Petrography and oxygen isotopic compositions in refractory inclusions from CO chondrites

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Abstract—Fine-grained Ca-Al-rich inclusions (FGIs) in Yamato-81020 (CO3.0) and Kainsaz (CO3.1–CO3.2) chondrites have been studied by secondary ion mass spectrometry. The FGIs from Yamato-81020 consist of aggregates of hibonite, spinel, melilitite, anorthite, diopside and olivine grains with no petrographic evidence of alteration. In contrast, the FGIs from Kainsaz commonly contain alteration products such as nepheline. From replacement textures and chemical compositions of altered and unaltered FGIs, we conclude that the alteration products formed by decomposition of melilitite and anorthite. All phases in the Yamato-81020 FGIs are enriched in \( ^{18}O \), with \( \delta^{18}O = \sim -40\%e \) except for one FGI that experienced melting. Oxygen isotopic compositions of melilitite, anorthite, some spinel and diopside in Kainsaz FGIs changed from \( \delta^{18}O = \sim -40\%e \) toward 0\%e by aqueous alteration. Alteration products in FGIs are depleted in \( ^{16}O \) relative to primary phases, with \( ^{17}O = \sim 0\%e \). These results show that FGIs in CO chondrites commonly had \( ^{18}O \)-rich compositions in the solar nebula. The original \( ^{16}O \)-rich FGIs were modified to \( ^{16}O \)-poor compositions during aqueous alteration in the parent body.

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1. INTRODUCTION

Refractory inclusions have been classified as Ca-Al-rich inclusions (CAIs) based on their petrographic and chemical characteristics (e.g., MacPherson et al., 1988). Previous O-isotope studies of coarse-grained CAIs (CGIs) from various types of carbonaceous chondrites have shown that oxygen isotopic compositions of CGI minerals are generally distributed along the carbonaceous chondrite anhydrous minerals (CCAM) line on a three-O isotope diagram (e.g., Clayton, 1993; Clayton and Mayeda, 1999). The O-isotopic distributions indicate that the spinel and Al-Ti-pyroxene (fassaite) in CGIs usually have \( \delta^{18}O = \sim -40\%e \), whereas melilitite and anorthite in CGIs mostly have \( \delta^{18}O = \sim 0\%e \). A recent study of the O-isotope microdistribution within and among minerals (Yurimoto et al., 1998) shows that multiple heating events in different O isotopic environments are essential to CGI formation.

Previous petrographic studies of chondrites revealed that various type of chondrites (ordinary chondrite [OC], enstatite chondrite [EC] and carbonaceous chondrite [CC]) usually contain FGIs in different abundances (e.g., Grossman et al., 1988). Previous oxygen isotopic studies of FGIs from different petrologic classes of chondrite (OC, EC, CI, CV, CM, CO, CH, CK, CR) usually reported \( ^{18}O \)-rich characteristics of spinel and diopside in FGIs (e.g., Huss et al., 1995; McKeegan et al., 1998; Hiyagon and Hashimoto, 1999; Sahijpal et al., 1999; Sakai and Yurimoto, 1999; Guan et al., 2000; Itoh et al., 2000; Fagan et al., 2001; Krot et al., 2001; Wasson et al., 2001; Yurimoto et al., 2001; Krot et al., 2002). However, the origin of the \( ^{16}O \)-poor nature of FGI minerals remained unclear because of the strong alteration effects for such small grains of FGIs compared with those of CGIs (e.g., Fagan et al., 2002), i.e., it remained unknown whether \( ^{16}O \)-poor FGI minerals were originally \( ^{16}O \)-rich or \( ^{16}O \)-poor.

CO chondrites contain many FGIs with sizes ranging from a few tens to hundreds of micrometers across (Tomeoka et al., 1992; Kojima et al., 1995; Russell et al., 1998). Many FGIs from CO3.0 meteorites (Y–81020, Colony) appear to be unaltered and retain their original characteristics. In contrast, effects of aqueous alteration gradually appear in FGIs with increasing petrographic subtype of host CO chondrite (Kojima et al., 1995; Wasson et al., 2001). The alteration appears to have resulted in the replacement of melilitite by a fine-grained mixture of nepheline and other phases such as andradite and hedenbergite. With increasing petrographic subtypes (>3.5), spinel grains in FGIs become more Fe-rich, reaching ~50–60 mol.% hercynite probably due to redistribution of FeO by thermal metamorphism (McSween, 1977a; Itoh and Tomeoka, 2003). Kojima et al. (1995) proposed that such alteration and metamorphism occurred in the parent body based on the observation that the degree of alteration and metamorphic effects observed in FGIs increase with petrographic subtypes of the host. This inference is supported by hydrothermal experiments that show that the Na-rich minerals (e.g., nepheline) typical of secondary alteration products in CAIs can be formed by aqueous alteration of melilitite with hydrothermal fluid (Nomura and Miyamoto, 1998).

