



# Nebular history of an ultrarefractory phase bearing CAI from a reduced type CV chondrite

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## Abstract

Ultrarefractory (UR) phases in calcium-aluminum-rich inclusions (CAIs) could have formed at higher temperature compared to common CAI minerals and thus they potentially provide constraints on very high temperature processes in the solar nebula. We report a detailed characterization of the mineralogy, petrology and oxygen isotopic composition of an UR phase davisite ( $\text{CaScAlSiO}_6$ ) bearing CAI from a reduced type CV chondrite. The CAI is an irregular-shaped, compound inclusion that consists of five units that are composed of melilite + spinel + Al, Ti-rich pyroxene  $\pm$  perovskite with various modal abundances of minerals and lithologies, and surrounded by the Wark-Lovering (WL) rim. Davisite occurs only in one lithological unit that consists of three chemically and isotopically distinct parts: (i)  $^{16}\text{O}$ -poor ( $-20\text{‰} \leq \delta^{18}\text{O} \leq 0\text{‰}$ ) regions with reversely zoned melilite and davisite; (ii)  $^{16}\text{O}$ -rich ( $-50\text{‰} \leq \delta^{18}\text{O} \leq -40\text{‰}$ ) regions consisting of unzoned, gehlenitic melilite, Al, Ti-rich diopside and spinel; and (iii) spinel framboids composed of  $^{16}\text{O}$ -rich spinel and  $^{16}\text{O}$ -poor melilite. Absence of secondary iron- and/or alkali-rich phases, occurrence of low-iron, manganese-enriched (LIME) olivine, and random distribution of the oxygen isotopic heterogeneity indicate that primitive chemical and isotopic compositions are preserved in the inclusion. The occurrence of chemical and isotopic heterogeneities with sharp boundaries in the CAI indicates formation of the inclusion by an aggregation of mineral assemblages formed and processed separately at different time and/or space in the solar nebula. Although isotope exchange between  $^{16}\text{O}$ -rich solids and  $^{16}\text{O}$ -poor gases prior to the final agglomeration of the CAI cannot be ruled out, we suggest that modification of chemical and isotopic composition of porous CAI precursors or aggregation of isotopically distinct mineral assemblages are alternative scenarios for the origin of oxygen isotopic heterogeneity in CAIs. In either case, coexistence of spatially and/or temporally distinct  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor gaseous reservoirs at the earliest stage of the solar system formation is required. The grain-scale oxygen isotopic disequilibrium in the CAI indicate that post-formation heating of the inclusion (i.e., the WL rim formation event) was short (e.g.,  $\leq 10^3$  h at 1400 K;  $\leq 10^5$  h at 1100 K), which can be achieved by rapid outward transport of the CAI. High  $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$  ratios of pyroxene from CAI interior and the rim and LIME composition of the olivine rim document that the entire CAI formation process took place under highly reducing conditions.

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## 1. INTRODUCTION

Calcium-aluminum-rich inclusions (CAIs) are the oldest dated solar system solids (Connelly et al., 2012) and the key objects for understanding of physicochemical processes in the earliest stage of the solar system evolution (e.g., MacPherson, 2014 and references therein). CAIs mostly occur as  $\mu\text{m}$ - to  $\text{cm}$ -sized inclusions in chondritic meteorites, especially in CV carbonaceous chondrites (e.g., Hezel et al., 2008), and consist of various kinds of refractory minerals (e.g., melilite, spinel, Al,Ti-rich diopside) that are predicted by thermodynamic models to be among the first solids to condense from a cooling gas of the solar composition (e.g., Grossman, 1972). They are considered to have formed during high-temperature processes including condensation, evaporation, aggregation and melting that occurred near the proto-Sun (e.g., McKeegan et al., 2000; Sossi et al., 2017). Shortly after their formation, CAIs were transported to the asteroid- or even comet-forming region (e.g., Zolensky et al., 2006) via X-winds (e.g., Shu et al., 1996), outwards turbulent flow (e.g., Ciesla, 2007), or disk winds (Van Kooten et al., 2016).

Bulk CAIs sometimes show the group II Rare Earth element (REE) patterns in which the most refractory (ultra-refractory–UR) and the most volatile REEs are depleted compared to moderately refractory ones (e.g., Tanaka and Masuda, 1973). Such a pattern can only be produced by fractional condensation in which earlier condensates were removed from a gas before the condensation is completed (Boynton, 1975). Therefore, the earlier condensates should be enriched in the UR elements. In some rare cases, UR phases such as davisite ( $\text{CaScAlSiO}_6$ ; Ma and Rossman, 2009a) and Zr and/or Y-rich perovskite form UR CAIs, whose bulk chemical composition show a large enrichment ( $> 1000 \times \text{CI}$ ) in the most refractory elements (e.g., Davis and Hinton, 1985; Simon et al., 1996; ElGoresy et al., 2002). UR phases also occur in a very minor population of CAIs which mostly consist of non-UR phases (e.g., Lin et al., 2003) and amoeboid olivine aggregates (AOAs) (Noonan et al., 1977; Ma et al., 2012; Komatsu et al., 2018). Since evaporation experiments have failed to reproduce the REE patterns observed in UR CAIs (Davis and Hashimoto, 1995; Davis et al., 1995) and the natural UR CAIs show no clear isotopic evidence for mass fractionation during evaporation (Simon et al., 1996), these inclusions are unlikely to be evaporation residues. In contrast, thermodynamic calculations demonstrated that the UR REE pattern could be produced by condensation (e.g., Davis and Grossman, 1979; Simon et al., 1996; Davis et al., 2018). As the UR phases are expected to have formed at higher temperatures compared to common CAI minerals, they can potentially provide constraints on physicochemical processes occurred in the beginning of the solar system formation (Krot et al., 2018a). However, due to their rare occurrences and small grain sizes, the detailed formation history of the UR phases is poorly understood.

Oxygen isotopes in CAI minerals show mass-independent fractionation (e.g., Clayton et al., 1977; Yurimoto et al., 2008 and references therein). On an oxygen three-isotope diagram, the individual CAI minerals

distribute along a slope  $\sim 1$  line, which is known as the carbonaceous chondrite anhydrous minerals (CCAM) line (Clayton et al., 1977), except for minerals in Fractionation and Unidentified Nuclear effects (FUN) CAIs (e.g., Krot et al., 2014). Most CAIs in unmetamorphosed (petrologic types  $\leq 3.0$ ) carbonaceous chondrites have uniformly  $^{16}\text{O}$ -rich compositions ( $-50\text{‰} \leq \delta^{18}\text{O} \leq -40\text{‰}$ ), suggesting that the majority of CAIs are originated in a solar-like,  $^{16}\text{O}$ -rich gaseous reservoir (McKeegan et al., 2011; Yurimoto et al., 2008 and references therein). On the other hand, mineral-scale oxygen isotopic heterogeneity is commonly observed in CAIs from CV and metamorphosed (petrologic types  $> 3.1$ ) chondrites (e.g., Yurimoto et al., 2008 and references therein). In most of these CAIs, spinel, hibonite, Al,Ti-rich diopside and forsterite are  $^{16}\text{O}$ -rich ( $-50\text{‰} \leq \delta^{18}\text{O} \leq -40\text{‰}$ ) whereas melilite, anorthite and secondary alkali- and/or iron-rich phases are  $^{16}\text{O}$ -poor ( $-30\text{‰} \leq \delta^{18}\text{O} \leq 10\text{‰}$ ). To date, several models have been proposed for a possible origin of the oxygen isotopic heterogeneity: (i) modification of isotope composition during fluid-assisted thermal metamorphism on the chondrite parent body (e.g., Wasson et al., 2001; Aléon et al., 2005); (ii) gas-melt isotope exchange during partial or disequilibrium melting in the solar nebula (e.g., Yurimoto et al., 1998; Aléon et al., 2002; Kawasaki et al., 2017b; Aléon, 2018); (iii) isotope exchange by solid-state diffusion during nebular reheating events (e.g., Clayton et al., 1977; Itoh and Yurimoto, 2003; Simon et al., 2011, 2016); and (iv) changes in the isotopic composition of a nebular gas during CAI condensation (e.g., Katayama et al., 2012; Kawasaki et al., 2012, 2017a; Park et al., 2012a).

The UR minerals sometimes show  $^{16}\text{O}$ -depletion (Ivanova et al., 2012, 2017; Zhang et al., 2015; Aléon et al., 2018), whose origin remains controversial. Ivanova et al. (2012) reported that UR oxide, Zr,Sc-rich pyroxene and Y-rich perovskite in an UR inclusion 3N-24 in a forsterite-bearing CAI from NWA 3118 (CV<sub>ox</sub>) are  $^{16}\text{O}$ -poor, whereas spinel and Al,Ti-rich diopside are  $^{16}\text{O}$ -rich. They also showed that in an UR inclusion 33E-1 in a fluffy type A CAI from Efremovka, UR oxide, davisite and Y-rich perovskite are depleted in  $^{16}\text{O}$ , and Al,Ti-rich diopside and spinel are enriched in  $^{16}\text{O}$ . The authors suggested that these inclusions originated in a  $^{16}\text{O}$ -rich gaseous reservoir and subsequently experienced isotope exchange in a  $^{16}\text{O}$ -poor gaseous reservoir, and they preferred post-crystallization isotope exchange in such UR phases due to their faster O self diffusion compared to spinel and diopside. However, the detailed mechanism and timing of the isotopic modification are unclear. Zhang et al. (2015) reported that an UR inclusion A0031 from Sayh al Uhaymir 290 (CH), which is composed of various UR phases such as panguite ( $(\text{Ti}^{4+}, \text{Sc}, \text{Al}, \text{Mg}, \text{Zr}, \text{Ca})_{1.8}\text{O}_3$ ; Ma et al., 2012), davisite and Sc-rich anosovite ( $(\text{Ti}^{4+}, \text{Ti}^{3+}, \text{Mg}, \text{Sc}, \text{Al})_3\text{O}_5$ ) associated with spinel, anorthite, and perovskite, is uniformly depleted in  $^{16}\text{O}$ . They concluded that the inclusion condensed from a  $^{16}\text{O}$ -depleted nebular gas. Ivanova et al. (2017) revealed that spinel and rubinite ( $\text{Ca}_3\text{Ti}_2^{3+}\text{Si}_3\text{O}_{12}$ ; Ma et al., 2017) are  $^{16}\text{O}$ -rich; Zr,Sc-bearing grossmanite ( $\text{CaTi}^{3+}\text{AlSiO}_6$ ; Ma and Rossman,

2009b) and melilite are  $^{16}\text{O}$ -poor; and perovskite is intermediate in an UR CAI 40E-1 in a compound CAI. Aléon et al. (2018) showed that in an UR compact type A CAI E101.1 from Efremovka ( $\text{CV}_{\text{red}}$ ), Zr,Sc-rich diopside and nepheline are similarly depleted in  $^{16}\text{O}$ , Zr,Sc-poor diopside is  $^{16}\text{O}$ -rich, and UR perovskite and melilite have variable oxygen isotopic compositions. The authors suggested crystallization of the Zr,Sc-rich diopside by interaction between  $^{16}\text{O}$ -poor melt and the UR perovskite, and relict origin for the  $^{16}\text{O}$ -rich diopside. They proposed that the CAI originated in a  $^{16}\text{O}$ -rich gas and experienced isotopic exchange with a  $^{16}\text{O}$ -poor gaseous reservoir during partial melting. Thus, the origin of oxygen isotopic heterogeneity observed in UR phase bearing CAIs can be variable among different inclusions but is not fully understood. Further isotopic studies on the UR phase bearing inclusions can provide us insights into the early solar system processes that provided isotopic heterogeneities in these highly refractory objects.

Here we report petrology, mineral chemistry and oxygen isotopic composition of an UR phase bearing CAI R3C-01-U1 from the reduced type CV chondrite Roberts Massif (RBT) 04143. In this inclusion, Ti,V-rich davisite coexists with common CAI minerals such as melilite, Al,Ti-rich diopside, and spinel, and they are isotopically heterogeneous. Based on the occurrence, mineral chemistry, and oxygen isotope compositions of Ti,V-rich davisite and associated phases including spinel frambooids (El Goresy et al., 1979), we discuss origin and thermal history of the CAI, and physicochemical conditions of the solar nebula.

