

Oxygen isotopic compositions in a plagioclase-olivine inclusion from Ningqiang: similar to those in Al-rich chondrules

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Abstract: We report the petrology and oxygen isotopic composition (using a Cameca NanoSIMS 50L ion microprobe) of a plagioclase-olivine inclusion, C#1, found in the Ningqiang carbonaceous chondrite. In addition to major phases (plagioclase, spinel and olivine), C#1 is also surrounded by a pyroxene rim (64 vol % Ca-rich and 36 vol % Ca-poor pyroxenes). On a three-isotope oxygen diagram, $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$, the compositions of individual minerals analyzed in C#1 fall along the CCAM line (carbonaceous chondrite anhydrous mineral line), and oxygen isotopic compositions in C#1 show significant variability in $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$. The oxygen isotopic compositions of the pyroxene rim minerals are similar to those of the other host minerals, which suggests that the rim likely formed from the same melting process as the host. The rim is considered to have formed as a result of interaction between an ^{16}O -poor gas and a melt. Some spinel grains are typical ^{16}O -rich and likely of relict origin, which is similar to the ^{16}O -rich Ca-, Al-rich inclusions that likely are the one of the precursor of C#1. The inclusion then likely melted in an ^{16}O -poor region where chondrules formation, accompanying by oxygen isotope exchange with an ^{16}O -poor gas. Some anorthite, pyroxene and spinel could have undergone fluid-assisted thermal metamorphism on the Ningqiang chondrite parent body. The oxygen isotope data and evolution of the C#1 plagioclase-olivine inclusion are similar with those of Al-chondrules in chondrites.

Key words: oxygen isotopes; plagioclase-olivine inclusion; Al-rich chondrules; Ningqiang chondrite; CAIs

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1 Introduction

Chondrites are complex aggregates of high temperature components that formed in the solar nebula 4.56 billion years ago: chondrules, Ca-, Al-rich inclusions (CAIs), amoeboid olivine aggregates (AOAs), and Fe-Ni metal alloy. CAIs are composed of refractory minerals (e.g. spinel, melilite and diopside), enriched in refractory elements, generally show an ^{16}O -rich oxygen isotopic composition ($\delta^{17,18}\text{O} \sim -50\%$), and they are the most extensively studied components of carbonaceous chondrites. Most minerals in CAIs show a signature of ^{16}O -rich which is similar to solar oxygen isotopic compositions (McKeegan et al., 2011; Kawasaki et al., 2017). In contrast to CAIs, those in ferromagnesian chondrules that are dominated by ^{16}O -poor signatures (Krot et al., 2006; Ushikubo et al., 2012; Tenner et al., 2013; Wakaki et al., 2013). The linear array defined by the oxygen isotope ratios of CAI minerals on a three isotope plot is referred to as the CCAM line (Clayton, 1993), which has a slope of 0.94 ± 0.02 as defined by CAIs from the Allende CV3 carbonaceous chondritic meteorite, in contrast to mass fractionation curves with slopes slightly greater than 0.5. The oxygen isotopes of CAIs in different chondrites groups exhibit a similar ^{16}O -rich oxygen isotopic reservoir (Guan et al., 2000a,b; Lin et al., 2003), whereas ferromagnesian chondrules show a large variation. Furthermore, chondrule silicates have ^{16}O -depleted compositions that confirm the existence of an ^{16}O -poor reservoir in the chondrule-forming region (Krot et al., 2006; Marrocchi and Chaussidon, 2015). Previous studies have demonstrated that in unmetamorphosed carbonaceous chondrites, the minerals in chondrules and CAIs present a wide range of non-mass-dependent oxygen isotope variations that are thought to reflect the existence of at least two reservoirs in the accretion disk with substantially different isotopic compositions (i.e., ^{16}O -rich and ^{16}O -poor) (Clayton, 2002).

CAIs are usually divided into coarse-grained and fine-grained texture. The most common coarse-grained inclusions are Type A (melilite-predominant), Type B (melilite-Ti-Al-Ca-pyroxene-rich), and Type C (Ti-Al-Ca-pyroxene-anorthite-rich). These CAIs are characterized by an igneous texture which formed by complete or partial melting and subsequent crystallization. The melting conditions of the igneous CAIs are estimated from crystallization experiments using igneous CAI analogs. Al-rich

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chondrules are rare components in primitive chondrites and contain one or more primary phases, including plagioclase, spinel, and Al-diopside, \pm Al-rich glass, in addition to olivine and Ca-poor pyroxene. Petrologic and oxygen isotopic studies of Al-rich chondrules in carbonaceous and ordinary chondrites (Russell et al., 2000; Krot and Keil, 2002; Krot et al., 2004; MacPherson and Huss, 2005) show that these chondrules may represent a transitional link between CAIs and ferromagnesian chondrules. The study of Al-rich chondrules therefore provides insights on the genetic among important primitive chondrites components (e.g. CAIs, AOAs and ferromagnesian chondrules).