Clayton and Mayeda (1999) suggested that the variation of bulk O-isotopic compositions in different petrologic subtypes (CO3.0–CO3.7) could be attributed to the variable degree of aqueous alteration. In our preliminary O-isotopic work (Itoh et al., 2000) we reported about the alteration effect for the minerals except melilitite of various petrographic FGI-types from different metamorphic grade CO3 chondrites. Other previous work has addressed changes in mineralogy and textures (McSween, 1977a; Chizmadia et al., 2002) and O-isotopic composition of a single phase (Wasson et al., 2001) over a large range of CO subtypes. In this study, we focus on the mineralogy and O-isotopic compositions near the onset of the metamorphic sequence to determine: (1) the original O-isotopic systematics of CO FGIs and (2) relationships between textural alteration...
Table 1. Representative compositions in Yamato-81020 inclusion.

<table>
<thead>
<tr>
<th>Type:</th>
<th>Spinel-mellilite-pyroxene</th>
<th>Spinel-mellilite-pyroxene</th>
<th>Melilite-rich inclusion</th>
</tr>
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<tr>
<td>Inclusion:</td>
<td>Y20-9</td>
<td>Y20-8</td>
<td>Y20-3</td>
</tr>
<tr>
<td>Mineral:</td>
<td>Diopside</td>
<td>Spinel</td>
<td>Melilite</td>
</tr>
<tr>
<td>No. in Fig. 1:</td>
<td>1</td>
<td>2</td>
<td>3</td>
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<tr>
<td>MgO</td>
<td>18.1</td>
<td>18.7</td>
<td>27.1</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.6</td>
<td>0.8</td>
<td>69.4</td>
</tr>
<tr>
<td>SiO2</td>
<td>53.9</td>
<td>55.4</td>
<td>n.d.</td>
</tr>
<tr>
<td>CaO</td>
<td>26.1</td>
<td>25.4</td>
<td>n.d.</td>
</tr>
<tr>
<td>FeO</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Total:</td>
<td>98.7</td>
<td>100.4</td>
<td>97.2</td>
</tr>
<tr>
<td>Na</td>
<td>0.99</td>
<td>1.00</td>
<td>0.98</td>
</tr>
<tr>
<td>Mg</td>
<td>0.03</td>
<td>0.03</td>
<td>1.99</td>
</tr>
<tr>
<td>Si</td>
<td>1.97</td>
<td>1.99</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ca</td>
<td>1.02</td>
<td>0.98</td>
<td>n.d.</td>
</tr>
<tr>
<td>O</td>
<td>6.00</td>
<td>6.00</td>
<td>4.00</td>
</tr>
<tr>
<td>Cations</td>
<td>4.01</td>
<td>4.00</td>
<td>2.99</td>
</tr>
<tr>
<td>$\delta^{18}O$</td>
<td>$-49.0$</td>
<td>$-41.5$</td>
<td>$-46.8$</td>
</tr>
<tr>
<td>$\delta^{17}O$</td>
<td>$-43.4$</td>
<td>$-43.0$</td>
<td>$-43.9$</td>
</tr>
<tr>
<td>$\alpha_{mean}^{18}O$</td>
<td>2.2</td>
<td>2.1</td>
<td>2.6</td>
</tr>
<tr>
<td>$\alpha_{mean}^{17}O$</td>
<td>1.2</td>
<td>1.1</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Ti-Al-Di = Ti-Al-rich diopside. Al-Di = Al-rich diopside. r-Di = diopside from rim of the inclusion. No. of Fig. 1: the numbers correspond to SIMS analyses position in Fig. 1. n.d. = not detected. n.m. = not measured due to small size. $\alpha_{mean}$: standard deviation of the mean determined by statistical variation of secondary ion intensities corresponding to precisions for a series of measurements.

and oxygen isotopic evolution in the CO chondrites. We discuss the oxygen isotopic signatures of FGIs from CO chondrites based on relationships between petrologic properties and chemical compositions for individual crystals in FGIs from two CO chondrites of different petrologic subtype, Y-81020 (CO3.0) and Kainsaz (CO3.1–CO3.2) (subtypes from Sears et al., 1991; Kojima et al., 1995; Shibata, 1996; Chizmadia et al., 2002).

2. EXPERIMENTAL PROCEDURES

2.1. Scanning Electron Microscopy and X-Ray Analysis

Polished thin sections of Yamato-81020 (#61-1) on loan from National Institute of Polar Research and of Kainsaz (TTK1) were used in this study. They were examined with a petrographic microscope and with a JEOL JSM-5310LV scanning electron microscope equipped with an Oxford LINK-ISIS energy dispersive X-ray spectrometer (SEM-EDS) at the Tokyo Institute of Technology (TiTech). Backscattered electron images and quantitative analyses were obtained with this system. X-ray intensities for major elements were collected at 15 keV with a beam current of 1 nA for quantitative analyses. The measurement time for each point was 100 seconds. ZAF corrections were applied to the X-ray data to obtain quantitative values.