## 2. ANALYTICAL METHODS

### 2.1. Scanning electron microscope analyses

Petrology and mineralogy of the CAI R3C-01-U1 in a polished thick section of the CV chondrite RBT 04143 were initially characterized with backscattered electron (BSE) imaging using Hitachi S-3400N scanning electron microscope (SEM) and JEOL JSM-7001F field-emission scanning electron microscope (FE-SEM) at Tohoku University (TU). Semi-quantitative analyses were performed using Oxford INCA energy-dispersive spectrometers (EDS) that were installed on both SEM, at an accelerating voltage of 15 kV and a beam current of 1.0–1.4 nA.

### 2.2. Electron probe microanalyzer analysis

Quantitative X-ray microanalyses of melilite, spinel, perovskite and pyroxene were performed at TU and Korea Polar Research Institute (KOPRI) using JEOL JXA-8530F field-emission electron probe microanalyzers (FE-EPMA) equipped with wavelength-dispersive X-ray spectrometers (WDS). All electron probe analyses are available as [Supplementary Information](#). A defocused electron beam of 3  $\mu\text{m}$  in diameter accelerated at 15 kV with a beam current of 10 nA was used to quantify 14 elements (Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, V, Zr, Hf, Sc and Y) in melilite, spinel and perovskite. The peak counting times were 10 s for Na; 20 s for Si, Al, Mg and Ca; and 40 s for Ti, Cr,

Fe, Mn, V, Sc and Y. Silicon, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, V and Sc were measured using *K $\alpha$*  and Zr, Hf and Y were quantified using the *L $\alpha$* . Natural and synthetic crystalline minerals were used as standards. Matrix corrections were applied using the atomic number (Z), absorption (A), and fluorescence (F) (ZAF) correction method. The detection limits were 0.01 wt% for  $\text{Cr}_2\text{O}_3$ , FeO, MnO, MgO, CaO,  $\text{Na}_2\text{O}$  and  $\text{Sc}_2\text{O}_3$ ; 0.02 wt% for  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ ; 0.03 wt% for  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Y}_2\text{O}_3$ ; and 0.05 wt% for  $\text{HfO}_2$ . Analyses with totals below 98 wt% and above 102 wt% were excluded from consideration. A focused electron beam accelerated at 10 kV with a beam current of 20 nA was used to quantify 13 elements (Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, V, Zr, Sc and Y) in pyroxene. The peak counting times were 10 s for Na and 20 s for other elements. Other conditions were similar to analyses of melilite, spinel and perovskite. Detection limits were 0.01 wt% for MgO, CaO and  $\text{Na}_2\text{O}$ ; 0.02 wt% for  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , MnO,  $\text{V}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{Sc}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$ ; and 0.03 wt% for  $\text{SiO}_2$ ,  $\text{TiO}_2$  and FeO. The amounts of  $\text{Ti}^{3+}$  in pyroxene with  $\text{TiO}_2 \geq 4$  wt% were calculated by assuming the pyroxene is ideally stoichiometric (4 cations per 6 oxygen atoms) and titanium is the only element with various valence states (Beckett, 1986). Quantitative chemical composition of olivine was measured using the JEOL JXA-8800 electron microprobe equipped with WDS detectors at TU. Analyses were conducted at an accelerating voltage of 15 kV and a beam current of 10 nA with a counting time 20 s for each element. 11 elements (Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, K and Ni) were quantitatively determined. Other conditions were similar to the aforementioned analyses. Detection limits are 0.02 wt% for  $\text{Al}_2\text{O}_3$ , MgO, CaO,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ; 0.03 wt% for  $\text{SiO}_2$ ,  $\text{Cr}_2\text{O}_3$ , FeO and MnO; and 0.04 wt% for  $\text{TiO}_2$  and NiO.

X-ray elemental maps of Si, Ti, Al, Fe, Mg, Ca, Na, V and Sc were obtained using FE-EPMA at TU and KOPRI. For both instruments, a focused electron beam was used at 15 kV accelerating voltage, 20–50 nA beam current and 20–100 ms per pixel dwell time. Obtained X-ray elemental maps were processed using ImageJ, Python and R.

The bulk chemical composition of R3C-01-U1 was obtained using average chemical compositions of each phase and their modal abundances and densities. The modal abundance of each mineral was calculated using high-resolution X-ray elemental maps processed using the ImageJ software and Python codes. A quantitative map of åkermanite content in melilite was obtained using spot EPMA data within a mapped area as referential composition.

### 2.3. Electron back-scatter diffraction analysis

Electron back-scatter diffraction (EBSD) analyses were performed to obtain crystal orientation maps of melilite using Oxford AZtec EBSD system on the FE-SEM at TU. Prior to the measurements, the sample surface was polished using 1  $\mu\text{m}$  alumina lapping film followed by a chemomechanical polish by a combination of colloidal silica and a Buehler VibroMet 2 Vibratory Polisher for 3 h. The polished sample was then coated with a thin layer of

carbon. Analyses were conducted at an acceleration voltage of 15 kV and beam current of 3.4 nA under a high vacuum. The grain boundaries of melilite crystals were identified based on crystallographic orientation maps, BSE images and X-ray elemental maps.

## 2.4. Oxygen isotope analysis

Spot oxygen isotope analyses were performed with the Cameca ims-1270 ion microprobe at Hokkaido University. A primary  $\text{Cs}^+$  ion with a beam current of 0.1 nA was used to achieve a count rate of  $\sim 5 \times 10^7$  cps for  $^{16}\text{O}^-$ . The  $\text{Cs}^+$  ions were accelerated with 20 kV to sputter the  $\sim 5\text{--}7$   $\mu\text{m}$  spot (in diameter) of the sample surface coated by gold. An electron flood gun was used for a charge compensation. Negative secondary ions were detected using a Faraday cup (for  $^{16}\text{O}^-$ ) and an electron multiplier (for  $^{17}\text{O}^-$  and  $^{18}\text{O}^-$ ). The mass resolution was set to  $M/\Delta M \sim 7000$  to resolve  $^{16}\text{O}^1\text{H}^-$  and  $^{17}\text{O}^-$ . Each mass peak in a cycle was measured for 1 s, 2 s and 1 s for  $^{16}\text{O}^-$ ,  $^{17}\text{O}^-$  and  $^{18}\text{O}^-$ , respectively, in the magnet peak switching mode. San Carlos olivine standard was used to correct instrumental mass fractionation. Results are reported using the conventional delta-notation relative to the Standard Mean Ocean Water (SMOW):

$$\delta^{17,18}\text{O} = \left( \frac{^{17,18}\text{O}_{\text{Sample}}}{^{17,18}\text{O}_{\text{SMOW}}} - 1 \right) \times 1000(\text{‰}). \quad (1)$$

Analytical uncertainties are estimated based on an internal error of each measurement and reproducibility of the standard measurements and are reported in  $2\sigma$ . The sample was investigated using the SEM to make sure that there was no contamination due to beam overlapping onto neighboring phases and the sampling area was free of cracks.

Quantitative oxygen isotope imaging (isotopograph) of melilite, spinel, perovskite and pyroxene was obtained using the isotope microscope system consisting of the Cameca ims-1270 ion microprobe and a high-efficiency Stacked CMOS-type Active Pixel Sensor (SCAPS) ion imager at Hokkaido University (Takayanagi et al., 1999; Yurimoto et al., 2003; Sakamoto et al., 2008). Analytical conditions were generally similar to those in Park et al. (2012a) and Zhang et al. (2015), otherwise described below. A  $\text{Cs}^+$  primary beam was set to  $\sim 65$   $\mu\text{m} \times 55$   $\mu\text{m}$  and intensity of  $\sim 3$  nA. Two measurement cycles were performed to obtain secondary ion images of  $^{16}\text{O}^-$  and  $^{18}\text{O}^-$ . Each cycle consists of 1 frame for  $^{16}\text{O}^-$  and 40 frames for  $^{18}\text{O}^-$  with each frame of 5 s. Before the oxygen isotope mapping,  $^{27}\text{Al}^{16}\text{O}^-$  was also mapped for 1 frame to identify the locations of minerals in the imaged area. The  $\delta^{18}\text{O}$  isotopograph was obtained by calculating the secondary ion ratios of  $^{18}\text{O}^-/^{16}\text{O}^-$  for each pixel and then calibrated with a spinel grain in the imaging area, whose oxygen isotopic composition was determined by the spot analysis. The obtained  $\delta^{18}\text{O}$  isotopograph was smoothed with a moving-average of  $3 \times 3$  pixels to reduce statistical error to be  $\pm 6\text{‰}$  ( $1\sigma$ ) in the processed image. Spatial resolution of isotopography is calculated to be  $\sim 1$   $\mu\text{m}$ , which corresponds  $\sim 4.3$  pixels (see [Supplementary Information](#) for more details).

## 3. RESULTS

### 3.1. Mineralogy and petrology

#### 3.1.1. Overview of mineralogy and petrology of R3C-01

The UR phase bearing CAI R3C-01-U1 ( $1.0 \times 0.6$  mm) is one of five lithological units (Table 1) that form an irregularly-shaped, compound CAI R3C-01 ( $1.5 \times 0.8$  mm; Fig. 1). Petrology and mineralogy of R3C-01-U1 are distinct from the common CAIs and the other four units of R3C-01: for instance, davisite and high concentration of spinel inclusions are observed only in this unit (Figs. 1–3 and A1). The detailed mineralogy and petrology of R3C-01-U1 is described later in this section.

Unit 2 of R3C-01 consists of melilite, irregular-shaped clusters of spinel grains, tiny perovskite and Al,Ti-rich diopside (Fig. A1f). Al,Ti-rich diopside commonly surrounds perovskite or it is associated with spinel but no davisite is observed in this unit. There are some spinel clusters in the Unit 2 which show frambooid-like texture, but their abundance is much lower than that in R3C-01-U1. The Unit 2 is separated from R3C-01-U1 by the Wark-Lovering (WL) rim. Unit 3 of R3C-01 is a less-irregular domain with melilite-rich core and spinel-rich mantle (Fig. A1g). The grain size of melilite is larger in the core ( $\sim 50$   $\mu\text{m}$  in diameter) than in the mantle ( $\leq 20$   $\mu\text{m}$ ). The core melilite show reverse zoning ( $\text{\AA}k_5$  and  $\text{\AA}k_{30}$  in the core and rim, respectively). The core contains some large cracks and pores, and the mantle has numerous tiny pores. No davisite grain occurs in this unit. Spinel occurs as euhedral small ( $\sim 10$   $\mu\text{m}$ ) grains, some of which are forming small ( $\sim 20\text{--}50$   $\mu\text{m}$ ) clusters. Perovskite occurs as irregular  $\sim$  sub-rounded grains embedded in the outer core of this unit, and its  $\text{V}_2\text{O}_3$  content is higher than that in R3C-01-U1 (0.7–1.3 wt% and 0.1–0.8 wt%, respectively), whereas  $\text{ZrO}_2$  concentration is lower in the Unit 3 (0.05–0.15 wt% and 0.15–0.35 wt%, respectively; Table 1). Irregular Al,Ti-rich pyroxene occurs in the mantle of this subinclusion. The continuous occurrence of spinel-rich mantle around the core distinguishes the Unit 3 from associated Unit 2 and Unit 4. Unit 4 consists of unzoned melilite, fine-grained spinel and Al,Ti-rich diopside intergrown with spinel (Fig. A1h). Melilite in this subinclusion show lower  $\text{\AA}k$  content ( $\text{\AA}k_{5-15}$ ) relative to melilite in the other units (Table 1). Spinel has lower  $\text{V}_2\text{O}_3$  content (0.1–0.2 wt%) than in other units (Table 1). Perovskite is rare and davisite is absent in this domain. Unit 5 consists of compact melilite, thick layers of spinel, perovskite and Al,Ti-rich diopside surrounding perovskite or intergrown with spinel (Fig. A1g). Based on these mineralogical and petrological observations, it is likely that R3C-01 is a compound of at least five melilite-rich CAIs. Note that the number of lithological units in the CAI is a minimum since we only see a 2D section of the inclusion.

Tiny grains of refractory metal nuggets (RMNs) are observed in each lithological unit. Secondary iron- and/or alkali-rich phases such as nepheline, sodalite and hydrous silicates are not observed in any units. The outer margin of the inclusion is surrounded by the multi-layered WL

Table 1

Summary of petrological and mineralogical characters used to distinguish five lithological units in R3C-01.

