</th>
<th>⁵⁵Mn/⁵²Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wells</td>
<td>Chondrule</td>
<td>0.1</td>
<td>4.1</td>
<td>4.8</td>
</tr>
<tr>
<td>ALH77034-1</td>
<td>Isolated mineral</td>
<td>0.2</td>
<td>1.8</td>
<td>33.2</td>
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<tr>
<td>ALH77304-2</td>
<td>Isolated mineral</td>
<td>-2.2</td>
<td>1.5</td>
<td>34.4</td>
</tr>
<tr>
<td>ALH77304-3</td>
<td>Isolated mineral</td>
<td>-1</td>
<td>1.5</td>
<td>28.3</td>
</tr>
<tr>
<td>Yamato 790256-1</td>
<td>Isolated mineral</td>
<td>2.7</td>
<td>2.1</td>
<td>142</td>
</tr>
<tr>
<td>Yamato 790256-2</td>
<td>Isolated mineral</td>
<td>3.2</td>
<td>3.3</td>
<td>220</td>
</tr>
</tbody>
</table>

7.4 Mn-Cr systematics

The initial ⁵⁵Mn/⁵²Mn ratio for Y790256 (LL6) was estimated to be (1.9 ± 2.5 (2σ))x10⁻⁶, where the error does not include the uncertainty due to the not-well-known RSF. The initial ratio of ~1.9x10⁻⁶ suggests that Y790256 may be about 2 Ma older than the Angra dos Reis (⁵⁵Mn/⁵²Mn = 1.25x10⁻⁶ after Lugmair and Shukolyukov, 1998), although the attached error is quite large. The time span between CAI formation and the Angra dos Reis formation is 13 Ma. (Lugmair and Shukolyukov, 2001). The time span between CAI formation and chondrule formation is about 2 Ma according to Al-Mg studies (Kita et al., 2000). From these age data, we can say that the Mn-Cr age of the ilmenite in Y790256 is significantly younger than that of chondrule formation and hence probably records Cr isotopic closure after the thermal metamorphism in the parent body. The other two chondrites do not provide meaningful age data because of the large errors.

At any rate, Cr isotopic compositions of these ilmenites, especially Y790256, are nearly normal, suggesting that the metamorphic events of these chondrites ended after the nearly complete decay of ⁵⁵Mn. Nevertheless, we predict that ilmenite can give significant age data, if we find coarse-grained ilmenite in very primitive chondrites.

### 8 Summary

1. Although ilmenite is rarely reported from ordinary chondrites, our systematic study shows that ilmenite is always present, at least in LL chondrites. In addition, we also found rutile, perovskite and an unknown Al-Ti-Zr oxide in the LL3.0-3.3 chondrites.

2. Ilmenite in LL3.0-3.3 has lower MnO contents than that in LL3.5-6. The low concentrations of MnO in LL3.0-3.3 are due to crystallization in chondrules at high
temperatures. On the other hand, ilmenite composition in LL3.5-6 reflects the metamorphism. The chemistry of ilmenite is a criterion for distinguishing petrologic type in ordinary chondrites.

(3) In chondrules of LL3.0-3.3 chondrites, ilmenite seems to be encountered only in FeO-rich chondrules, type II. The Mg/Fe ratio of ilmenite weakly depends on the bulk composition of the host chondrule in LL3.0-3.3.

(4) We measured Mn-Cr systematics of ilmenite for the first time. The data obtained here are indicative of a metamorphic age of 2 Ma earlier than the formation of angrites.

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