2.2. Secondary Ion Mass Spectrometry (SIMS)

In situ oxygen isotopic analysis was performed with the TiTech CAMECA ims 1270 SIMS instrument. The primary ion beam was mass-filtered positive $^{133}$Cs ions accelerated to 20 keV and the beam spot size was adjusted to 3–5 µm in diameter. Negative secondary ions of the $^{16}$O, $^{17}$O, $^{18}$O, $^{17}$OH and $^{18}$O were analyzed at a mass resolution power of 3000, sufficient to eliminate the hydride interference on the $^{17}$O peak. Other analytical conditions and data calibration methods have been described elsewhere (Yurimoto et al., 1998). The reported precision of each analysis was determined by secondary ion stability (Tables 1–3). The overall analytical accuracy is estimated as $\pm 5\%$ (1σ). Since the FGI minerals are fine-grained, we carefully evaluated overlapping of the primary beam among mineral phases by scanning electron microscope after SIMS analysis. Data affected by beam overlap on multiple phases show intermediate O isotopic values.

3. RESULTS AND DISCUSSION

3.1. Petrography and Oxygen Isotope Characteristics


About 37 mm$^2$ of thin section #61-1 of Y-81020 CO3 chondrite have been carefully observed by SEM-EDS in this study. In this area, 169 FGIs, $\sim$4.6 particles/mm$^2$, were iden-
tified. The FGIs from Yamato-81020 have a size range of 50–200 μm across by optical microscope (Fig. 1). Individual mineral grains are difficult to discern by optical microscope (i.e., categorized as FGIs; MacPherson et al., 1988). We analyzed chemical and oxygen isotopic compositions at the same points in each mineral (Table 1). All FGIs contain Fe-free spinel (FeO < 0.1 wt.%; Table 1) and are free of alteration products such as nepheline, hedenbergite and andradite. All O-isotope ratios of these FGI minerals generally plot on the CCAM line and are enriched in $^{16}O$, with $^{17}O_\text{SMOW} = -40\%$ (Fig. 2). Based on mineralogy, the FGIs have been classified into four groups: (1) spinel-mellite-pyroxene (Sp-Mel-Px) inclusions (73 particles; 43%), (2) mellite-rich inclusions (4 particles; 3%), (3) hibonite-pyroxene-olivine (Hib-Px-Ol) inclusions (2 particles; 1%) and (4) spinel-anorthite-pyroxene (Sp-An-Px) inclusions (90 particles; 53%). The characteristics of each FGI type are described below.

### 3.1.1. Spinel-mellite-pyroxene inclusions

Sp-Mel-Px inclusions (Fig. 1a) are irregularly-shaped with sizes up to 200 μm across. Sp-Mel-Px inclusions always have a core of spinel enclosed by a mellite layer completely surrounded by a diopside layer. This type of inclusion rarely contains hibonite and grossite grains enclosed by the mellite layer. Similar inclusions have been described previously in CO3 chondrites including Y-81020 in this study (Y-81020: Kojima et al., 1995; Colony: Russell et al., 1998, and Wasson et al., 2001). Rare Sp-Mel-Px inclusions contain an anorthite layer between the mellite and diopside layers. All phases from this type of inclusion are enriched in $^{16}O$, with $^{17}O_\text{SMOW} = -40\%$ (Table 1).

#### 3.1.1.1. Spinel-mellite-pyroxene inclusions

The FGIs from CO3 chondrites have a size range of 50–200 μm across by optical microscope (Fig. 1). Individual mineral grains are difficult to discern by optical microscope (i.e., categorized as FGIs; MacPherson et al., 1988). We analyzed chemical and oxygen isotopic compositions at the same points in each mineral (Table 1). All FGIs contain Fe-free spinel (FeO < 0.1 wt.%; Table 1) and are free of alteration products such as nepheline, hedenbergite and andradite. All O-isotope ratios of these FGI minerals generally plot on the CCAM line and are enriched in $^{16}O$, with $^{17}O_\text{SMOW} = -40\%$ (Fig. 2). Based on mineralogy, the FGIs have been classified into four groups: (1) spinel-mellite-pyroxene (Sp-Mel-Px) inclusions (73 particles; 43%), (2) mellite-rich inclusions (4 particles; 3%), (3) hibonite-pyroxene-olivine (Hib-Px-Ol) inclusions (2 particles; 1%) and (4) spinel-anorthite-pyroxene (Sp-An-Px) inclusions (90 particles; 53%). The characteristics of each FGI type are described below.

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Aldrich diopside. p- = primary area. a- = alteration area. c- = core. r- = rim. No. of Fig. 3: the numbers correspond to SIMS analyses position in Fig. 3. n.d. = not detected. n. m. = not measured due to small size. \( \sigma_{\text{mean}} \) standard deviation of the mean determined by statistical variation of secondary ion intensities corresponding to precisions for a series of measurements. * overlapping spinel (20%) and Al-rich diopside (80%). * overlapping spinel (50%) and hibonite (50%); the reported data means one spot analysis. ‘ overlapping of anorthite (50%) and alteration mineral (50%). * overlapping of Al-rich diopside (50%) and alteration mineral (50%).