Unit	1 (R3C-01-U1)	2	3	4	5
Size (mm)	1.5 × 0.8	0.7 × 0.4	0.3 × 0.3	0.3 × 0.2	0.3 × 0.2
Shape	Irregular	Irregular	Subrounded	Subrounded	Nodular
Core-mantle structure	–	–	+	–	–
Typical grain size of melilite (μm)	20–50	~20	~50 (core); ~15 (mantle)	~10	~50
Davite	+	–	–	–	–
Spinel framboids	++	+	+	–	–
Irregular-shaped Al,Ti-rich pyroxene	++	–	+	++	+
Reversely-zoned melilite	+	–	+	–	+
Perovskite	++	+	++	–	–
Åk (mol%) in melilite	5–30	5–25	5–30	5–15	10–30
V <sub>2</sub> O <sub>3</sub> (wt%) in spinel	0.1–0.8	0.3–0.4	0.3–0.4	0.1–0.2	~0.2
ZrO <sub>2</sub> (wt%) in perovskite	0.15–0.35	0.10	0.05–0.15	–	–
V <sub>2</sub> O <sub>3</sub> (wt%) in perovskite	0.1–0.8	NA	0.7–1.3	–	–

NA—not available.

rim (Wark and Lovering, 1977) composed of spinel, Al,Ti-rich/poor diopside and olivine + Fe,Ni-metal layers (Figs. 1 and A1d). Based on the constant thickness of the olivine layer, we consider it as a part of the WL rim rather than a forsterite-rich accretionary rim, which is commonly observed around CV CAIs with a highly variable thickness that is controlled by the topography of the host inclusion (e.g., Krot et al., 2001). High Ca content in the olivine (up to 0.8 wt%) is also distinct from those in common forsterite-rich accretionary rim (mostly < 0.4 wt%; e.g., Krot et al., 2001).

### 3.1.2. Mineralogy and petrology of R3C-01-U1

R3C-01-U1, the largest part of the compound CAI R3C-01, mainly consists of fine-grained (<50 μm) melilite and spinel, with minor perovskite, Al,Ti-rich pyroxene (Figs. 1–4 and A1a–e), and RMNs. The CAI does not show

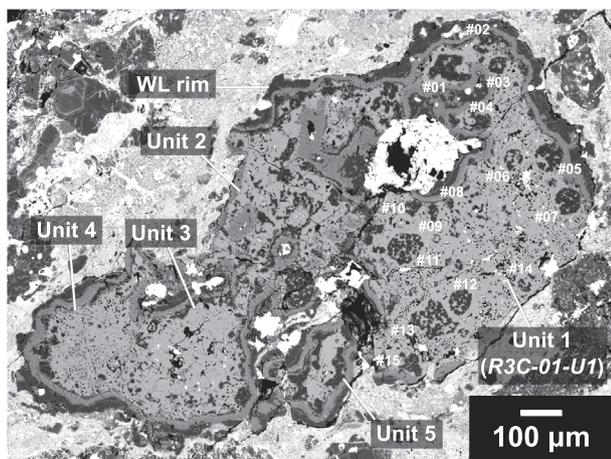


Fig. 1. BSE image of the compound CAI R3C-01 from RBT 04143. Spinel framboids in R3C-01-U1 (#01–15) are indicated by labels. Enlarged image of a part of the CAI is shown in Figs. 2–4. Some holes and cracks in the thick section are filled with a gold, which had been coated for previous SIMS study and could not be removed by polishing. Abbreviations: WL rim—Wark-Lovering rim.

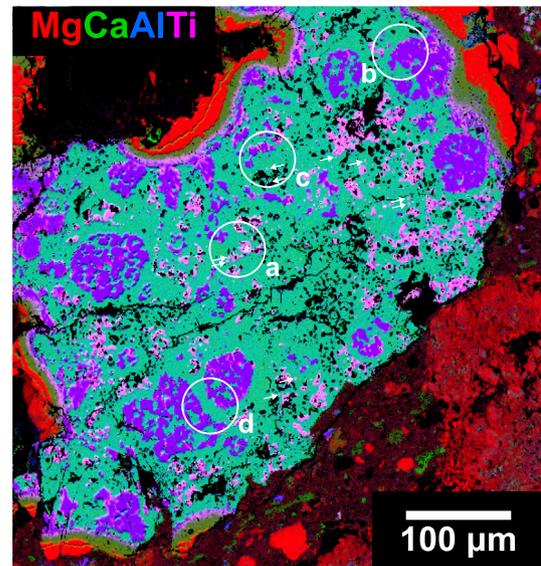


Fig. 2. Combined elemental map in Mg (red), Ca (green), Al (blue) and Ti (pink) K $\alpha$ X-rays image of R3C-01-U1. The analysis areas for isotopography (Fig. 4) are also shown by white circles with labels. Arrows show occurrences of Ti,V-rich davite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

any obvious core-mantle structure (Figs. 1 and 2). Representative microprobe analyses of minerals in R3C-01-U1 are listed in Tables 2 and 3 and A1–A4.

The X-ray elemental map and EBSD crystal orientation map show that R3C-01-U1 consists of small (<50 μm) grains of reversely-zoned, relatively Åk-rich melilite (typically Åk<sub>15–20</sub> in the core and Åk<sub>5</sub> at the rim) and unzoned Åk-poor melilite (typically Åk<sub>5</sub>), with random crystal orientation and 120° triple junctions at some grain boundaries (Fig. 4).

Al,Ti-rich pyroxene in the interior R3C-01-U1 shows various occurrences (Figs. 3 and A1a–e). Most Al,Ti-rich pyroxene in R3C-01-U1, which occurs as irregularly-shaped grains of <5 μm in diameter attached to perovskite

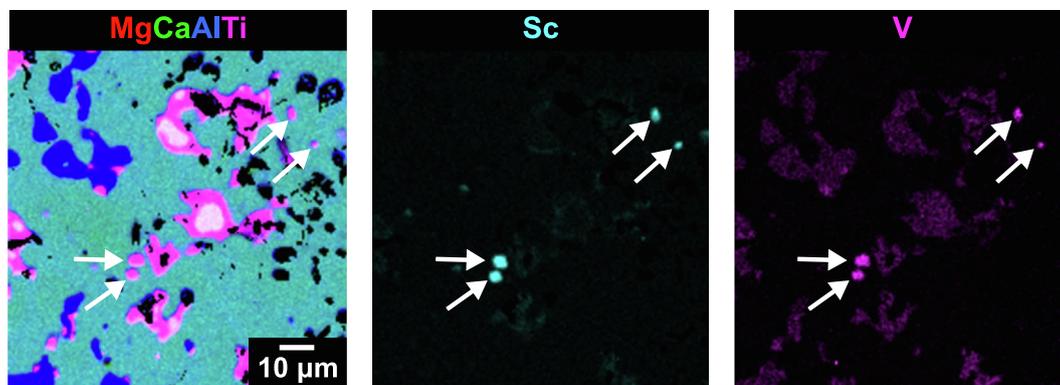


Fig. 3. Combined X-ray map in Mg (red), Ca (green), Al (blue) and Ti (pink) and elemental maps in Sc and V  $K\alpha$  X-rays of R3C-01-U1 (area a in Fig. 2). Arrows show occurrences of Ti, V-rich davisite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

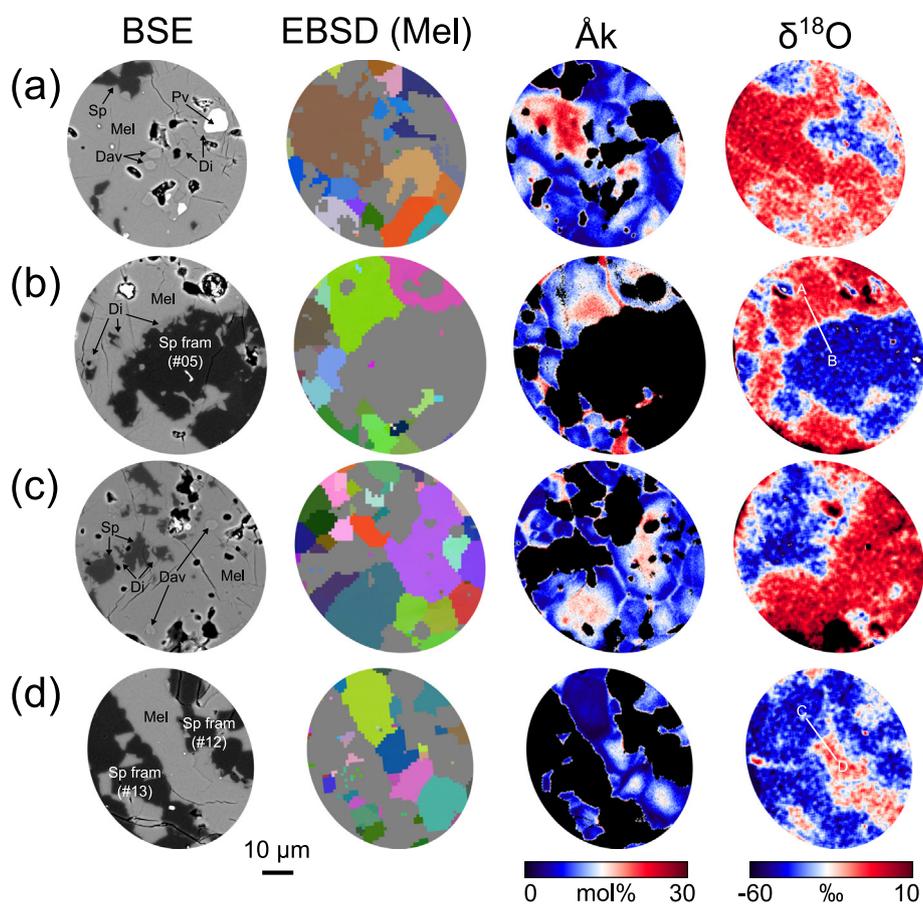


Fig. 4. BSE image, EBSD crystal orientation map of melilite, åkermanite (Åk) content map of melilite and  $\delta^{18}\text{O}$  isotopograph for each analyzed areas. In EBSD maps, similar colors indicate similar crystal orientations. Line profiles along lines A–B and C–D are shown in Fig. B1 and Fig. 11, respectively. The  $\delta^{18}\text{O}$  value around pores and cracks could be affected by differences in topography of the sample surface (Park et al., 2012b). Abbreviations: Dav–davisite; Di–diopside; Mel–melilite; Pv–perovskite; Sp–spinel; Sp fram–spinel framboïd. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and/or spinel, is a member of Al,Ti-rich diopside with 20.9–25.2 wt%  $\text{Al}_2\text{O}_3$ ; 10.2–17.0 wt%  $\text{TiO}_2^{\text{tot}}$  ( $= \text{Ti}_2^{3+}\text{O}_3 + \text{Ti}^{4+}\text{O}_2$ ); 0.1–0.5 wt%  $\text{Sc}_2\text{O}_3$ ; 0.2–1.4 wt%  $\text{V}_2\text{O}_3$ ; and 0–0.3 wt%  $\text{ZrO}_2$  (Fig. 5 and 6 and Table 2). On the other

hand, euhedral pyroxene grains ( $<5\ \mu\text{m}$ ; mostly 2–3  $\mu\text{m}$ ) isolated in reversely-zoned melilite are Ti, V-rich davisite with 20.8–22.8 wt%  $\text{Al}_2\text{O}_3$ ; 10.8–13.6 wt%  $\text{TiO}_2^{\text{tot}}$ ; 6.2–8.9 wt%  $\text{Sc}_2\text{O}_3$ ; 2.2–3.7 wt%  $\text{V}_2\text{O}_3$ ; and 0.5–0.7 wt%  $\text{ZrO}_2$

Table 2  
Major element composition of Al,Ti-rich pyroxene in R3C-01-U1.