Plagioclase-olivine inclusions (POIs) are a type of aggregates that mainly consist of plagioclase, olivine, pyroxene, and spinel. However, the link to coarse-grained CAIs (Lin and Kimura, 1997; Lin et al., 2006) and Al-rich chondrules (MacPherson and Huss, 2005) remain controversial. POIs are distinguished from typical CAIs by the absence of melilite, more abundant sodic plagioclase and olivine. Compared with ferromagnesian chondrules, POIs have more plagioclase and spinel. POIs are distinguished from other typical inclusions and ferromagnesian chondrules based on their petrography, chemistry, and isotopic compositions. They therefore likely represent intermediate assemblages between more refractory inclusions and chondrules (Sheng et al., 1991), similar to Al-rich chondrules.

Ningqiang carbonaceous chondrite shares similar petrologic and mineralogic characteristics with oxidized CV and CK chondrites (Kallemeyn et al., 1991), but exhibits unique features that differ from any other known subtype of carbonaceous chondrites (Rubin et al., 1988; Wang and Lin, 2007). As a result, Ningqiang has been classified as an ungrouped carbonaceous chondrite (Wang et al., 2007). Previous studies have addressed the petrography, mineral chemistry, and Al-Mg isotopic characteristics of POIs (Sheng et al., 1991; Lin and Kimura, 1997; Hsu et al., 2003), but their oxygen isotopic composition remains unreported. Preserved oxygen isotopic heterogeneities, especially in CAIs and chondrules from metamorphosed carbonaceous chondrites, are interpreted as the result of mixing between two or more oxygen reservoirs that existed prior to or during the formation of chondritic materials (Clayton, 1993). The main purpose of this study is to constrain the precursor and formation history of POIs by studying their petrography and oxygen isotopes.

2 Samples and Experiments Method

We studied a POI labeled C#1 from the Ningqiang carbonaceous chondrite with a size of 2.6×3.0 mm. Backscattered electron images of C#1 are provided in Lin and Kimura (1997).

The POI was first investigated using a petrographic microscope and interesting areas were photographed and characterized using a JSM-7200F scanning electron microscope (SEM) at the National Astronomical Observatories of the Chinese Academy of Sciences.

A Cameca NanoSIMS 50L ion microprobe at the Key Laboratory of Earth and Planetary Physics, Institute of Geology and Geophysics of the Chinese Academy of Sciences was used to measure the oxygen isotope ratios in C#1. A Cs^+ primary beam of 16 keV, ~ 100 pA was scanned over the surface to produce a spot of about 1.5×2 μm . ^{16}O and ^{18}O were simultaneously measured using a multi-collection Faraday Cup (FC) and ^{17}O was simultaneously measured using a mono-collection electron multiplier (EM), respectively. The instrument was set to give a mass resolving power (MRP) ~ 6000 (Cameca NanoSIMS definition), based on the measured peak width containing 80% of the ion beam (e.g. Hoppe et al. 2013) on the ^{17}O detector, which is sufficient to resolve the ^{16}OH peak from that of ^{17}O (contribution of ^{16}OH typically ≤ 25 ppm) (Lin et al., 2014). Oxygen isotopic compositions were reported as per mil deviations from standard mean ocean water (SMOW) and as ^{16}O excesses relative to terrestrial samples ($\Delta^{17}\text{O} = \square^{17}\text{O} - 0.52\square\square^{18}\text{O}$). Under the applied analytical conditions, the internal (2σ) precision of individual oxygen isotope analyses was typically better than 1 ‰ for $\square^{18}\text{O}$ and < 2 ‰ for $\square^{17}\text{O}$. □

The following standards were used during the NanoSIMS analyses: San Carlos olivine, Burma spinel and single crystals of anorthite and pyroxene. The elemental composition of each standard was measured using a FEI Quanta 200 3D electron-dispersive X-ray spectrometer, and their O isotope ratios were measured by laser-assisted fluorination at the Key Laboratory of Earth and Planetary Physics, Institute of Geology and Geophysics, Chinese Academy of Sciences following the method described in Miller et al. (1999) and Lin et al. (2014).

3 Results

3.1 Petrography

The C#1 POI contains 59 vol% plagioclase, 14 vol% spinel, 14 vol% olivine, 7 vol% Ca-rich pyroxene, 5 vol% Ca-poor pyroxene, 1 vol% Ti-rich oxides, and other accessory phases (Lin and Kimura, 1997). The plagioclase in C#1 is euhedral and coarse-grained (up to 380 μm in size) (Fig. 1a). The olivine shows two occurrence types. Most of the olivine is subhedral to euhedral in form, with sizes ranging from 50 to 240 μm , and is associated with or enclosed within plagioclase in the marginal areas of the inclusion (Fig. 1a). The remaining grains are anhedral to subhedral with sizes < 35 μm and

are associated with abundant spinel in the central area, labeled as the spinel-olivine-rich zone. The spinels in C#1 are euhedral, <20 μm in size, and occur as inclusions in plagioclase and olivine but predominantly in the spinel-olivine-rich zone (Lin and Kimura, 1997). C#1 consists of a pyroxene rim (100–150 μm wide) that partially surrounds the inclusion host (Fig. 1b). The pyroxene rim is mainly composed of Ca-poor and Ca-rich pyroxenes (64 and 36 vol%, respectively) with a few grains of plagioclase (<40 μm) (Lin and Kimura, 1997). Ca-poor pyroxene is generally mantled by Ca-rich pyroxene, both of which are in close contact with the plagioclase and olivine of the host (Fig. 1b). Mineral chemistry composition of C#1 are described in detail by Lin and Kimura (1997).