### 3.1.1.4. Spinel-anorthite-pyroxene inclusions.

Two textural subtypes of Sp-An-Px inclusions were recognized. One type (e.g., Y20-6; Fig. 1d) is characterized by irregular shapes and consists of aggregates of grains, suggesting condensation products from vapor to solid. This type of FGI shows a concentric structure with a core of spinel enclosed by anorthite and surrounded by diopside. The FGIs often contain small Al-rich diopside grains (<5 µm) enclosed by anorthite. Previous studies have proposed that the anorthite was produced by the reaction between precondensed melilite and high temperature nebula gas (Lin and Kimura, 1998). Similar textures have been previously described in Al-rich inclusions in amoeboid olivine aggregates (AOAs) from CV (McSween, 1977b; Kornacki and Wood, 1984; Hashimoto and Grossman, 1987; Komatsu et al., 2001) and from CO chondrites, including Y-81020 in this study (McSween, 1977a; Chizmadia et al., 2002; Itoh et al., 2002). All phases of Y20-6 FGI are enriched in \( ^{18} \)O, with \( \delta^{18} \)O of \(-33.6 \) ‰ (Table 1). The O-isotopic distribution of these inclusions is consistent with crystallization of the type-C melt. This type of FGI might have originated from melting of Sp-An-Px inclusions without igneous texture. All phases of Y20-1 except spinel grains are relatively depleted in \( ^{16} \)O, but spinel is enriched in \( ^{16} \)O.

### Table 2. Representative compositions in Kainsaz Ca-Al-rich inclusions.

<table>
<thead>
<tr>
<th>Inclusion</th>
<th>Spinel-Alteration-Pyroxene</th>
<th>Spinel-Alteration-Pyroxene</th>
<th>spinel-alteration-pyroxene</th>
</tr>
</thead>
<tbody>
<tr>
<td>TK1-16</td>
<td>Diopside</td>
<td>Spinel</td>
<td>spinel</td>
</tr>
<tr>
<td>TK1-1</td>
<td>Diopside</td>
<td>Perovskite</td>
<td>Al-Di</td>
</tr>
<tr>
<td>TK1-19</td>
<td></td>
<td>graftomite</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral</th>
<th>No. in Fig. 3</th>
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<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>18.1</td>
<td>15.2</td>
<td>17.6</td>
<td>17.9</td>
<td>0.6</td>
<td>n.d.</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Al2O3</td>
<td>6.0</td>
<td>8.6</td>
<td>67.0</td>
<td>67.2</td>
<td>35.9</td>
<td>34.3</td>
<td>32.0</td>
<td>32.0</td>
</tr>
<tr>
<td>SiO2</td>
<td>53.9</td>
<td>49.4</td>
<td>n.d.</td>
<td>n.d.</td>
<td>40.7</td>
<td>41.8</td>
<td>24.2</td>
<td>24.2</td>
</tr>
<tr>
<td>CaO</td>
<td>26.1</td>
<td>24.8</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.7</td>
<td>39.9</td>
<td>n.d.</td>
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</tr>
<tr>
<td>TiO2</td>
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<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>FeO</td>
<td>1.3</td>
<td>13.4</td>
<td>14.1</td>
<td>1.7</td>
<td>2.3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Total</td>
<td>98.7</td>
<td>100.6</td>
<td>99.1</td>
<td>98.8</td>
<td>98.8</td>
<td>97.8</td>
<td>98.0</td>
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</table>

\( \sigma_{\text{mean}} \) and \( \sigma_{\text{mean}}^{18} \)O are determined by statistical variation of secondary ion intensities corresponding to precisions for a series of measurements. * overlapping spinel (20%) and Al-rich diopside (80%). * overlapping spinel (50%) and hibonite (50%); the reported data means one spot analysis. ‘ overlapping of anorthite (50%) and alteration mineral (50%).

The FGI shows a poikilitic texture, with spinel enclosed in subhedral anorthite and subhedral diopside. The FGIs commonly contain small (<5 µm) Al-rich diopside grains enclosed by diopside. The bulk chemical compositions (MgO, 12.4 wt.%; Al2O3, 22.2 wt.%; SiO2, 42.5 wt.%; CaO, 21.2 wt.%; TiO2, 1.5 wt.%; Cr2O3, 0.4 wt.%; FeO, 0.6 wt.%)) correspond to the type-C CAI field of Stolper’s diagram (Stolper, 1982; Wark, 1987). The petrographic texture is consistent with crystallization of the type-C melt. This type of FGI might have originated from melting of Sp-An-Px inclusions without igneous texture. All phases of Y20-1 except spinel grains are relatively depleted in \( ^{16} \)O, but spinel is enriched in \( ^{16} \)O, with \( \delta^{16} \)O of \(-33.6 \) ‰ (Table 1). The O-isotopic distribution and igneous texture suggest that spinel is a relict phase and the other phases (Al-diopside, diopside and anorthite) crystallized from melt with \( \delta^{17} \)O of \(-33.6 \) ‰.
FGIs in Kainsaz is ~4.4 particles/mm². They have a size range of 20–400 µm across. Typical textures are shown in Figures 3 and 4. All of the Kainsaz FGIs contain alteration products such as nepheline. The FGIs have been classified into five groups: (1) spinel-alteration-pyroxene (Sp-Alt-Px) inclusions, including one extremely altered FGI, TK1-3 (22 particles; 55%); (2) spinel-alteration (Sp-Alt) inclusions (3 particles; 8%); (3) pyroxene-alteration (Px-Alt) inclusions (12 particles; 30%); (4) melilite-alteration-pyroxene inclusions (Mel-Alt-Px) (2 particles; 5%); and (5) hibonite-pyroxene inclusions (Hib-Px) (1 particle; 3%). All groups correspond to those in Y-81020 if anorthite. We analyzed chemical and oxygen isotopic compositions at the same points in each mineral (Tables 2 and 3). Oxygen isotopic analyses of minerals from each of these FGI types generally plot on the CCAM line (Fig. 5). The characteristics of each FGI type and the heavily altered FGI are described below.