wt%	77 <sup>a</sup>	163 <sup>a</sup>	86 <sup>b</sup>	84 <sup>b</sup>	103 <sup>c</sup>	178 <sup>c</sup>	75 <sup>d</sup>	172 <sup>d</sup>	283 <sup>e</sup>	366 <sup>e</sup>	13 <sup>f</sup>	14 <sup>f</sup>	23 <sup>f</sup>
SiO <sub>2</sub>	28.4	29.5	27.7	27.6	24.9	29.1	28.6	29.8	38.9	37.3	37.4	42.0	52.9
TiO <sub>2</sub> <sup>tot</sup>	16.6	15.5	17.4	17.7	19.0	15.2	16.4	16.2	8.4	11.0	10.4	4.3	0.1
Ti <sub>2</sub> O <sub>3</sub>	8.5	6.9	8.4	9.7	10.1	5.8	8.2	8.6	7.4	8.4	5.7	1.8	n.a.
TiO <sub>2</sub>	7.1	7.8	8.0	7.0	7.7	8.8	7.3	6.6	0.2	1.7	4.1	2.3	0.1
Al <sub>2</sub> O <sub>3</sub>	24.5	24.2	24.5	25.3	25.6	25.7	24.4	23.2	19.0	19.6	17.9	17.2	4.6
Cr <sub>2</sub> O <sub>3</sub>	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.1	b.d.	0.1	0.0	0.0
FeO	0.0	0.1	b.d.	0.1	0.0	0.1	b.d.	b.d.	0.1	0.1	b.d.	0.1	b.d.
MnO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.0	0.0	b.d.	b.d.
MgO	4.8	5.2	4.9	4.3	3.0	6.3	5.2	5.7	8.8	8.6	8.9	10.6	16.4
CaO	24.9	25.9	24.8	24.8	24.6	24.5	24.7	24.5	24.1	23.9	25.4	25.7	25.9
Na <sub>2</sub> O	b.d.	b.d.	0.0	b.d.	0.0	0.0	b.d.	0.1	b.d.	0.0	b.d.	0.1	0.1
V <sub>2</sub> O <sub>3</sub>	1.0	0.6	0.5	0.5	1.8	0.5	1.0	0.7	0.4	0.2	0.6	0.3	0.0
ZrO <sub>2</sub>	0.1	0.1	0.2	0.2	0.3	0.1	0.2	0.1	0.0	0.1	0.0	b.d.	0.0
Sc <sub>2</sub> O <sub>3</sub>	0.5	0.0	0.5	0.5	1.2	0.0	0.6	0.2	0.1	0.0	0.2	0.1	0.0
Y <sub>2</sub> O <sub>3</sub>	b.d.	b.d.	0.0	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	b.d.	b.d.
Total	99.8	100.5	99.6	100.0	99.4	101.0	100.3	99.5	99.1	100.1	100.5	100.2	100.2
<i>Cations per 24 oxygen</i>													
Si	1.1	1.1	1.1	1.1	1.0	1.1	1.1	1.1	1.4	1.5	1.4	1.5	1.9
Ti <sup>3+</sup>	0.3	0.2	0.3	0.3	0.3	0.2	0.3	0.3	0.2	0.3	0.2	0.1	n.a.
Ti <sup>4+</sup>	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.0	0.0	0.1	0.1	0.0
Al	1.1	1.1	1.1	1.1	1.2	1.1	1.1	1.0	0.8	0.9	0.8	0.7	0.2
Cr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	n.a.	0.0	0.0	0.0
Fe	0.0	0.0	n.a.	0.0	0.0	0.0	n.a.	n.a.	0.0	0.0	n.a.	0.0	n.a.
Mn	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0	0.0	n.a.	n.a.
Mg	0.3	0.3	0.3	0.2	0.2	0.3	0.3	0.3	0.5	0.5	0.5	0.6	0.9
Ca	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Na	n.a.	n.a.	0.0	n.a.	0.0	0.0	n.a.	0.0	n.a.	0.0	n.a.	0.0	0.0
V	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Zr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	n.a.	0.0
Sc	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Y	n.a.	n.a.	0.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0	n.a.	n.a.
Ti <sup>3+</sup> /Ti <sup>tot</sup>	0.57	0.50	0.54	0.61	0.59	0.42	0.56	0.59	0.97	0.84	0.61	0.47	n.a.

b.d.– below detection limit; n.a.– not available.

<sup>a</sup> Px attached to Pv.

<sup>b</sup> Px attached to Pv + Sp.

<sup>c</sup> Px attached to Sp.

<sup>d</sup> Px attached to pore.

<sup>e</sup> Px WL Sp layer in WL rim.

<sup>f</sup> Px in WL rim.

(Fig. 5 and 6, Table 3). The calculated Ti<sup>3+</sup>/Ti<sup>tot</sup> ratios mostly range from 0.3 to 0.8 for Al,Ti-rich diopside and from 0.6 to 0.9 for Ti,V-rich davisite (Fig. 5 and 6 and Tables 2,3). Note that quantitative analyses of Al,Ti-rich pyroxene attached to spinel described above are possibly contaminated by beam overlapping onto spinel due to tiny grain size of pyroxene, as seen in their elevated Al and Mg contents and lower Ti<sup>3+</sup>/Ti<sup>tot</sup> ratio (open symbols in Fig. 5). Thus, its Ti<sup>3+</sup>/Ti<sup>tot</sup> ratio should be considered as the lower limit for its true ratio (Dyl et al., 2011). Importantly, measurements of pyroxene which is not attached to spinel (filled symbols or asterisks in Fig. 5) do not show clear contamination by other phases.

Spinel in R3C-01-U1 occurs as euhedral grains (<20 μm) and its chemical composition is nearly pure MgAl<sub>2</sub>O<sub>4</sub> with FeO and Cr<sub>2</sub>O<sub>3</sub> ≤ 0.2 wt% (Table A2). Most spinel grains form framboidal aggregates (Figs. 1, 2 and A1a,b,e). Fifteen framboids (#01–15) are identified in R3C-01-U1. Palisade

bodies, spheroidal shells of spinel enclosing typical CAI minerals that commonly coexist with framboids (Simon and Grossman, 1997), are apparently absent in this inclusion. All framboids are surrounded by relatively coarse (>10 μm), reversely-zoned melilite (typically Åk<sub>15–20</sub> in the core and Åk<sub>5</sub> at the rim) and unzoned melilite (typically Åk<sub>5</sub>) grains and enclose tiny melilite (<10 μm) (Fig. 4b, d). In most framboids, spinel occurs with small amounts of Al,Ti-rich diopside (<5 μm), whereas tiny perovskite is also associated with spinel and Al,Ti-rich diopside in one framboid (#13; Fig. 4d). Vanadium oxide content of spinel in framboids ranges between 0.2 to 0.8 wt%, but the value is nearly constant within each framboids (Fig. 7 and Table A2). Framboidal spinel attached to the rim show lower V<sub>2</sub>O<sub>3</sub> contents compared to those from the inner part of the CAI, and spinel in the WL rim shows the lowest value. The V content in spinel is not correlated well with abundances of other elements (e.g., Ti, Cr).

Table 3  
Major element composition of davisite in R3C-01-U1.

wt%	226	227	228	229	230	293	294	295	296	297
SiO <sub>2</sub>	27.2	28.9	27.4	27.3	28.5	29.5	28.6	28.6	28.7	29.0
TiO <sub>2</sub> <sup>tot</sup>	11.3	13.6	12.4	11.6	11.0	11.8	10.8	11.0	11.0	11.7
Ti <sub>2</sub> O <sub>3</sub>	7.1	9.4	8.1	6.7	6.5	9.0	8.4	8.8	8.5	8.9
TiO <sub>2</sub>	3.4	3.2	3.4	4.2	3.7	1.8	1.4	1.3	1.6	1.7
Al <sub>2</sub> O <sub>3</sub>	21.6	20.8	21.9	22.8	21.7	21.1	20.9	21.4	21.4	21.0
Cr <sub>2</sub> O <sub>3</sub>	0.1	0.1	0.2	b.d.	0.1	0.1	0.1	0.2	b.d.	0.1
FeO	0.1	b.d.	0.1	0.1	0.1	0.1	b.d.	b.d.	0.1	b.d.
MnO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.1	b.d.	b.d.
MgO	3.0	3.8	3.4	3.3	3.6	3.7	2.8	3.0	3.3	3.6
CaO	23.8	24.2	23.4	24.1	24.3	23.9	24.1	23.6	23.5	23.6
Na <sub>2</sub> O	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
V <sub>2</sub> O <sub>3</sub>	3.7	3.2	2.5	2.9	2.8	2.5	3.7	2.7	2.2	2.3
ZrO <sub>2</sub>	0.7	0.5	0.6	0.7	0.5	0.6	0.6	0.6	0.5	0.6
Sc <sub>2</sub> O <sub>3</sub>	8.1	6.2	7.8	8.5	8.6	7.6	8.8	8.9	8.3	8.2
Y <sub>2</sub> O <sub>3</sub>	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Total	99.0	100.3	98.8	100.8	100.6	99.9	99.5	99.2	98.0	99.1
<i>Cations per 24 oxygen</i>										
Si	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Ti <sup>3+</sup>	0.2	0.3	0.3	0.2	0.2	0.3	0.3	0.3	0.3	0.3
Ti <sup>4+</sup>	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.1
Al	1.0	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cr	0.0	0.0	0.0	n.a.	0.0	0.0	0.0	0.0	n.a.	0.0
Fe	0.0	n.a.	0.0	0.0	0.0	0.0	n.a.	n.a.	0.0	n.a.
Mn	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0	n.a.	n.a.
Mg	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Ca	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Na	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
V	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Zr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sc	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Y	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ti <sup>3+</sup> /Ti <sup>tot</sup>	0.70	0.76	0.73	0.64	0.66	0.85	0.87	0.88	0.85	0.85

b.d.– below detection limit; n.a.– not available.

Perovskite in R3C-01-U1 is smaller than 10  $\mu\text{m}$  and mostly surrounded by Al,Ti-rich diopside (Figs. 4a and A1b,c,e). Minor element concentration in perovskite in the inclusion (e.g., <0.3 wt% ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> and <0.8 wt % V<sub>2</sub>O<sub>3</sub>; Table A3) is in the range of those in typical non-UR CAIs (e.g., Brearley and Jones, 1998).

The innermost layer of the WL rim surrounding R3C-01-U1 and other units is semi-continuous, ribbon-like spinel layer with 0.1–0.2 wt% V<sub>2</sub>O<sub>3</sub> (Fig. 7) with thickness of <10  $\mu\text{m}$  and intergrown with tiny Al,Ti-rich diopside grains (Fig. A1d). The second layer consists of intergrowths of melilite and spinel, which is surrounded by diopside layer thereafter. The diopside layer is  $\sim$ 10  $\mu\text{m}$  in thickness and compositionally zoned outward from Al,Ti-rich to Al,Ti-poor (Fig. 5, Table 2). Similar to Al,Ti-rich pyroxene in the CAI interior, the rim pyroxene shows high Ti<sup>3+</sup>/Ti<sup>tot</sup> ratio (0.4–1.0). Anorthite (An<sub>~100</sub>) rarely occurs along cracks as thin layers (<10  $\mu\text{m}$ ) between melilite in inner CAI and the WL rim. The outermost layer of the WL rim is compact-textured olivine rim (Figs. 1 and 2), with highly forsteritic composition (mostly Fa<sub>0.5–1</sub>) (Fig. 8 and Table A4). Some olivine grains from the outermost part of the rim have the low-iron, manganese-enriched (LIME)

compositions with MnO/FeO  $\sim$  1 and FeO <1 wt% (Fig. 9a and Table A4). CaO contents in olivine decreases from the inner to the outer rim whereas MnO contents gradually increases (Fig. 9b). The continuous changes in CaO and MnO contents in olivine match a model composition of forsterite condensed from a cooling nebular gas of solar composition at 10<sup>-4</sup> bar (Sugiura et al., 2009).

In the diagram of Al<sub>2</sub>O<sub>3</sub>-Ca<sub>2</sub>SiO<sub>4</sub>-Mg<sub>2</sub>SiO<sub>4</sub>, bulk compositions of R3C-01 and R3C-01-U1 are similar to that of type A CAIs (Fig. A2). The CI-normalized bulk composition of R3C-01-U1 is distinguished from those of previously studied UR inclusions in abundances of highly refractory elements such as Zr, Hf, Sc, Y, and Ti (Fig. A3).