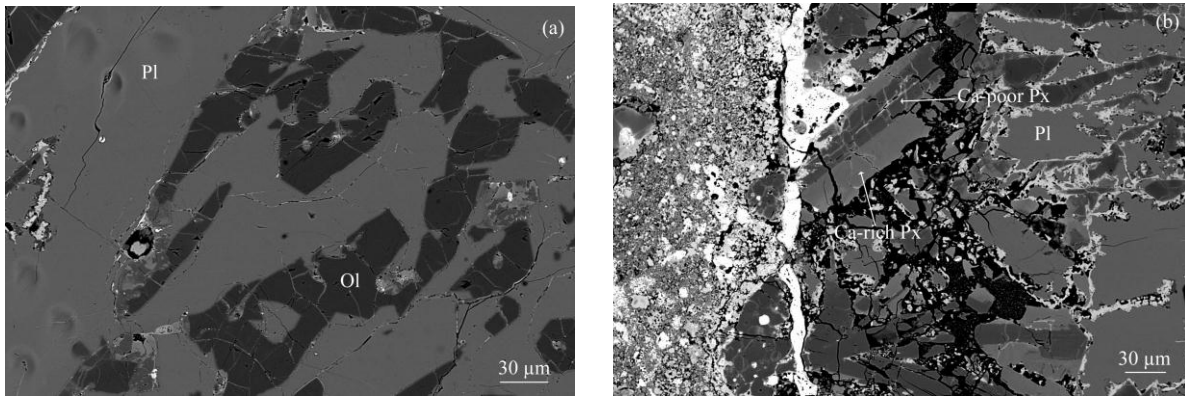


Fig. 1. Back scattered electron images of plagioclase (Pl), olivine (Ol) and pyroxene (Px) in C#1 inclusion. (a) Pl is euhedral and coarse-grained, Ol is coarse-grained and subhedral to euhedral; (b) The pyroxene rim (W-L rim) is predominantly composed of Ca-poor and Ca-rich pyroxenes, Ca-poor pyroxene is generally mantled by Ca-rich pyroxene.

3.2 Oxygen isotopic compositions

The oxygen isotopic compositions of C#1 are listed in Table 1 and 2 and plotted in Fig. 2. On a three-isotope oxygen diagram, all oxygen isotope measurements for the minerals plot slightly off or along the CCAM line within error limits (Fig. 2). This indicates that C#1 has not been significantly affected by mass-dependent fractionation processes.

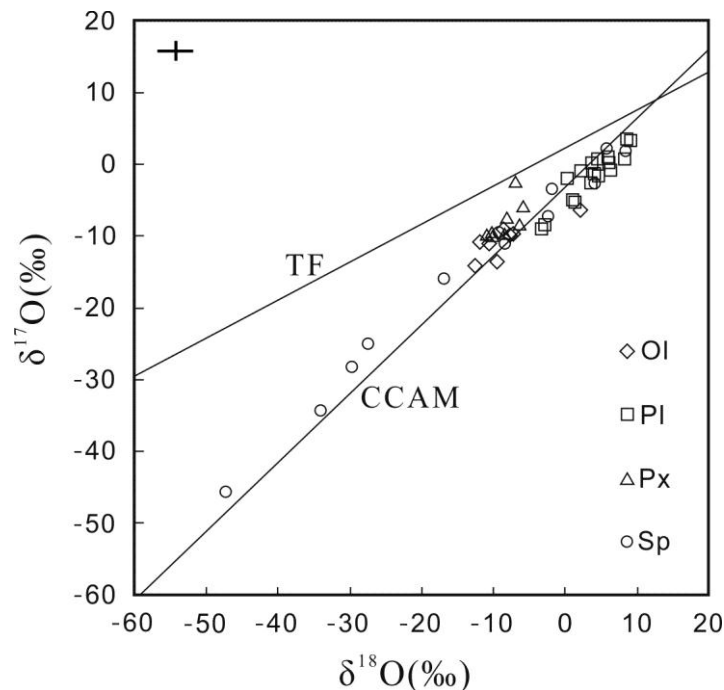


Fig. 2. Oxygen-isotope compositions of individual minerals in C#1 inclusion. The data are plotted on a three-isotope oxygen diagram. +: error bars.