3.1.2.1. Spinel-alteration-pyroxene inclusions. Sp-Alt-Px inclusions (Fig. 3a) are compact objects consisting of layered aggregates ~10–20 µm across, with fine spinel grains (5–75 mol.% hercynite) enclosing 1–5 µm perovskite, hibonite laths, grossite and ilmenite grains. Aggregates of fine melilite enclosed by nepheline layers were rarely observed. From the inside to outward, the spinel grains are surrounded by a 2–10-µm layer of diopside (Al₂O₃ = ~5 wt.%). A thin alteration layer (2 to ~10 µm) is present between the spinel core and diopside layer. The alteration layer consists of nepheline or unidentifiable Na-Ca-Al-rich silicates. The diopside layer contains troilite grains. Throughout the inclusions are veins of Fe-rich material that may be due to terrestrial weathering. Spinel and diopside are generally enriched in 16O, with δ18O = ~0‰. The 16O-poor melilite grains are similar to those from Ornans FGIs (Wasson et al., 2001). Comparing the texture and O isotopic compositions between Kainsaz and Y-81020, this inclusion type corresponds to Sp-Mel-Px and/or Sp-An-Px inclusions of Y-81020, in which melilite and anorthite have been altered to nepheline.
measurement.

The standard deviation of the mean determined by statistical variation of secondary ion intensities corresponding to precisions for a series of measurements.

**Table 3. Representative compositions in TK1-3 Kainsaz Ca-Al-rich inclusions**

<table>
<thead>
<tr>
<th>Mineral:</th>
<th>Spinel</th>
<th>Diopside</th>
<th>Hibonite</th>
<th>Grossite</th>
</tr>
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<tr>
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<td>sp#A2</td>
<td>sp#A3</td>
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<tr>
<td>MgO</td>
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<td>Al₂O₃</td>
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<td>58.2</td>
<td>59.6</td>
<td>59.3</td>
</tr>
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<td>n.d.</td>
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<td>0.4</td>
</tr>
<tr>
<td>FeO</td>
<td>32.2</td>
<td>32.6</td>
<td>31.9</td>
<td>33.5</td>
</tr>
<tr>
<td>Total:</td>
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<td>100.4</td>
<td>99.7</td>
</tr>
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<td>0.27</td>
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<td>1.94</td>
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<td>n.d.</td>
</tr>
<tr>
<td>Ti</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Cr</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<tr>
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<tr>
<td>Zn</td>
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<tr>
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<tr>
<td>d_mean(¹⁸O²⁷O)</td>
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<td>2.4</td>
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</tr>
<tr>
<td>σ_mean(¹⁸O²⁷O)</td>
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<td>1.1</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>FeAl₂O₄ (%)</td>
<td>73</td>
<td>71</td>
<td>71</td>
<td>74</td>
</tr>
</tbody>
</table>

No. of Fig. 4: the numbers correspond to SIMS analyses position in Fig. 4. n.d. = not detected. n.m. = not measured due to small size. σ_mean; standard deviation of the mean determined by statistical variation of secondary ion intensities corresponding to precisions for a series of measurements.

3.1.2.2. Spinel-alteration inclusions. Sp-Alt inclusions (Figs. 3b and 3c) are irregularly-shaped. The cores of these inclusions consist of fine-grained spinel (40–70 mol.% hercynite) that often encloses perovskite, ilmenite, ulvöspinel and laths of hibonite. The spinel grains are surrounded by an altered zone consisting of a fine-grained mixture of nepheline, diopside, and troilite (Fig. 3c). In unaltered spinel ± hibonite-bearing FGIs from Y-81020, this domain adjacent to spinel consists of melilite and anorthite (Fig. 1a). This texture suggests that the altered layer formed from decomposition of melilite and anorthite. In addition, high hercynite contents of spinel indicate that the degree of alteration of this inclusion is relatively high. These observations are consistent with previous reports which showed similar type inclusions tend to have high hercynite contents of spinel (Tomeoka et al., 1992; Kojima et al., 1995; Russell et al., 1998). The area of mixed spinel and hibonite shows δ²⁷O = −30‰ (Table 2). In contrast, the alteration phase has an oxygen isotopic composition of δ²⁷O = −10‰ (Table 2). Comparing the texture and O-isotopic compositions between FGIs in Kainsaz and Y-81020, this inclusion type corresponds to Sp-Mel-Px inclusions of Y-81020 in which the original spinel was altered.