### 3.2. Oxygen isotopes

On the oxygen three-isotope diagram, spinel in two frambooids (#01 and #05) from R3C-01-U1 and the WL rim minerals (Al-diopside and olivine) plot on the CCAM line (Fig. 10 and Table A5), showing no evidence for a mass-dependent fractionation of oxygen isotopes as observed in FUN CAIs (e.g., Krot et al., 2014). All of these

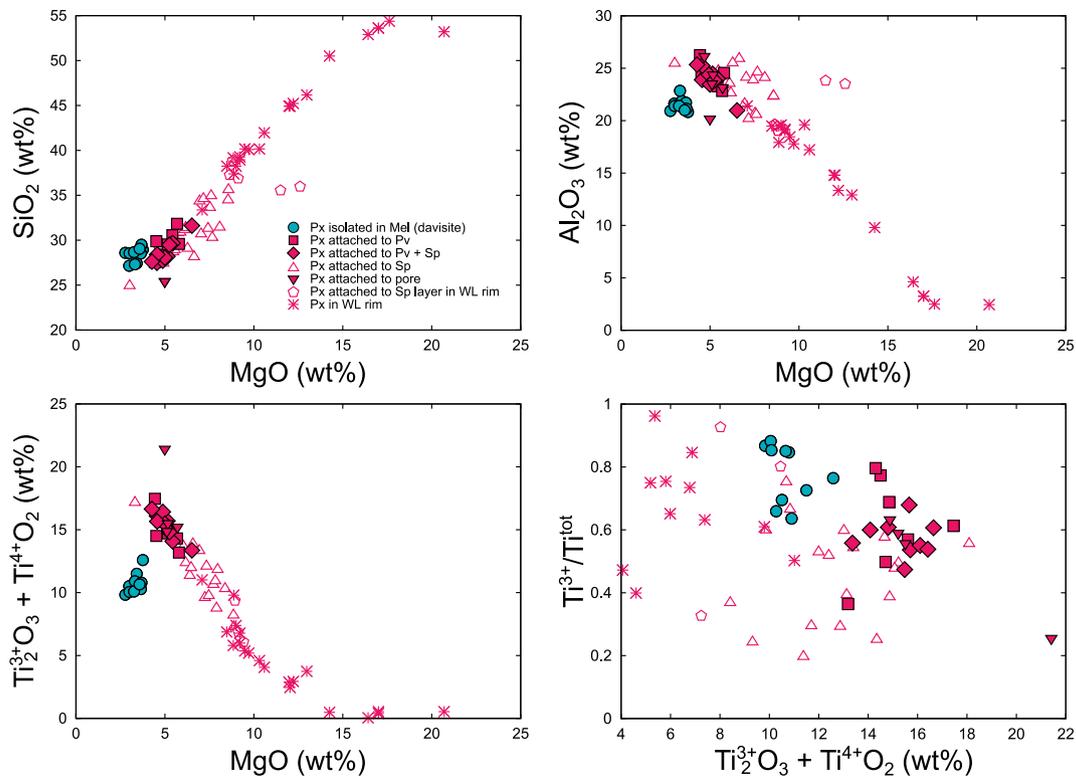


Fig. 5. Major elemental composition of Al,Ti-rich pyroxene in R3C-01-U1. Note that quantitative analyses of Al,Ti-rich pyroxene attached to spinel described above are possibly contaminated by beam overlapping onto spinel due to tiny grain size of pyroxene, as seen in their elevated Al and Mg contents and lower  $Ti^{3+}/Ti^{tot}$  ratios (open symbols). Importantly, measurements of pyroxene which is not attached to spinel (filled symbols or asterisks) do not show clear contamination by other phases. Abbreviations are as in Fig. 4.

minerals are enriched in  $^{16}O$ , with  $\delta^{18}O$  of  $\sim -47\text{‰}$  for spinel,  $\sim -40\text{‰}$  for Al-diopside and olivine in the WL rim.

We obtained 4 isotopographs (areas (a)–(d)) from R3C-01-U1 (Fig. 2 and 4). These areas include Ti,V-rich davisite, melilite, Al,Ti-rich diopside, spinel and perovskite. As O-isotopes of spinel in the CAI lay on the slope-1 line (Fig. 10), low- and high- $\delta^{18}O$  areas in isotopographs can be regarded as  $^{16}O$ -rich and -poor regions, respectively. The obtained isotopographs of R3C-01-U1 minerals show that this inclusion is mostly composed of three mineralogically and isotopically distinct regions: (i)  $^{16}O$ -poor ( $-20\text{‰} \leq \delta^{18}O \leq 0\text{‰}$ ) regions with reversely-zoned melilite and Ti,V-rich davisite; (ii)  $^{16}O$ -rich ( $-50\text{‰} \leq \delta^{18}O \leq -40\text{‰}$ ) regions consisting of unzoned, gehlenitic melilite, Al,Ti-rich diopside and spinel; and (iii) spinel framboids composed of  $^{16}O$ -rich spinel and  $^{16}O$ -poor melilite. These three chemically and isotopically distinct regions show clear boundaries and seem to be distributed randomly in this inclusion.

In the area (a), some reversely-zoned melilite, spinel and Al,Ti-rich diopside are enriched in  $^{16}O$  ( $\delta^{18}O \sim -40\text{‰}$ ) (Fig. 4a). On the other hand, Ti,V-rich davisite and most reversely-zoned melilite are depleted in  $^{16}O$  ( $\delta^{18}O \sim 0\text{‰}$  for Ti,V-rich davisite;  $\delta^{18}O \sim -10$  to  $0\text{‰}$  for melilite). A perovskite grain rimmed by  $^{16}O$ -rich Al,Ti-rich diopside is depleted in  $^{16}O$  ( $\delta^{18}O \sim -20\text{‰}$ ). The  $\delta^{18}O$  values change

sharply at the grain boundaries between  $^{16}O$ -rich regions and  $^{16}O$ -poor regions.

In the area (b), reversely-zoned melilite grains surrounding a spinel framboid are uniformly depleted in  $^{16}O$  ( $\delta^{18}O \sim -10\text{‰}$ ) (Fig. 4b). Tiny melilite grains enclosed in the spinel framboid are also depleted in  $^{16}O$ . On the other hand, all spinel grains and Al,Ti-rich diopside grains enclosed in melilite or surrounding the spinel framboid are uniformly enriched in  $^{16}O$  ( $\delta^{18}O \sim -47\text{‰}$ ).

In the area (c), unzoned  $\dot{A}k$ -poor melilite in the upper-left region of the area, spinel and Al,Ti-rich diopside are uniformly  $^{16}O$ -rich ( $\delta^{18}O \sim -45\text{‰}$ ) (Fig. 4c). In contrast, Ti,V-rich davisite and relatively coarse ( $\sim 30 \mu\text{m}$ ) reversely-zoned melilite are uniformly depleted in  $^{16}O$  ( $\delta^{18}O \sim -5\text{‰}$ ). The  $\delta^{18}O$  values change clearly at the grain boundaries.

In the area (d), spinel grains from two framboids and unzoned  $\dot{A}k$ -poor melilite between these framboids are enriched in  $^{16}O$  ( $\delta^{18}O \sim -45\text{‰}$ ) (Fig. 4d). In contrast, reversely-zoned melilite between these framboids are depleted in  $^{16}O$  ( $\delta^{18}O \sim -15\text{‰}$ ). Line profiles in the two melilite grains revealed a possible narrow zoning of oxygen isotopic composition at their grain boundaries (Fig. 11). Tiny reversely-zoned or unzoned melilite enclosed in a spinel framboid (#12) show moderate depletion in  $^{16}O$  ( $\delta^{18}O \sim -25\text{‰}$ ).

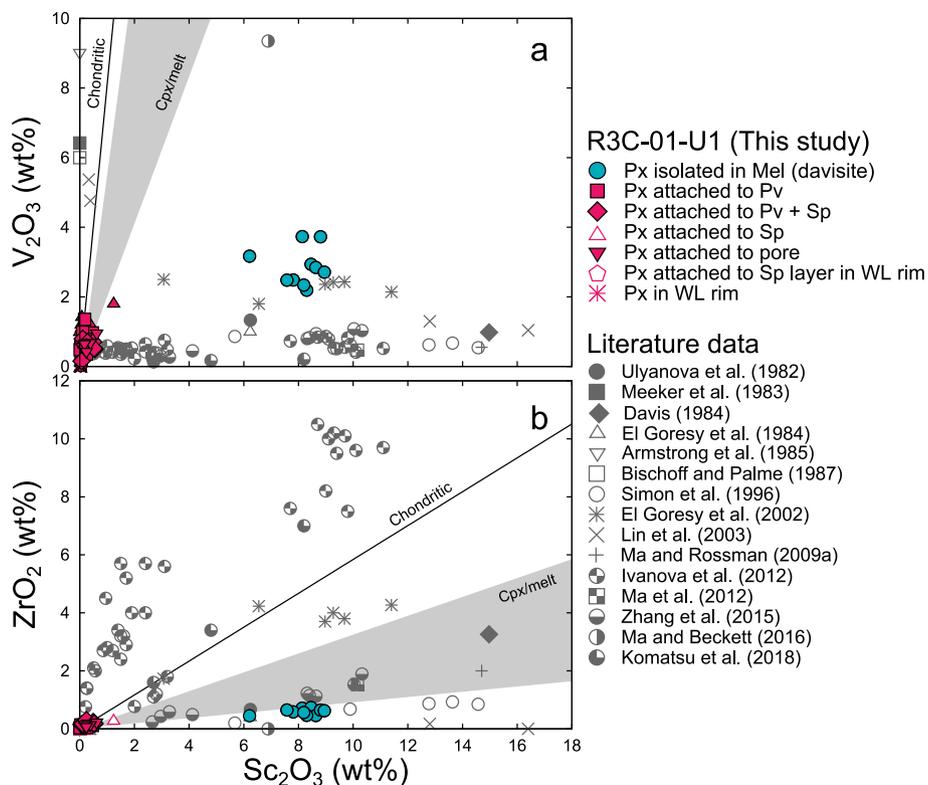


Fig. 6. Plots of (a)  $V_2O_3$  vs  $Sc_2O_3$  and (b)  $ZrO_2$  vs  $Sc_2O_3$  of pyroxene in R3C-01-U1. Compositions of Sc-, V-, and/or Zr-rich pyroxene from previous studies (Ulyanov et al., 1982; Meeker et al., 1983; Davis, 1984; El Goresy et al., 1984; Armstrong et al., 1985; Bischoff and Palme, 1987; Simon et al., 1996; El Goresy et al., 2002; Lin et al., 2003; Ma and Rossman, 2009a; Ivanova et al., 2012; Ma et al., 2012; Zhang et al., 2015; Ma and Beckett, 2016; Komatsu et al., 2018) and chondritic ratios (Lodders, 2003) are also shown. Gray areas correspond clinopyroxene/melt fractionation ratio determined by previous studies (Simon et al., 1991; Hart and Dunn, 1993). Abbreviations are as in Fig. 4.

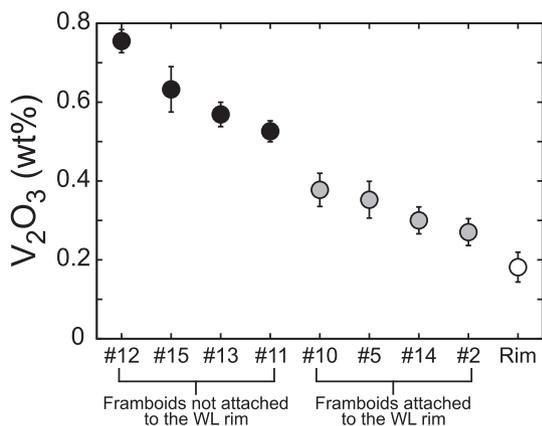


Fig. 7.  $V_2O_3$  contents in spinel in frambooids and WL rim in R3C-01-U1. Error bars represent  $1\sigma$  standard deviation ( $n = 5$  for each frambooids and 10 for the rim, respectively).

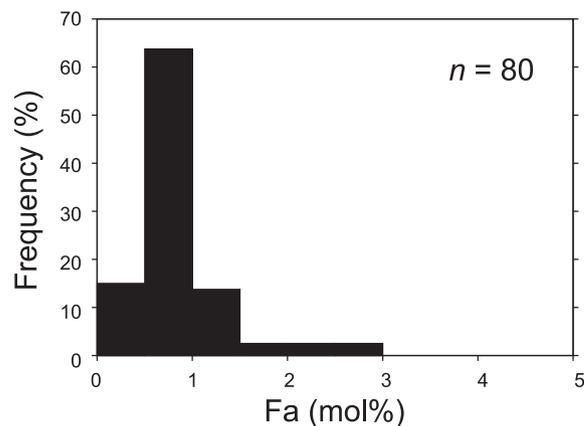


Fig. 8. Histogram of Fa contents of olivine in the WL rim on R3C-01-U1.

## 4. DISCUSSION

### 4.1. Origin of oxygen isotopic heterogeneity in R3C-01-U1

Here we discuss five possible scenarios for the origin of grain-scale O-isotopic heterogeneity observed in R3C-01-

U1, based on combination of the oxygen isotope mapping with micron-scale petrology and mineralogy of the inclusion.