Table 1 Oxygen isotopic data of olivine(Ol), pyroxene(Px) and spinel(Sp) in C#1

Analysis number	$\delta^{18}\text{O}$ (‰)	2 σ	$\delta^{17}\text{O}$ (‰)	2 σ	$\delta^{17}\text{O}$ (‰)	2 σ
Ol-01	-7.1	0.76	-9.5	0.36	-5.8	0.56
Ol-02	-7.7	0.86	-10	0.38	-6	0.62
Ol-03	-9.6	0.82	-13.4	0.42	-8.4	0.62
Ol-04	-12.6	0.94	-14	0.38	-7.5	0.66
Ol-05	2.1	0.98	-6.3	0.34	-7.4	0.66
Ol-06	-10.6	0.86	-11	0.36	-5.5	0.61
Ol-07	2.3	0.84	-1.1	0.38	-2.3	0.61
Ol-08	-8.5	0.84	-8.9	0.38	-4.5	0.61
Ol-09	-11.8	0.88	-10.8	0.38	-4.6	0.63
Ol-10	-8.6	0.84	-9.2	0.4	-4.7	0.62
Px-01	-10.2	0.84	-9.3	0.34	-4	0.59
Px-02	-7	0.96	-2.3	0.46	1.3	0.71
Px-03	-5.9	0.8	-5.7	0.38	-2.6	0.59
Px-04	-8.2	0.78	-7.4	0.38	-3.1	0.58
Px-05	-8	0.88	-7.3	0.4	-3.1	0.64
Px-06	-6.4	0.86	-8.2	0.36	-4.8	0.61
Px-07	-8.6	0.92	-9.2	0.42	-4.8	0.67
Px-08	-10	0.9	-10.1	0.36	-4.9	0.63
Px-09	-10.9	0.82	-9.7	0.38	-4	0.6
Sp-01	-27.5	0.82	-24.8	0.34	-10.5	0.58
Sp-02	-29.8	0.86	-28.1	0.4	-12.6	0.63
Sp-03	-1.9	0.88	-3.3	0.4	-2.3	0.64
Sp-04	-17	0.82	-15.8	0.4	-7	0.61
Sp-05	5.6	0.86	2.2	0.38	-0.7	0.62
Sp-06	-47.3	0.96	-45.5	0.38	-20.9	0.67
Sp-07	-34.1	0.82	-34.2	0.4	-16.4	0.61
Sp-08	8.4	0.86	1.9	0.38	-2.5	0.62
Sp-09	4.1	0.82	-2.7	0.36	-4.8	0.59
Sp-10	-8.5	0.82	-10.9	0.36	-6.5	0.59
Sp-11	-2.4	0.78	-7.1	0.34	-5.8	0.56
Sp-12	-9.3	0.8	-9.4	0.34	-4.6	0.57

Table 2 Oxygen isotopic data of plagioclase in C#1

Analysis number	$\delta^{18}\text{O}$ (‰)	2 σ	$\delta^{17}\text{O}$ (‰)	2 σ	$\delta^{17}\text{O}$ (‰)	2 σ
Pl-01	3.4	0.88	-2.2	0.36	-4.0	0.62
Pl-02	4.5	0.80	-1.5	0.34	-3.9	0.57
Pl-03	0.9	0.82	-4.9	0.44	-5.3	0.63
Pl-04	6.3	0.86	-0.7	0.38	-4.0	0.62
Pl-05	-2.9	0.86	-8.1	0.42	-6.6	0.64
Pl-06	1.4	0.84	-5.1	0.36	-5.8	0.6
Pl-07	-3.4	0.84	-8.9	0.38	-7.1	0.61
Pl-08	-3.1	0.86	-8.5	0.34	-6.9	0.6
Pl-09	2.9	0.94	-1.3	0.38	-2.8	0.66
Pl-10	3.6	0.80	-0.2	0.36	-2.0	0.58
Pl-11	9.1	0.80	3.4	0.38	-1.3	0.59
Pl-12	8.8	0.88	3.7	0.38	-0.9	0.63
Pl-13	5.8	0.84	1.3	0.40	-1.7	0.62
Pl-14	2.1	0.86	-1.0	0.36	-2.1	0.61
Pl-15	4.5	0.84	0.1	0.38	-2.2	0.61
Pl-16	5.5	0.82	1.3	0.38	-1.5	0.6
Pl-17	2.2	0.86	-0.8	0.36	-2.0	0.61
Pl-18	4.1	0.84	0.3	0.36	-1.8	0.6
Pl-19	0.2	0.82	-1.8	0.38	-1.9	0.6
Pl-20	3.7	0.90	0.3	0.38	-1.6	0.64
Pl-21	4.5	0.84	0.7	0.36	-1.6	0.6
Pl-22	8.5	0.90	3.5	0.38	-0.9	0.64
Pl-23	4.9	0.88	-0.3	0.36	-2.8	0.62
Pl-24	4.8	0.86	-0.2	0.38	-2.6	0.62
Pl-25	6.0	0.84	0.3	0.38	-2.8	0.61
Pl-26	-8.9	0.80	-9.9	0.36	-5.3	0.58
Pl-27	3.1	0.74	-0.6	0.38	-2.2	0.56
Pl-28	8.3	0.84	0.8	0.36	-3.5	0.6
Pl-29	3.9	0.76	-1.2	0.34	-3.3	0.55