3.1.2.3. Pyroxene-alteration inclusions. Px-Alt inclusions (Fig. 3d) are irregularly-shaped and are divided into diopside and alteration layer. The diopside layer often rims the inclusions of this type. The alteration layer is a mixture of nepheline, unidentified Na-Al-Si-rich silicates, diopside, Al-rich diopside (Al₂O₃ = ~20 wt.%), TiO₂ (~10 wt.%) and FeS. Some samples of this inclusion type contain spinel grains (~2 µm) with corroded texture, which is similar in texture to the spinel-alteration-pyroxene inclusions. The corroded texture of the small spinel grains suggests that spinel has been partially decomposed during alteration. The diopside is enriched in ¹⁶O, with δ²⁷O = −30‰ (Table 2), whereas the Na-Al-Si-rich silicates and nepheline have oxygen isotopic compositions of δ²⁷O = −0‰ (Table 2). This inclusion type might correspond to spinel-anorthite-pyroxene and spinel-melilite-pyroxene inclusions from Y-81020 in which spinel, melilite and anorthite were changed to unidentified Na-Al-Si-rich silicates and nepheline.

3.1.2.4. Melilite-alteration-pyroxene inclusions. Mel-Alt-Px (Figs. 3e–3g) inclusions are irregularly-shaped. These FGIs consist of small melilite grains that are enclosed by nepheline and rare anorthite, surrounded by Al-rich diopside (Al₂O₃ = ~13 to ~18 wt%; Table 2). Al-rich diopside grains are in contact with matrix and also occur in the interior of these FGIs. Parts of the TK1-12 Mel-Alt-Px FGI are heavily altered and other parts are not (Figs. 3e–3g). In the area with abundant primary phases (Fig. 3f), the melilite and Al-rich diopside have O-isotopic compositions of about δ²⁷O = −30‰, whereas anorthite is relatively depleted in ¹⁶O, with δ²⁷O = −15‰ (Table 2). In the area with abundant alteration products (Fig. 3g), much of the melilite and anorthite has been converted to nepheline. Melilite in
Fig. 1. Representative back-scattered electron (BSE) images of several CAIs in Y-81020. The numbers in the figure correspond with analyses of chemical and O-isotopic compositions reported in Table 1. Mineral abbreviations: Mel, melilite; Pv, perovskite; Sp, spinel; Di, diopside; Al-Di, Al-rich diopside; An, anorthite; Hib, hibonite; Ol, olivine. (a) Compact Sp-Mel-Px inclusion, Y20-9, 150 μm across. The CAI consists of a core of fine spinel aggregates (FeO < 0.1 wt.%) surrounded by melilite (Åk_k<sub>10</sub>). The rim consists of diopside (Al<sub>2</sub>O<sub>3</sub> = ~0.5 wt.%). The CAIs are compact but many pores are observed in the sp-mel core. Perovskite grains 1 to 5 μm in size occur in the core. (b) Melilite-rich inclusion, Y20-3, 100 μm across. The CAI is irregularly shaped, and mostly composed of melilite (Åk_k<sub>2</sub>–10) that encloses small patches of perovskite and diopside. (c) Hib-Px-OI inclusion, Y20-7, 80 μm across. The CAI is ellipse shaped, and is composed of laths of hibonite (TiO<sub>2</sub> = ~2–3 wt.%) that are enclosed by Ti-Al-rich diopside (TiO<sub>2</sub> = ~1.4 wt.%, Al<sub>2</sub>O<sub>3</sub> = ~24 wt.%) and Al-rich diopside (TiO<sub>2</sub> = ~0.4 wt.%, Al<sub>2</sub>O<sub>3</sub> = ~19 wt.%). Aggregates of olivine grains (~5 μm) partly enclose the diopside core. The diopside has sector zoning of Ti. The lighter areas of diopside have high Ti contents. (d) An irregularly shaped Sp-An-Px inclusion, Y20-6, 150 μm across. The CAI consists of a core of fine spinel aggregates (FeO < 0.1 wt.%) and Al-rich diopside (Al<sub>2</sub>O<sub>3</sub> = ~30 wt.%) enclosed by anorthite. A rim of diopside encloses the CAI (Al<sub>2</sub>O<sub>3</sub> = ~18 wt.%). (e) High magnification BSE image corresponds to the white square area of Figure 1d. All minerals indicate the anhedral texture. (f) An irregularly shaped compact Sp-An-Px inclusion, Y20-1, 150 μm across. The CAI is composed of subhedral diopside (Al<sub>2</sub>O<sub>3</sub> = ~13 wt.%), small patches of Al-rich diopside (Al<sub>2</sub>O<sub>3</sub> = ~22 wt.%), and subhedral anorthite enclosing spinel aggregates (FeO = ~0.5 wt.%). Some of the anorthite and diopside grains have euhedral angular crystal margins. Small rounded perovskite grains are often observed. They are rimmed by 2–10 μm crystals of diopside (Al<sub>2</sub>O<sub>3</sub> = ~6 wt.%). SIMS analysis spots appear in diopside as sputtered craters.
3.1.2.6. Heavily altered inclusion.