#### 4.1.1. Parent-body processes

R3C-01-U1 consists of three chemically and isotopically distinct regions: (i)  $^{16}O$ -poor ( $-20\text{‰} \leq \delta^{18}O \leq 0\text{‰}$ ) regions

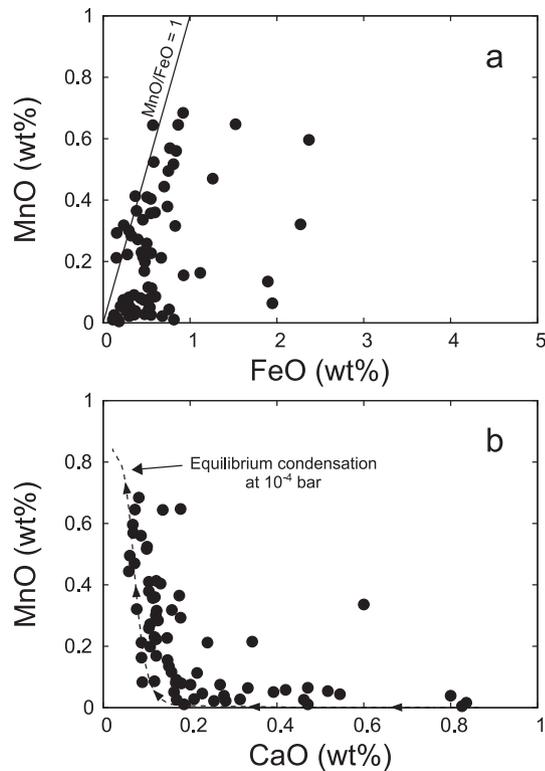


Fig. 9. Plot of (a) MnO vs FeO and (b) MnO vs CaO for olivine in the WL rim on R3C-01-U1. A broken line in (b) shows a model composition of forsterite formed by equilibrium condensation at a cooling gas of solar composition at  $10^{-4}$  bar traced from Sugiura et al. (2009).

with reversely-zoned melilite and Ti,V-rich davite; (ii)  $^{16}\text{O}$ -rich ( $-50\text{‰} \leq \delta^{18}\text{O} \leq -40\text{‰}$ ) regions consisting of unzoned, gehlenitic melilite, Al,Ti-rich diopside and spinel; and (iii) spinel framboids composed of  $^{16}\text{O}$ -rich spinel and  $^{16}\text{O}$ -poor melilite (Figs. 2–4). It has been recognized that most CV3 chondrites have experienced various degrees of thermal metamorphism assisted by  $^{16}\text{O}$ -poor fluid on their parent bodies (e.g., Brearley and Krot, 2013; Krot et al., 2018b). During the parent-body processes, primary anhydrous CAI minerals such as melilite, anorthite and forsteritic olivine are replaced by alkali- and/or iron-rich,  $^{16}\text{O}$ -poor phases such as nepheline, sodalite, fayalitic olivine and phyllosilicates (e.g., Hashimoto and Grossman, 1985; Krot et al., 1995; Brearley and Krot, 2013). In addition, alteration by  $^{16}\text{O}$ -poor thermal fluid could also result in  $^{16}\text{O}$ -depletion in melilite compared to other phases in CAIs (e.g., Fagan et al., 2004a,b; Itoh et al., 2004; Krot et al., 2018b), because oxygen diffuses much rapidly in melilite among the common CAI phases (Yurimoto et al., 1989; Ryerson and McKeegan, 1994).

R3C-01 lacks clear evidence for a fluid-driven thermal metamorphism in the CV parent body. Presence of intact melilite and anorthite, the most fragile phases that are easily replaced by secondary minerals during parental body processes (Hashimoto and Grossman, 1985; Krot et al., 1995), and absence of iron- and/or alkali-rich phases in R3C-01 documents that this inclusion largely escaped

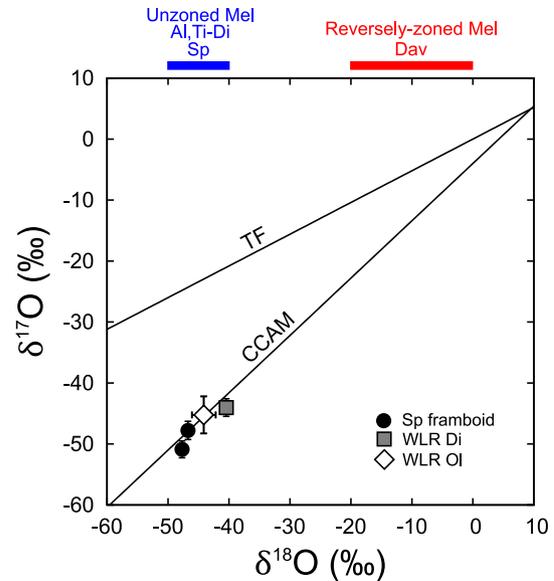


Fig. 10. Oxygen three-isotope plots of minerals in R3C-01-U1 measured by spot analysis. Error bars are shown as  $1\sigma$ . The terrestrial fractionation (TF) line and carbonaceous chondrite anhydrous mineral (CCAM) line (Clayton et al., 1977) are shown for references.  $\delta^{18}\text{O}$  values of CAI minerals determined by isotope imaging (Fig. 4) are also shown. Abbreviations: Dav–davite; Di–diopside; Mel–melilite; Ol–olivine; Sp–spinel; WLR–Wark-Lovering rim.

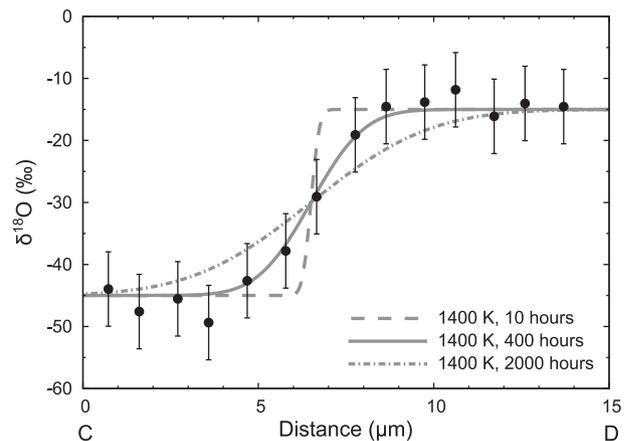


Fig. 11. Line  $\delta^{18}\text{O}$  profile for the line C–D in Fig. 4d. Error bars are shown as  $1\sigma$ . Gray curves show the modeled oxygen isotopic zoning in melilite grains heated at 1400 K for 10, 400 and 2000 h, respectively.

fluid-assisted thermal metamorphism on the CV parent body. The fayalite content of olivine rim surrounding R3C-01 (mostly  $\text{Fa}_{0-1}$ ; Fig. 8) is similar to that in AOAs from unmetamorphosed carbonaceous chondrites (e.g., Krot et al., 2004). The presence of LIME olivine in the rim (Fig. 9) is also inconsistent with thermal-fluid metamorphism that would result in increase of FeO content and decrease of MnO/FeO ratio of silicates (e.g., Komatsu et al., 2015). Unlike an Allende CAI that shows clear evidence for parent-body alteration (Park et al., 2012a), the

$^{16}\text{O}$ -poor region in R3C-01-U1 is not spatially related to cracks or pores and the  $\delta^{18}\text{O}$  value clearly changes at grain boundaries between primary CAI minerals (Fig. 4). The coexistence of  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor melilite grains with similar Åk content at their grain boundaries (Fig. 4c,d) rules out the asteroidal modification scenario, because the oxygen isotopic exchange should occur similarly in the chemically comparable melilites if their isotopic compositions were originally similar. The occurrence of uniformly  $^{16}\text{O}$ -rich WL rim minerals also strongly suggest that there was no subsequent parent-body processing driven by a  $^{16}\text{O}$ -poor thermal fluid (e.g., Matzel et al., 2013; Bodénan et al., 2014; Ushikubo et al., 2017; Krot et al., 2017b). Thus, it is suggested that the oxygen isotopic heterogeneity in R3C-01-U1 did not result from fluid-rock interaction on CV parent body. Considering that RBT 04143 is a brecciated chondrite (Ishida et al., 2012; Lunning et al., 2016), it is inferred that the clast in which the CAI occurs escaped the parent body processing. R3C-01 is likely to be one of the most pristine CV CAIs which preserve primitive mineralogical, petrological and isotopic features, as CAIs from pristine chondrites do (e.g., Itoh et al., 2004; Krot et al., 2008; Makide et al., 2009; Bodénan et al., 2014; Ushikubo et al., 2017; Simon et al., 2018).

#### 4.1.2. Progressive isotopic evolution of a nebular gas

Significant variation in oxygen isotopic compositions within single grains is not observed in R3C-01-U1 (Fig. 4), demonstrating that the oxygen isotopic heterogeneity in this inclusion does not reflect gradual changes of isotopic compositions of a nebular gas (Katayama et al., 2012; Kawasaki et al., 2012, 2017a; Park et al., 2012a).

#### 4.1.3. Partial melting in the solar nebula

The irregular shape without any apparent core-mantle structure and fine-grained nature of R3C-01-U1 (Figs. 1 and 2) is distinct from typical igneous CAIs (e.g., Brearley and Jones, 1998 and references therein), indicating an igneous origin of this sub-inclusion is unlikely. In R3C-01-U1, reversely-zoned melilite and Ti,V-rich davisite enclosed in the melilite are depleted in  $^{16}\text{O}$  (Fig. 4a, c). MacPherson and Grossman (1984) suggested that formation of reversely zoned melilite crystals in unmelted CAIs cannot be explained by crystallization from a melt, but by direct condensation from a gas with decreasing pressure. If this is the case for reversely-zoned melilite in R3C-01-U1, they are expected to record oxygen isotopic compositions of the nebular gas in which the melilite condensed. On the other hand, Grossman et al. (2002) suggested that reversely-zoned melilite could be crystallized from an incomplete melt accompanied by a melt evaporation. Although we cannot exclude the melt evaporation scenario for the origin of reversely-zoned melilite in R3C-01-U1, it is less likely given that significant Mg isotopic fractionation has never been observed in reversely-zoned melilite in the melilite-rich CAIs like R3C-01-U1 (e.g., Kawasaki et al., 2017a) and this scenario requires evaporation and crystallization of melilite grains without grain coarsening before aggregation of R3C-01-U1. In addition, uniform oxygen

isotopic compositions of individual melilite grains with sharp changes in  $\delta^{18}\text{O}$  values at their grain boundaries (Fig. 4) suggest that  $^{16}\text{O}$ -depletion in R3C-01-U1 did not result from partial melting that could produce abrupt oxygen isotope variation within a single crystal (Yurimoto et al., 1998). Furthermore, the lack of Ti-V correlation in spinel also indicates that the inclusion has never experienced partial melting or subsolidus equilibration (Connolly et al., 2003; Connolly and Burnett, 2003). The compact texture of minerals with triple junctions in R3C-01 (Figs. 1 and 2) can be achieved with a subsolidus heating of less than few hours (Karato, 1989; Nichols and Mackwell, 1991; Faul and Scott, 2006; Whattam et al., 2008; Komatsu et al., 2009) and does not require partial melting. Thus, oxygen isotope exchange during nebular partial melting processes is unlikely for the origin of oxygen isotopic heterogeneity in R3C-01-U1.

On the other hand, it is possible that other lithological units in R3C-01 (e.g., the Unit 3 with a core-mantle structure; Fig. 1) have experienced partial melting before aggregation of R3C-01 so that the irregular shape of R3C-01 is originated in a coagulation of igneous and non-igneous CAIs (Rubin, 2012). Although it is beyond the scope of the present work to test this possibility, further isotopic study of this inclusion will provide us insights into formation process of irregularly-shaped CAIs.

#### 4.1.4. Solid-state isotopic exchange during nebular heating

The oxygen isotopic composition of melilite in R3C-01-U1 does not correlate with the distance from the outer margin of the inclusion (Figs. 2 and 4). The sharp isotopic changes at grain boundaries of melilite and the random distribution of  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor regions are apparently inconsistent with gas-solid isotopic exchange from the outer edge of the inclusion during nebular heating processes (Simon et al., 2011, 2016).

Importantly, the grain boundary diffusion is much faster than the volume diffusion (e.g., Zhang, 2010). Small grain sizes in R3C-01-U1 indicate that the grain boundary diffusion could have been more effective in the CAI. Furthermore, since compact-textured CAIs are likely the result of annealing of once porous aggregates of mineral grains, surface diffusion also should not be ignored as the effective diffusion mechanism in the pre-annealed CAIs.