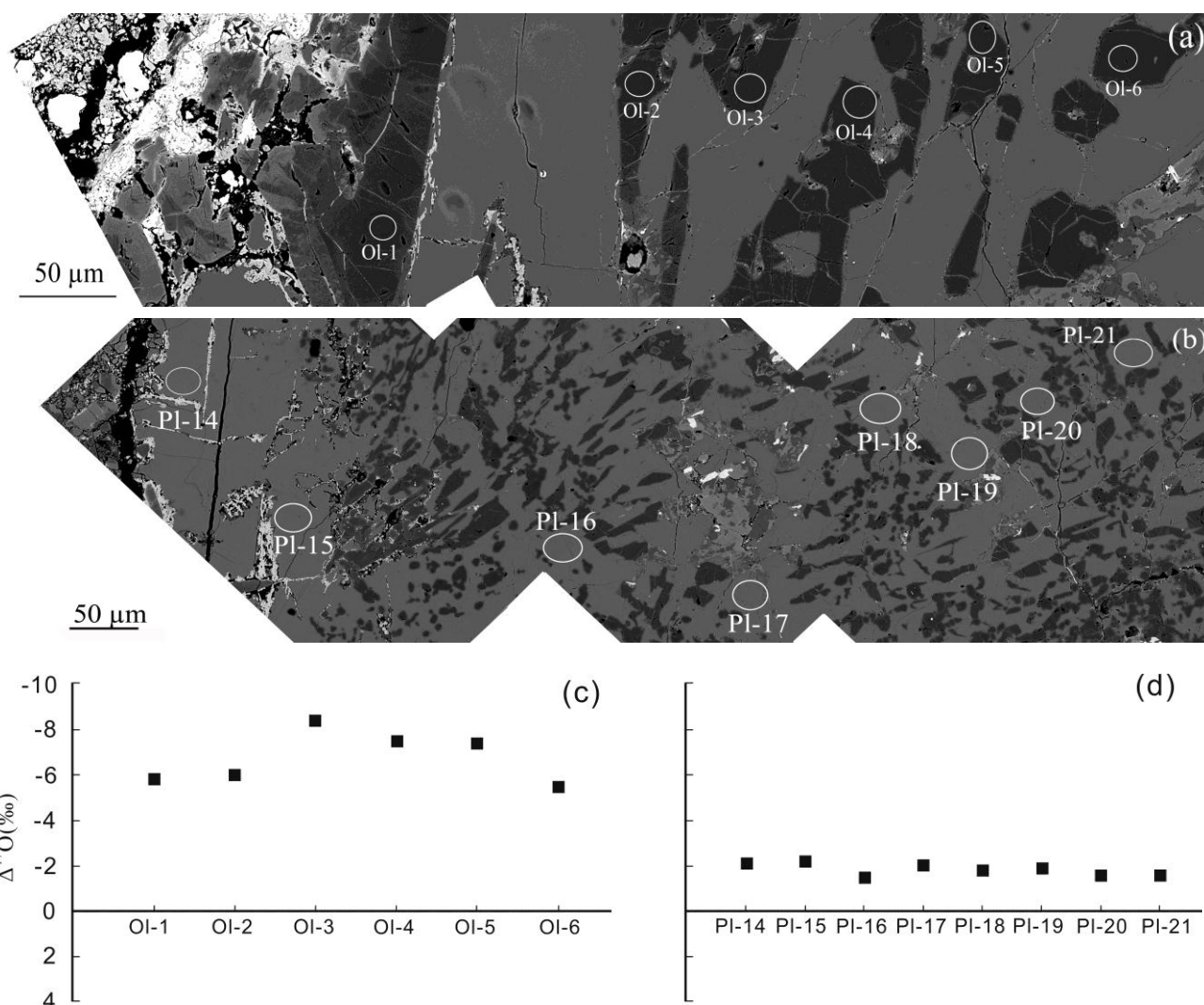


Fig. 3. $\Delta^{17}\text{O}$ value of olivine (Ol) and plagioclase (Pl) from the rim to the core in C#1 inclusion.

(a) The locations of olivine (Ol) oxygen isotope analysis from the rim to the core; (b) The locations of plagioclase (Pl) oxygen isotope analysis from the rim to the core; (c) $\Delta^{17}\text{O}$ value of olivine (Ol) from the rim to the core; (d) $\Delta^{17}\text{O}$ value of plagioclase (Pl) from the rim to the core. $\Delta^{17}\text{O}$ of olivine and plagioclase do not show a regular change from the rim to the core.

The oxygen isotopic compositions of minerals from C#1 mostly fall into an ^{16}O -poor cluster, aside from some ^{16}O -rich spinels. The olivine and Ca-rich and Ca-poor pyroxene are ^{16}O -poor ($\square\square\square\text{O} > -12.6\text{‰}$, $\square\square\square\text{O} > -14.0\text{‰}$, $\Delta^{17}\text{O} > -8.4\text{‰}$) (Table 1), and the plagioclase exhibits a trend toward the most ^{16}O -poor compositions ($\square\square\square\square\square\text{O} > -9.9\text{‰}$, $\Delta^{17}\text{O} > -7.1\text{‰}$) (Table 2). The oxygen isotopic compositions of spinel falls in a range of $\square\square\square\text{O}$: -47.3‰ – 8.4‰ , $\square\square\square\text{O}$: -45.5‰ – 2.2‰ , and $\Delta^{17}\text{O}$: -20.9‰ – -0.7‰ (Table 1 and Fig. 2).