TK1-3 is classified as a Sp-Alt-Px inclusion (Figs. 4a–4c) but it appears to be more heavily altered than the other Kainsaz FGIs and is described separately here. The spinel in this inclusion has the highest FeO content (~75 mol.% hercynite) of any spinel in the Kainsaz FGIs (Table 3). The spinel core is divided into a porous part (Sp#A) and a smooth part (Sp#B) (Fig. 4). The FeO content of spinel in the porous part (~70 mol.% hercynite) is higher than that in the smooth part (~50 mol.% hercynite; Table 3). ZnO contents are ~1 wt.% in the smooth part and are below detection in the porous part (Table 3). The two parts have contrasting O-isotopic compositions; the smooth part has δ17,18O_{SMOW} = ~−40‰, and the porous part has δ17,18O_{SMOW} = ~0‰. The diopside is porous and has 18O-poor compositions with δ17,18O_{SMOW} = ~−10‰, in contrast to those of other inclusions in Y-81020 and Kainsaz. The only 18O-poor spinel and diopside identified in this study are porous grains in this heavily altered FGI.

3.2. Comparison of Alteration of CAIs in Y-81020 and Kainsaz

3.2.1. Petrologic and isotopic evidence of thermal metamorphism and aqueous alteration

CAIs in Y-81020 consist of primary high-temperature phases such as hibonite, melilite, spinel, Al-rich diopside, diopside and anorthite, while most CAIs in Kainsaz contain major amounts of alteration products that probably replaced primary melilite and anorthite. Therefore, CAIs from Y-81020 show pristine textures and compositions of FGIs, whereas FGIs from Kainsaz show the effects of alteration. These petrographic and chemical descriptions are consistent with those of previous work on CO chondrites (Kojima et al., 1995; Chizmadia et al., 2002). Because the previous studies (Kojima et al., 1995; Chizmadia et al., 2002) suggest that the characteristics result from aqueous alteration in the parent body and evidence of aqueous alteration in the CO parent body has been observed in dark inclusions (Itoh and Tomeoka, 2003), it is plausible that the alteration observed in this study is due to the same processes. The degree of alteration varies among individual CAIs even within thin sections of meteorites of the same petrographic classification. Some of the heterogeneity of alteration may be due to a parent body brecciation effect. However, degree of alteration varies within a single FGI (Fig. 3e). Therefore, alteration progressed heterogeneously on a mm-scale in the CO parent body and alteration effects varied in different locations and/or at different times in this parent body.

Aqueous alteration of FGIs begins with 18O-depletion of originally 18O-rich melilite and anorthite. Melilite-alteration-pyroxene inclusions from Kainsaz in this study (Fig. 3e) and in Wasson et al. (2001) experienced O-isotopic exchange. After O-isotopic exchange, the melilite and anorthite reacted with aqueous fluid to form alteration products, mainly nepheline (Figs. 3a, 3b, 3d, and 3e). Secondary phases have 18O-poor isotopic compositions near the SMOW value, consistent with the variation in bulk compositions of CO chondrites with increasing petrographic subtype (Clayton and Mayeda, 1999).

FGIs from Kainsaz commonly contain diopside having a porous texture or interfingered alteration phases along grain boundaries (Figs. 3e and 3h). Such diopside has not been observed in the Y-81020 FGIs. Porous diopside is poorer in Al2O3 than massive diopside but it retains its 18O-rich nature (Table 2). Our results indicate that the process of aqueous alteration changes textures and chemical compositions of diopside without significant O-isotopic exchange in this stage.

Hercynite contents of spinel grains range from 5 to 75 mol.% in Kainsaz FGIs, compared to < 2 mol.% in spinel from Y-81020 (Fig. 6). The high hercynite contents are inconsistent with equilibrium condensation from a solar gas at high temperatures (e.g., Grossman, 1972). Kojima et al. (1995) and Russell et al. (1998) reported that the hercynite content of...
Spinel increases with increasing petrologic subtype in CO chondrites. In addition, hercynite contents of spinel are higher in FGIs without diopside rims (Fig. 3b; Table 2: hercynite mol.%/H11005/H11011 70 mol.%) than in those having diopside rims (Fig. 3a; Table 2: hercynite mol.%/H11005/H11011 30). These results suggest that the diopside rims inhibit Fe diffusion into FGIs and Fe diffusion generates high hercynite contents of spinel. It is plausible that Fe diffusion was caused by metamorphic processes in parent body (McSween, 1977a; Scott and Jones, 1990; Greenwood et al., 1992; Kojima et al., 1995; Russell et al., 1998). In spite of the large Fe-Mg exchanges, most spinel grains retain their original O-isotopic compositions (δ17O ≈ −20 to −50‰) (Fig. 7). The contrast in degree of exchange between Fe-Mg and O isotopes is consistent with the diffusivity contrast; Fe-Mg diffusion in spinel is about 10 orders of magnitude faster than that of oxygen self-diffusion (Ando and Ohishi, 1974; Freer and O'Reilly, 1980).