Here we assume that R3C-01-U1 was originally porous aggregates of fine-grained minerals. If such an object experienced solid-state isotope exchange with an external gaseous reservoir, oxygen atoms are transported by diffusion in the gas between crystals, followed by the volume diffusion in each mineral crystal. In this case, diffusion profiles correlate with a distance from grain boundaries, rather than with a distance from the outer edge of the object. Thus, difference in diffusivity between phases can result in variation in degree of chemical and isotopic modification of the minerals. The diffusion coefficient of oxygen ( $D^{\text{Ox}}$ ) in åkermanite is higher than that of gehlenite (Yurimoto et al., 1989). Since the melting temperature ( $T_m$ ) of åkermanite is lower than that of gehlenite (Osborn and Schairer, 1941), Yurimoto et al. (1989) suggested that  $D_{\text{Mel}}^{\text{Ox}}$  and  $T_m$  follow the relationship  $\log D \propto -T_m/T$ , which has been demon-

strated in general solid solution systems of alloys and semiconductors (Flynn's rule; Flynn, 1972). Nagasawa et al. (2001) demonstrated that  $D$  value of interdiffusion of Al + Al vs Mg + Si can be the same order with that of oxygen self-diffusion in melilite at  $> 1200$  K, and the  $D_{\text{Mel}}^{\text{AlAl-MgSi}}$  value also follows the Flynn's rule. Therefore, if unzoned Åk-rich melilite coexisted with uniformly Åk-poor one and they experienced gas-solid interaction with another gaseous reservoir, selective modification of chemical and isotopic composition of the Åk-rich one is possible. When both original Åk-rich and Åk-poor melilite grains were originally  $^{16}\text{O}$ -rich and they reacted with Al-rich,  $^{16}\text{O}$ -poor gaseous reservoir, occurrence of reversely-zoned,  $^{16}\text{O}$ -poor melilite adjacent to Åk-poor,  $^{16}\text{O}$ -rich melilite can be achieved. In this case, the reversely-zoned melilite should have been originally more Åk-rich than their present core. Alternatively, it is possible that the precursor of the reversely-zoned,  $^{16}\text{O}$ -poor melilite was originally  $^{16}\text{O}$ -rich and it has experienced solid state isotopic (and chemical?) modification with the ambient gas before aggregation of R3C-01-U1. Thus, subsolidus processes between crystals and  $^{16}\text{O}$ -poor gaseous reservoir at several stages of the CAI formation could have resulted in the oxygen isotopic heterogeneity. In contrast, the uniform  $^{16}\text{O}$ -enrichment in minerals of the WL rim (Fig. 10) that seems to have completely surrounded R3C-01 before its fragmentation indicates that the solid-state isotopic and chemical modification might predate formation of the WL rim.

A key issue with the gas-solid exchange model for the origin of  $^{16}\text{O}$ -depletion ( $\pm$  reverse zoning) in the reversely-zoned, Åk-rich melilite is the occurrence of  $^{16}\text{O}$ -depleted davisite (i.e., Sc-rich pyroxene) in a center of some of these melilite grains (Fig. 3 and 4). Diffusion coefficients of oxygen in diopside is much lower than in melilite (Ryerson and McKeegan, 1994) although a diffusion coefficient of oxygen in davisite has not yet been determined. If pyroxene also follows the Flynn's rule, davisite ( $T_m \sim 1534$  °C at 1 atm; Ohashi, 1978) can have much lower oxygen diffusivity than diopside ( $T_m \sim 1390$  °C; Bowen, 1914). In this case, solid-state isotopic modification of davisite discussed above is less likely for the origin of  $^{16}\text{O}$ -depletion of this phase and associated melilite. Experimental determination of diffusivity of oxygen in davisite is a key to understand the origin of  $^{16}\text{O}$ -depletion in the CAI.

#### 4.1.5. Aggregation of isotopically distinct mineral assemblages

Alternatively, the heterogeneous chemical and oxygen isotopic composition in R3C-01-U1 can be explained by another scenario: aggregation of crystals formed separately in physicochemically and isotopically distinct gaseous reservoir. Mineralogy and chemical and oxygen isotopic composition of spinel frambooids suggest a separate origin of spinel frambooids in R3C-01-U1 (see Section 4.5), which is another evidence for the accumulation of mineral assemblages that formed separately. Even in the gas-solid isotopic (and chemical) modification model, aggregation of at least three mineralogically distinct mineral assemblages (Åk-rich meli-

lite + davisite, Åk-poor melilite + Al,Ti-rich diopside + spinel, and spinel frambooids) is required. Therefore, it is suggested that R3C-01-U1 consists of mineral assemblages that formed separately in different gaseous reservoir under variable physicochemical conditions. We suggest that this scenario will be supported if the oxygen diffusivity in pyroxene follows the Flynn's rule.

#### 4.1.6. Implications for the oxygen isotopic reservoirs in the early solar system

In either scenario (gas-solid exchange and aggregation of isotopically distinct materials; Sections 4.1.4 and 4.1.5), it is highly likely that oxygen isotopic composition of minerals in the interior of R3C-01-U1 was established before the WL rim formation since the rim minerals are uniformly enriched in  $^{16}\text{O}$  (Fig. 10). Thus, it is suggested that there were temporally and/or spatially distinct  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor gaseous reservoirs when the UR phase bearing CAI formed. This suggestion is consistent with the coexistence of an  $^{16}\text{O}$ -rich gaseous reservoir whose oxygen isotopic composition is close to that of the Sun ( $\delta^{18}\text{O} \sim \delta^{17}\text{O} \sim -60\%$ ; McKeegan et al., 2011) and a planetary-like,  $^{16}\text{O}$ -poor gaseous reservoir ( $\delta^{18}\text{O} \sim \delta^{17}\text{O} \sim 0\%$ ; e.g., Clayton, 1993) in the earliest stage of the solar system formation (e.g., Krot et al., 2002; Krot et al., 2017a; Aléon et al., 2018), which is considered to have formed during photochemical self-shielding effects in CO occurred in the protosolar molecular cloud (Yurimoto and Kuramoto, 2004; Lee et al., 2008), the inner protoplanetary disk (Clayton, 2002), or the outer protoplanetary disk (Lyons and Young, 2005).

## 4.2. Thermal processing of CAIs in the solar nebula

The occurrence of high-temperature, multilayered WL rim and compact texture of minerals in R3C-01 indicate that the inclusion has experienced heating event(s) after its aggregation. Decreasing refractoriness of mineralogy outwards the WL rim on R3C-01 (spinel + melilite + Al, Ti-rich diopside  $\rightarrow$  Al,Ti-rich diopside  $\rightarrow$  Al,Ti-poor diopside  $\rightarrow$  Ca-rich, Mn-poor olivine  $\pm$  Fe,Ni-metal  $\rightarrow$  Ca-poor, Mn-rich olivine  $\pm$  Fe,Ni-metal) (Figs. 2, 5 and 9) is generally consistent with the predictions of thermodynamic calculations of condensation from a cooling nebular gas (e.g., Petaev and Wood, 2005; Ebel, 2006). Thus, the WL rim surrounding R3C-01 likely have formed by a condensation from a cooling nebular gas (e.g., Wark and Lovering, 1977; Bolser et al., 2016; Krot et al., 2017b).

On the other hand, the oxygen isotopic heterogeneity in the CAI interior (Fig. 4) indicates that the subsequent heating of the CAI (i.e., the WL rim formation event) was short enough to preserve the grain-scale isotopic disequilibrium. Although most of  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor regions show clear isotopic boundaries, some melilite grains possibly have experienced micron-scale oxygen isotope exchange (Fig. 11). Thus, the duration of subsequent heating of the CAI can be estimated assuming that the observed isotopic zoning in melilite has resulted from this event. Here we consider a homogeneously  $^{16}\text{O}$ -rich ( $\delta^{18}\text{O} \sim -45\%$ ) melilite

occurred adjacent to an isotopically unzoned  $^{16}\text{O}$ -poor ( $\delta^{18}\text{O} \sim -15\%$ ) melilite grain before the WL rim formation. We assume that the temperature of the CAI interior is uniformly similar to that of the ambient gas due to high thermal diffusivity of minerals (e.g.,  $> 10^{-6} \text{ m}^2/\text{sat}$   $> 1000 \text{ K}$ ; Clauser and Huenges, 1995). The duration of subsequent heating of the inclusion required to achieve the  $\mu\text{m}$ -scale isotopic zoning (Fig. 11) can be calculated by solving the diffusion equation

$$\frac{\partial}{\partial t} c(x, t) = D(T) \frac{\partial^2}{\partial x^2} c(x, t), \quad (2)$$

where  $c$  is concentration of species  $i$  of interest,  $x$  is distance from the grain boundary,  $t$  is time,  $D(T)$  is the diffusion coefficient of oxygen in melilite

$$D(T) = D_0 e^{-\frac{Q}{RT}}, \quad (3)$$

where  $D_0$  is the pre-exponential factor,  $Q$  is the activation energy,  $R$  is the universal gas constant, and  $T$  is temperature. Since both  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor melilite grains in R3C-01-U1 are highly gehlenitic at their rim ( $\dot{A}k_5$ ; Fig. 4), we use the diffusion coefficient for gehlenitic ( $\dot{A}k_0$ ) melilite (Yurimoto et al., 1989) in the calculation. Temperature conditions of the WL rim formation event can be constrained based on mineralogy of the rim: in the WL rim sequence, spinel is the highest temperature condensate (1397 K at  $10^{-4}$  bar; Lodders, 2003) and the LIME olivine is the lowest ( $\sim 1100 \text{ K}$  at  $10^{-4}$  bar; Ebel et al., 2012). By fitting the model curve to the observed isotopic zoning, the duration of the WL rim formation event is estimated to be  $\sim 400 \text{ h}$  at 1400 K (Fig. 11) and  $\sim 3 \times 10^4 \text{ h}$  at 1100 K. Since it is possible that some of the micron-scale isotopic zoning was achieved by nebular heating before the WL rim formation, these estimates are upper limits of heating duration of R3C-01 during the WL rim formation.

Our estimate of timescale of the WL rim formation is also in harmony with the  $^{26}\text{Al}$ - $^{26}\text{Mg}$  systematics of CAIs and their rims, which demonstrated that a time interval between initial CAI crystallization and the WL rim formation was 0–2 Myr (Taylor et al., 2004, 2005; Cosarinsky et al., 2005; Simon et al., 2005; Mane et al., 2015, 2016; Matzel et al., 2015; Kawasaki et al., 2017a; Aléon et al., 2018), although Aléon et al. (2018) suggested that the secondary processes and Mg self-diffusion could have resulted in longer duration estimates. Furthermore, the compact texture of minerals in R3C-01 (Figs. 1 and 2) can be achieved with a subsolidus heating of less than few hours (Karato, 1989; Nichols and Mackwell, 1991; Faul and Scott, 2006; Whattam et al., 2008; Komatsu et al., 2009), supporting the short timescale of heating during the WL rim formation.

The short duration of post-formation heating of CAIs suggests that the high-temperature materials were rapidly removed from hot inner region of the solar nebula by outward transport processes (e.g., Ciesla, 2007; Van Kooten et al., 2016). This rapid transport process might have transported CAIs beyond several AU before proto-Jupiter formation, which created a pressure bump and hindered inward drift of CAIs to the inner solar system (Kruijer

et al., 2017; Desch et al., 2018; Scott et al., 2018), and thus caused a refractory element enrichment in carbonaceous meteorites compared to non-carbonaceous ones (e.g., Rubin, 2011, 2018).

#### 4.3. Redox conditions of the solar nebula

The presence of  $\text{Ti}^{3+}$  in Ti-bearing phases in refractory inclusions (e.g., diopside, hibonite, spinel and forsterite) reflects highly reducing condition in the solar nebula ( $\log f_{\text{rmO}_2} \sim \text{IW} - 6.8$ ; Grossman et al., 2008).  $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$  ratios in  $^{16}\text{O}$ -rich, Al,Ti-rich diopside and  $^{16}\text{O}$ -poor, Ti,V-rich davisite (0.3–0.8 and 0.6–0.9, respectively; Fig. 5 and Tables 2,3) are similar to those of Ti-rich pyroxene in the interior of other CAIs investigated so far (e.g., Simon et al., 1991, 2005, 2007; Simon and Grossman, 2006, 2011; Grossman et al., 2008; Dyl et al., 2011; Ma et al., 2012, 2013; Zhang et al., 2015), suggesting solar-like, highly reducing settings for both  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor gaseous reservoirs in which these pyroxenes formed.