We analyzed the oxygen isotopes of olivine and plagioclase from rim to core in C#1. The ranges of $\square\square\square\text{O}$, $\square\square\square\text{O}$, and $\Delta^{17}\text{O}$ of the olivine are -12.6‰ – 2.1‰ , -14.0‰ – 6.3‰ , and -5.5‰ – 8.4‰ , respectively (Table 1), and those for plagioclase are 0.2‰ – 8.5‰ , -1.8‰ – 3.5‰ , and -0.9‰ – 2.2‰ (Table 2). The oxygen isotopes of the olivine and plagioclase do not show a regular change from the rim to the core (Fig. 3).

4 Discussion

4.1 Formation of the pyroxene rim in C#1

Lin and Kimura (1997) suggested that C#1 had once melted, which is justified by the following evidence: (i) C#1 is a spherical shape. (ii) Most plagioclase crystals are euhedral, olivine are oriented and enclosed in plagioclase, which are consistent with those crystallized from a melt (Sheng et al., 1991). (iii) The occurrence of Ca-rich pyroxene mantling Ca-poor pyroxene in the inclusion is also typical of crystallization from a melt. (iv) The crystallization sequences of minerals based on textural observations are spinel - olivine - plagioclase - pyroxene from core to rim in C#1, which differs with a nebular condensation sequence (Yoneda and Grossman, 1995; Lin and Kimura, 2000, 2003).

The pyroxene rim in C#1 is predominantly composed of Ca-poor and Ca-rich pyroxenes and differs from a typical Warkling-Lovering rim, which is a layered object that surrounds CAIs and composed of refractory minerals (e.g., hibonite, spinel, melilite, anorthite, diopside, and olivine). Low-Ca pyroxene is not usually present in Warkling-Lovering rim. From the texture, the pyroxene rim in C#1 appears to have crystallized from a melt. Lin and Kimura (1997) reported two possibilities for the formation of the pyroxene rim: (i) it formed from the same melt as the host or (ii) it formed by melting of an accretionary rim on the host. In this work, we analyzed the oxygen isotopic composition of the pyroxene rim (Table 1 and Fig. 2). All of the oxygen isotope measurements for the pyroxene rim minerals (Ca-poor and Ca-rich pyroxenes) plot within error on the CCAM line, and the oxygen isotopic composition is similar to those of the other host minerals (Fig. 2). As a result, the pyroxene rim probably formed from the same melt as the host (Aléon, 2016; Dai et al., 2016). The precursors of the pyroxene rim and interior minerals in C#1 probably formed from the same ^{16}O -rich reservoir that the CAIs originated. However, the pyroxene rim is uniformly ^{16}O -depleted (Table 1), which suggests that subsequent isotope exchange occurred in an ^{16}O -poor reservoir. This exchange could have occurred in the solar nebula during C#1 remelting. The rim therefore formed from the host melt as a result of ^{16}O -poor gas and melt interaction (Tissandier et al., 2002; Libourel et al., 2006).

4.2 Oxygen isotopic compositions in C#1: similar to those in Al-rich chondrules

Early oxygen isotope studies of unequilibrated chondrite chondrules (Clayton, 1993) showed significant variability in $\square^{18}\text{O}$ and $\square^{17}\text{O}$. Many chondrule data (Clayton, 1993; Krot et al., 2006) plot on or near a slope ~ 1 line on a three-isotope oxygen diagram ($\square^{18}\text{O}$ vs. $\square^{17}\text{O}$), similar to the CCAM line derived from CAI analyses. Oxygen isotopic compositions in C#1 vary significantly in $\square^{18}\text{O}$ and $\square^{17}\text{O}$ ($\square^{18}\text{O}$: from -47.3% to 9.1% , $\square^{17}\text{O}$: from -45.5% to 3.7%). The C#1 oxygen isotopic compositions are generally similar to those of POIs in other chondrite groups (Rout et al., 2009). On a three-isotope oxygen diagram, all of the studied minerals in C#1 plot along a mass-independent fractionation line with a slope of ~ 1 .

The oxygen isotopic compositions ($\delta^{17,18}\text{O}$: from -15% to $+5\%$) of minerals in Al-rich chondrules from ordinary chondrites (Russell et al., 2000) and enstatite chondrites (Guan et al., 2006) are closely related to those of ferromagnesian chondrules. Olivine, plagioclase, Ca-rich pyroxene, and Ca-poor pyroxene in C#1 are uniformly ^{16}O -depleted and heterogeneous ($\Delta^{17}\text{O} = -8.4\%$ – -1.3% , with an average of -3.7%), and spinel is comparatively more ^{16}O -rich than other minerals in C#1. Melilite is a mineral that typically shows ^{16}O -depletion in the isotopically heterogeneous CAIs from metamorphosed CV and CO chondrites; however, none of the measured C#1 minerals contain melilite likely owing to replacement by secondary minerals during alteration and thermal metamorphism (Itoh et al., 2004; MacPherson et al., 2008). The $\delta^{17,18}\text{O}$ ($\square^{18}\text{O}$: from -12.6% to 9.1% , $\square^{17}\text{O}$: from -14.0% to 3.7%) of C#1 are similar to Al-rich chondrules in those ordinary chondrites and enstatite chondrites (except for some ^{16}O -rich spinel).