Petrography and O-isotopic characteristics indicate that melilite and anorthite in Kainsaz FGIs altered heterogeneously. On the other hand, O-isotopic compositions of spinel and diopside in the FGIs are almost always enriched in 16O, indicating that these phases usually kept their pristine O-isotopic compositions despite aqueous alteration in the parent body. However, the spinel and diopside are expected to become 16O-poor if aqueous alteration is very extensive. A heavily altered FGI contains spinel and diopside that appear to be altered in texture, chemical and O-isotopic compositions (Fig. 4 and Table 3). These results indicate the following alteration sequence of FGI spinel in CO chondrites: (1) Fe diffuses into spinel crystals by lattice diffusion mechanism; (2) aqueous fluid partially dissolves spinel and pyroxene, resulting in increasing porosity; (3) because the effective grain size becomes smaller, O self-diffusion leads to O-isotopic exchange; and (4) at the same time, recrystallization also enhances the O isotopic exchange.

Similar O isotopic exchange by aqueous alteration has been reported in olivine crystals of amoeboid olivine aggregates.
Porous diopside grains are also observed in a rim of TK1-3. These results indicate that the alteration process is the same as in the case of spinel.

3.3. Primary Characteristics of CAIs in CO Chondrites

Clear evidence of chemical alteration of Yamato 81020 FGIs has not been observed. The FGIs seem to have preserved pristine O isotopic compositions, with $\delta^{17}$\textsubscript{O} $\approx -40$ to

![Fig. 4. BSE images of irregularly-shaped FGI, TK1–3. The numbers in the figure indicate locations of chemical and O-isotopic analyses reported in Table 3. (a) TK1-3 consists mainly of a spinel core with an incomplete diopside rim. Micrometer-sized patches of perovskite, hibonite and grossite grains exist in spinel core. Alteration products exist between the spinel and diopside rim. The alteration products contain sodium, potassium and sulfur. (b) Spinel in the core in TK1-3 has two different textures: one is porous (Sp#A), the other is smooth (Sp#B). The mean FeO content of Sp#A (~73 hercynite %) is higher than that of Sp#B (~56 hercynite %) (Table 3). (c) The diopside layer has a porous texture like Sp#A. The rim diopside is higher in FeO, Al$_2$O$_3$, TiO$_2$ and Cr$_2$O$_3$ than diopside in the core (Di#2; Table 3). Elliptical marks in figure denote SIMS analyses spots. Hib: hibonite. Gr: grossite. Alt: Na-S-K-Fe-rich unknown phases.

![Fig. 5. Oxygen isotopic compositions of minerals from FGIs in TTK1 (Kainsaz). Analyses from all the FGI types of Kainsaz are plotted. Alteration denotes nepheline, graftonite, and unknown very fine-grained alteration minerals. Multi-phase is consistent with the overlap of data in Table 2.

![Fig. 6. Hercynite content distribution in spinel in FGIs from Y-81020 and Kainsaz.](image)

(Imai and Yurimoto, 2003). Porous diopside grains are also observed in a rim of TK1-3. These results indicate that the alteration process is the same as in the case of spinel.
ment of FGI spinel from Y-81020 and TTK1. The 16 O-enrichment is relatively depleted in 16 O (\(\delta^{16}O = -0 \) to \(-15\%\)). Textures are consistent with formation of the FGIs by solid condensation from gas. Therefore, the FGIs seem to have condensed from 16 O-rich gas. However, we found one remarkable FGI with remelted texture (Y20-1). The O-isotopic composition of the igneous minerals (diopside and anorthite) is relatively depleted in 16 O (\(\delta^{17}O = \sim -40 \) to \(-50\%\)). These results indicate that the 16 O-rich precursor solids were partially melted and the O-isotopic compositions of the melt became 16 O-poor before solidification. Therefore, the remelting occurred in an 16 O-poor environment, which was different from the environment in which most Y-81020 FGIs formed. The existence of such an 16 O-isotope change in the solar nebula was proposed by Yurimoto et al. (2001).

4. CONCLUSIONS

Fine-grained CAIs from the Y-81020 CO3.0 chondrite are characterized by the absence of alteration textures, the presence of Mg-rich spinel and 16 O-rich mineral compositions. One exception with relatively 16 O-poor diopside and anorthite with distinct igneous textures was identified. In contrast, FGIs from Kainsaz (CO3.1–CO3.2) have Mg-rich spinel and abundant very fine-grained Na-rich phases that appear to have formed from alteration of melilite and anorthite. The Kainsaz FGIs show a mineral-dependent pattern of isotopic compositions with alteration products and melilitic consistently depleted in 16 O relative to spinel, pyroxene and other primary phases.

These observations are interpreted to mean that: (1) all the primary phases of fine-grained CAIs in CO chondrites (hibonite, spinel, melilitic, anorthite, Al-rich diopside, diopside and olivine) crystallized from 16 O-rich gas. (2) Some CAIs with igneous textures in CO3 chondrites formed by partial melting during reheating events in 16 O-poor gas in the solar nebula. (3) The CO3 chondrites, except for petrologic subtype 3.0, were subjected to parent-body metamorphism generating Fe-, Na-rich and 16 O-poor minerals in the CAIs. (4) Aqueous alteration on the parent body changed the O isotopic composition of all mineral species in CO3 fine-grained CAIs from \(16^0\)O-rich to 16 O-poor.

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