We also observed clear evidence for the presence of  $\text{Ti}^{3+}$  in Al,Ti-rich diopside in the WL rim on R3C-01 ( $\text{Ti}^{3+}/\text{Ti}^{\text{tot}} \sim 0.4$ –1.0; Fig. 5 and Table 2) There is no clear variation of  $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$  ratios between pyroxenes from interior and WL rim, as reported by J. Simon et al. (2005) and Dyl et al. (2011), suggesting that the redox condition of a nebular gas remained highly reducing until the pyroxene layer formation. Occurrence of the LIME olivine at the outer edge of the WL rim (Fig. 9) also supports highly reducing conditions during the WL rim formation, since the LIME olivine can condense only in a very reducing gas of solar composition (e.g.,  $\log f_{\text{rmO}_2} < \text{IW} - 4.17 \pm 0.06$  at total pressure of  $10^{-4}$  bar; Komatsu et al., 2015). These results suggest that  $f_{\text{rmO}_2}$  of the nebular gas remains at solar-like redox condition ( $\log f_{\text{rmO}_2} \sim \text{IW} - 6.8$ ; e.g., Grossman et al., 2008) during the entire formation process of R3C-01.

CAIs likely have experienced outward transport after their formation near the proto-Sun (Brownlee et al., 2006; McKeegan et al., 2006; Zolensky et al., 2006; Simon et al., 2008), although the mechanism is still controversial. The X-wind model (e.g., Shu et al., 1996) is one of the possible scenarios in which objects formed close to the Sun is transported by a bipolar outflow. However, as pointed out by Krot et al. (2009) and Desch et al. (2010), in the X-wind model, high-temperature materials (e.g., CAIs) form in a dust-rich, hydrogen-depleted nebular setting, which is inconsistent with highly reducing condition during the entire R3C-01 formation inferred from our observation. Therefore, the X-wind model is unlikely and we support turbulent flow (e.g., Ciesla, 2007) or disk winds (Van Kooten et al., 2016) as the possible transportation mechanism of R3C-01.

#### 4.4. Possible scenarios for formation of Ti,V-rich davisite

Here we discuss two possible origin of  $^{16}\text{O}$ -poor, Ti,V-rich davisite isolated in  $^{16}\text{O}$ -poor, reversely-zoned melilite in R3C-01-U1 (Figs. 3 and 4): condensation from a gas and relict of pre-existing CAIs. Melt origin of Ti,V-rich

davite can be ruled out since their V/Sc and Zr/Sc ratios are different from clinopyroxene/melt ratios (Simon et al., 1991; Hart and Dunn, 1993) and partial melting of R3C-01-U1 is unlikely (see Section 4.1.3).

#### 4.4.1. Condensation origin

As discussed in Section 4.1.3, the reversely-zoned melilite is likely to be a nebular condensate (MacPherson and Grossman, 1984). Occurrence of davite indicates its formation prior to the condensation of melilite. Although condensation temperature of davite has never been constrained due to lack of knowledge of its thermodynamic properties, high concentration of very refractory elements such as Ti and Sc in davite might have stabilized davite at temperature higher than condensation temperature of diopside (1347 K at  $10^{-4}$  bar; Lodders, 2003) and melilite (1529 K). The high condensation temperature of davite is also inferred from common occurrence of davite with UR phases in the UR CAIs in which lower temperature condensate such as melilite and diopside are not abundant (see Table 1 of Ivanova et al. (2012); e.g., Davis, 1984; Simon et al., 1996; Ma and Rossman, 2009a; Zhang et al., 2015).

In the  $^{16}\text{O}$ -poor region of R3C-01-U1, phases that are expected to condense at higher (e.g., perovskite, hibonite and UR element rich phases) and lower temperature (e.g., Ti-poor pyroxene) than melilite are absent (Fig. 4). Spinel that possibly condenses in the similar temperature range with melilite and Al,Ti-rich pyroxene under equilibrium conditions is also absent. These results could be attributed to condensation from a gas of fractionated, non-solar composition and/or disequilibrium condensation due to isolation of earlier condensates (e.g., Petaev and Wood, 1998).

Ti,V-rich davite in R3C-01-U1 shows higher V/Sc and lower Zr/Sc values compared to davite in the UR inclusions previously studied (Fig. 6). The 50% condensation temperature of elements in a gas of solar composition at  $10^{-4}$  bar are 1741 K for Zr, 1659 K for Sc, and 1429 K for V (Lodders, 2003), suggesting that the Zr/Sc ratio of a condensate decreases with increasing V/Sc value as a nebular gas temperature decreases. Therefore, the condensation temperature of Ti,V-rich davite in R3C-01-U1 might be lower than davite in the previously-reported UR inclusions. The relatively lower condensation temperature of Ti,V-rich davite in R3C-01-U1 and absence of any other high-temperature condensates in the inclusion suggest that higher temperature condensates had been isolated from a gas before the condensation of Ti,V-rich davite.

#### 4.4.2. Relict origin

Lin et al. (2003) observed Sc- or V-rich Al,Ti-diopside grains isolated in melilite in compact type A CAIs and suggested that these grains are relicts of UR pyroxene grains from pre-existing UR inclusions (e.g., ElGoresy et al., 2002). In davite-bearing UR CAIs reported so far, the mineral occurs with other refractory phases that are more refractory than Al,Ti-rich diopside and melilite, such as Zr- and/or Y-rich perovskite (Ulyanov et al., 1982; Davis, 1984; Simon et al., 1996; ElGoresy et al., 2002; Ivanova et al., 2012), hibonite (Ulyanov et al., 1982; Davis, 1984),

and/or other Zr-, Sc-, and/or Y-rich minerals (Ma and Rossman, 2009a, Ma et al., 2011, 2012, 2013, 2017, Ivanova et al., 2012, 2017, Ma, 2012, Krot et al., 2015, Zhang et al., 2015, Daly et al., 2017, Komatsu et al., 2018). Therefore, it is expected that davite is associated with these highly refractory phases if the mineral is relict that originated in pre-existing UR inclusions. However, such highly refractory phases are completely absent in R3C-01-U1, suggesting that a relict origin of Ti,V-rich davite in the CAI is unlikely.

#### 4.5. Origin of spinel framboids

In some cases, spinel occurs as “palisade bodies” and “framboids” in CAIs, whose origins remain controversial (e.g., El Goresy et al., 1979; Wark and Lovering, 1982; Simon and Grossman, 1997; Kim et al., 2002). Palisade bodies are spheroidal shells of spinel enclosing typical CAI minerals such as melilite, spinel, Al,Ti-rich diopside and anorthite. Based on mineralogical investigations of natural occurrences and experimental works, Simon and Grossman (1997) suggested that they have formed *in situ* in their host inclusions as a result of crystallization of spinel around the vapor-melt interfaces of vesicles. In contrast, Kim et al. (2002) showed that oxygen isotopic composition of palisade bodies and associated phases cannot be reconciled with this scenario and suggested an external origin of these bodies. Framboids are tightly packed spheroidal clusters of spinel enclosed within phases such as melilite, Al,Ti-rich diopside and anorthite. El Goresy et al. (1979) suggested that framboids are direct condensates from the nebular gas crystallized around pre-existing phases like pyroxene, melilite and anorthite. On the other hand, Simon and Grossman (1997) interpreted framboids as polar sections of palisade bodies and concluded that there is no genetic distinction between them. A furnace experimental study by Wark and Lovering (1982) showed that framboids likely formed by near-solidus annealing rather than liquid crystallization.

Concentration of framboids only in one lithological unit (R3C-01-U1) of the compound CAI R3C-01 and absence of palisade bodies (Fig. 1) suggest that formation of framboids predated the aggregation of R3C-01, and there is no genetic relationship between framboids and palisade bodies. Systematic variations in  $\text{V}_2\text{O}_3$  contents of spinel (Fig. 7) and associated Ca,Ti-rich phases (perovskite  $\pm$  Al,Ti-rich pyroxene) among framboids cannot be explained by co-crystallization of all framboids in a single process. Therefore, *in situ* formation scenario of framboids during annealing (Wark and Lovering, 1982) or melting (Simon and Grossman, 1997) that took place after aggregation of R3C-01 are unlikely for the origin of framboids in R3C-01-U1. The lack of Ti-V correlation in spinel is also inconsistent with the *in situ* formation scenario (Connolly et al., 2003; Connolly and Burnett, 2003).

The mineralogical and chemical variations among spinel framboids very likely reflect difference in formation conditions and/or chemical composition of precursor of each framboid. Distinct occurrence, chemistry and oxygen iso-

topic composition of melilite enclosed in and surrounding frambooids (Fig. 4b, d) also support separate and complex origin of frambooids. Therefore, it is suggested that formation of spinel frambooids took place separately prior to the formation of their host CAI R3C-01-U1. This scenario is consistent with the formation of R3C-01-U1 by aggregation of mineral assemblages formed separately in the solar nebula (see Section 4.1).

The fine grain size of melilite enclosed in frambooids, absence of glasses and textural and mineralogical zoning are distinct from known terrestrial and extraterrestrial igneous objects such as igneous CAIs and chondrules (e.g., Wark and Lovering, 1982). Although the spheroidal shape could have been achieved by partial melting before incorporation into R3C-01-U1, this process would have resulted in grain coarsening. Therefore, we prefer non-igneous, condensation origin for the frambooids (El Goresy et al., 1979). The oxygen isotopic disequilibrium between spinel and melilite inside frambooids might have resulted from gas-solid or gas-melt interaction between originally  $^{16}\text{O}$ -rich minerals in proto-frambooids and  $^{16}\text{O}$ -poor gaseous reservoir, or aggregation of isotopically distinct minerals. Systematically lower  $\text{V}_2\text{O}_3$  content observed in frambooids attached to the WL rim and the spinel layer in the rim sequence implies that the V-poor spinel formed later than V-rich spinel. Although V becomes less refractory at oxidizing conditions (Kornacki and Fegley, 1986), multiple observations indicate a highly reducing condition during the whole formation process of R3C-01-U1 (Section 4.3). We suggest that vanadium can increase the condensation temperature of spinel.

The origin of spheroidal shape of frambooids is beyond the scope of this paper, but some irregularly-shaped frambooids (e.g., frambooid #01; Fig. 1) might be affected by deformation of R3C-01-U1. Since the thickness of the WL rim remains to be constant even regions near the irregularly-shaped frambooids, it is suggested that the deformation event took place in the nebula before the WL rim formation.

## 5. CONCLUSIONS

The petrological, mineralogical and isotopic characteristics of R3C-01 suggest the following formation history:

1. Three chemically distinct mineral assemblages (reversely-zoned or unzoned, Åk-rich melilite + Ti,V-rich davisite; unzoned, gehlenitic melilite + Al,Ti-rich diopside + spinel; and spinel frambooids) formed and processed separately in the solar nebula under various physicochemical conditions. They can originate in isotopically distinct gaseous reservoirs (solar-like,  $^{16}\text{O}$ -rich reservoir and planetary-like,  $^{16}\text{O}$ -poor one), or formed in the  $^{16}\text{O}$ -rich reservoir and subsequently experienced solid-state modification of oxygen isotopic composition during subsolidus heating in the solar nebula before and/or during the aggregation of R3C-01-U1.
2. Assemblages of  $^{16}\text{O}$ -poor and  $^{16}\text{O}$ -rich minerals aggregated to form R3C-01-U1.
3. R3C-01-U1 and four (or more) melilite-rich CAIs that formed separately aggregated to form the compound CAI R3C-01.
4. A multi-layered Wark-Lovering (WL) rim condensed onto R3C-01 from a cooling  $^{16}\text{O}$ -rich nebular gas. The duration of the WL rim formation process was  $< 10^3$  h at 1400 K and  $< 10^5$  h at 1100 K.
5. All of the formation processes mentioned above occur under highly reducing conditions in which  $\text{Ti}^{3+}$ -rich pyroxene and low-iron, manganese-enriched (LIME) olivine can be stable.
6. R3C-01 was transported outward by the turbulent flow or the disk winds to the region of CV chondrite formation and incorporated into the RBT 04143 parent body.

In this study, two scenarios for the origin of oxygen isotopic heterogeneity commonly observed in a variety of CAIs are proposed: (i) solid-state isotopic exchange between  $^{16}\text{O}$ -rich porous CAI precursors and  $^{16}\text{O}$ -poor gaseous reservoir via grain boundary and/or surface diffusion followed by volume diffusion during subsolidus heating in the solar nebula, and (ii) agglomeration of isotopically distinct mineral assemblages. These scenarios can be tested by experimental determination of oxygen diffusivity in davisite, which has not yet been determined. In either scenario, it is strongly indicated that spatially and/or temporally distinct  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor gaseous reservoirs existed in the period of UR phases and UR CAI formation.

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## APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.gca.2019.02.034>.

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