Interestingly, a few spinel grains are ^{16}O -rich to various degrees. Similar ^{16}O -rich isotopic compositions in Al-rich chondrule spinel or olivine have also been previously reported (Hiyagon and Hashimoto, 1999; Jones et al., 2004; Ushikubo et al., 2012; Tenner et al., 2013; Zhang et al., 2014) and are likely of relict origin, although Jones et al. (2004) also proposed an alternative interpretation that the earliest nebular solids from which chondrules formed had $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values around -50% . The relict origin for these spinel grains could be similar to the origin of the ^{16}O -rich olivine (Kobayashi et al., 2003) because both phases have comparably slow oxygen diffusion rates under chondrule-forming conditions (Ryerson et al., 1989; Ryerson and McKeegan, 1994). The ^{16}O -rich spinel in C#1 could also be of relict origin owing to incomplete melting during the chondrule-forming event.

4.3 Oxygen isotope exchange of the C#1

Previous studies have indicated that CAIs originated in an ^{16}O -rich gaseous reservoir (Krot et al., 2002), including those in ordinary, enstatite, and carbonaceous chondrite groups (McKeegan et al., 1998; Guan et al., 2000a,b; Itoh et al., 2004; Williams et al., 2017). In this study, the minerals in C#1 have an ^{16}O -poor composition, except for some spinels. It means that subsequent isotopic exchange occurred in an ^{16}O -poor reservoir. This exchange could have occurred in the solar nebula, e.g., during C#1 remelting (Yurimoto et al., 1998; Itoh et al., 2004; Krot et al., 2005, 2008), and/or during fluid-assisted thermal metamorphism on the Ningqiang chondrite parent body, as has been proposed for the majority of CAIs, amoeboid olivine aggregates (AOAs), and Al-rich chondrules from metamorphosed carbonaceous chondrites (Wasson et al., 2001; Imai and Yurimoto, 2003; Itoh et al., 2004; Zhang et al., 2014; Krot et al., 2018).

The oxygen isotopic compositions of olivine and plagioclase were measured from rim to core. The $\Delta^{17}\text{O}$ range in olivine is -8.4% to -5.5% (with an average of -6.8%), whereas the plagioclase range is -2.2% to -1.5% (with an average of -1.8%) (Tables 1 and 2, Fig. 3). This indicates that the oxygen isotopes of these minerals are equilibrated and likely crystallized from a melt with a homogeneous oxygen isotopic composition. However, the $\Delta^{17}\text{O}$ range of all of the studied olivine is -8.4% – -2.3%

(with an average of -5.7‰) and the plagioclase range is -7.1‰ – -0.9‰ (with an average of -3.1‰), which indicates that these minerals are not in isotopic equilibrium. The reason for this disequilibrium is post-crystallization oxygen isotopic exchange experienced by C#1 (Krot, 2019). The spinel in C#1 is comparatively more ^{16}O -rich than other minerals, whereas the coexisting plagioclase and olivine are ^{16}O -poor. This suggests that oxygen isotopic exchange between plagioclase and olivine could have occurred owing to melting in an ^{16}O -poor gas during formation of the Ningqiang chondrite chondrules, or that plagioclase and olivine crystallized from an ^{16}O -poor melt. The spinel grains in C#1 partly preserve the original ^{16}O -rich composition, consistent with a slow dissolution rate of spinel in the C#1 melts (Beckett and Stolper, 1994) and the slow oxygen self-diffusion rate in spinel (Ryerson and McKeegan, 1994). Olivine, plagioclase, Ca-rich pyroxene, Ca-poor pyroxene, and spinel portions in C#1 are uniformly ^{16}O -depleted (Fig. 2) to a level commonly observed in chondrules from carbonaceous chondrites (Krot et al., 2006). Similarly, ^{16}O -depleted CAIs have been previously reported in enstatite, CB, CH, and CR chondrites (Guan et al., 2000b; Fagan et al., 2001; Lin et al., 2003; Krot et al., 2008). We infer that C#1 underwent a large degree of partial melting and isotopic exchange in an ^{16}O -poor nebular gas. The ^{16}O -poor composition of most components in C#1 can be explained by oxygen isotopic exchange between the melt and ^{16}O -poor nebular gas during melting in the C#1 forming regions; whereas some anorthite, pyroxene, and spinel could have experienced further oxygen isotopic exchange with a relatively ^{16}O -poor reservoir on the parent body, likely during fluid-assisted thermal metamorphism.

4.4 Evolution and precursors of C#1

The petrography, mineral chemistry, bulk compositions (Lin et al., 2003, 2006; Dai et al., 2004, 2015), oxygen isotopes (McKeegan et al., 1998; Guan et al., 2000a,b; Fagan et al., 2001), Al-Mg isotopic system, (Huss et al., 2001; Hsu et al., 2003), and rare earth elements (Lin et al., 2003) suggest the same ^{16}O -rich reservoir of CAIs in various chemical groups of chondrites. The bulk compositions of the fluffy CAIs plot along the condensation trajectory for the solar nebula. Hibonite-bearing Type As tends to sample gas-solid condensates at high temperatures, followed by hibonite-free Type As, and then by spinel-pyroxene inclusions (Lin and Kimura, 2003). The AOAs probably formed during the same processes as refractory inclusions but at lower temperature (Lin and Kimura, 2003; Krot et al., 2004; Wang et al., 2007).

CAIs are generally believed to have formed in an ^{16}O -rich nebular region at ambient temperature ($>1350\text{ K}$), possibly near the proto-Sun ($<1\text{ AU}$) (Shu et al., 1996; Krot et al., 2008), whereas chondrules are usually ^{16}O -poor (Yurimoto et al., 2008). The fractionated refractory trace element compositions of the CAIs indicate that certain CAIs (or their precursors) formed by condensation (Davis and Grossman, 1979; Lin and Kimura 2003). A few previous investigations (Maruyama et al., 1999; Yurimoto and Wasson, 2002; Maruyama and Yurimoto, 2003; Jones et al., 2004) have reported that some minerals in chondrules also have ^{16}O -rich compositions. However, most of these studies suggested that the ^{16}O -rich features could be related to relict materials from CAIs or AOAs. In this study, we believe that the ^{16}O -rich feature of the spinel in C#1 provides additional evidence that the precursor material is related to CAIs.

We suggest that the precursors of C#1 formed near the proto-Sun in the presence of an ^{16}O -rich nebular gas and were probably fine-grained inclusions from gas-solid condensation. As a result, the precursors of C#1 were ^{16}O -rich. It is generally accepted that there is an age difference of $\sim 1\text{--}2\text{ Myr}$ between the formation of CAIs and chondrules in different chondrite groups based on the ^{26}Al - ^{26}Mg systematics of chondrules (Amelin et al., 2002; Connelly et al., 2008). The difference in oxygen isotopic composition of the CAIs and chondrules may provide evidence for oxygen isotope evolution in the inner solar system—the most likely region of CAI and chondrule formation (Krot et al., 2005, 2006; Zhang et al., 2014).

CAIs formed near the Sun at the beginning of the Solar System (i.e., 4.56 billion years ago), were subsequently transported to the entire protoplanetary disk where chondrules formed, and finally accreted onto the chondrite parent asteroids. Some CAIs experienced melting during chondrule formation and recycling. In the case of C#1, CAI(s) (fine-grained and/or igneous objects such as Type B, which are difficult to discern without measuring other isotopes such as Mg or trace elements) remelted together with other ferromagnesian materials during chondrule heating. The melt's oxygen isotopic composition was controlled by the amount of melted CAI material, and oxygen isotope exchange between the gas and melt. Olivine in C#1 is more abundant than in typical coarse-grained CAIs. Some ferromagnesian materials are therefore precursors of C#1 besides CAIs (Wakaki et al., 2013; Zhang et al., 2020). We infer that the precursors of C#1 are probably CAIs + ferromagnesian chondrules, and that they remelted in the region where chondrules formed and that the oxygen isotopic composition was ^{16}O -poor. After accretion into the parent body of Ningqiang, some anorthite, pyroxene, and spinel in C#1 experienced oxygen isotopic exchange with relatively ^{16}O -poor fluid during fluid-assisted thermal metamorphism.

5 Conclusions

On a three-isotope oxygen diagram, all oxygen isotope measurements for the pyroxene rim and interior minerals in C#1 plot slightly off or along the CCAM line within error. The pyroxene rim and host therefore probably formed from the same melt. The pyroxene rim is also uniformly ^{16}O -depleted, which indicates that isotopic exchange occurred in an ^{16}O -poor reservoir.

The oxygen isotopic compositions in C#1 are similar to those in Al-rich chondrules. All of the minerals (except for some ^{16}O -rich spinel) in C#1 are uniformly ^{16}O -depleted and heterogeneous, which indicates that C#1 underwent isotopic exchange in an ^{16}O -poor nebular reservoir. We conclude that C#1 experienced a high degree of partial melting and that the spinel is likely of relict origin.

Some spinel grains are typical ^{16}O -rich, which supports that the precursor material of C#1 is related to CAIs. We suggest that the C#1 precursors are probably CAIs + chondrules. CAIs formed near the proto-Sun in the presence of an ^{16}O -rich nebular gas reservoir. Some CAIs were subsequently transported to the protoplanetary disk where chondrules formed. Finally, CAIs and some ferromagnesian chondrules remelted in the ^{16}O -poor region. Some the anorthite, pyroxene, and spinel could have undergone further oxygen isotopic exchange with a relatively ^{16}O -poor fluid on the parent body. The oxygen isotope data and formation history of C#1 are similar to those in Al-rich chondrules.

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