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Chronological study of oxygen isotope composition for the solar protoplanetary disk recorded in a fluffy Type A CAI from Vigarano

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ABSTRACT

Fluffy Type A Ca-Al-rich inclusions (CAIs) containing reversely zoned melilite crystals are suggested to be direct condensates from solar nebular gas. We conducted an investigation of ²⁶Al–²⁶Mg systematics of a fluffy Type A CAI from Vigarano, named V2-01, with known oxygen isotopic distributions of reversely zoned melilite crystals; we also conducted oxygen isotope measurements of coexisting minerals. Two of six reversely zoned melilite crystals show continuous variations in magnesium isotopic composition, with $\delta^{25}\text{Mg}$ becoming small along the inferred direction of crystal growth, which supports the idea that they originated through condensation. Petrography suggests that the constituent minerals of V2-01 formed in the following order: first spinel and fassaite enclosed by melilite, then reversely zoned melilite crystals, and spinel and diopside in the Wark-Lovering rim. The spinel enclosed by melilite has ¹⁶O-rich compositions ($\Delta^{17}\text{O} \sim -24\text{‰}$) and an initial value of $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$. The fassaite enclosed by melilite crystals shows variable oxygen isotopic compositions ($\Delta^{17}\text{O} \sim -12\text{‰}$ and -17‰) and plots on an isochron with $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$. The oxygen isotopic compositions of reversely zoned melilite showed continuous variations in $\Delta^{17}\text{O}$ along the inferred direction of crystal growth, suggesting that surrounding nebular gas, during the formation of the reversely zoned melilite, changed from ¹⁶O-poor ($\Delta^{17}\text{O}$ values larger than -10‰) to ¹⁶O-rich ($\Delta^{17}\text{O} \sim -25\text{‰}$). The six

reversely zoned melilite crystals show indistinguishable initial $^{26}\text{Al}/^{27}\text{Al}$ values with an average $(^{26}\text{Al}/^{27}\text{Al})_0$ of $(4.7 \pm 0.3) \times 10^{-5}$, which is clearly distinguishable from the value of enclosed spinel and fassaite, indicating a younger formation age than the enclosed spinel and fassaite. The spinel and diopside from the Wark-Lovering rim shows ^{16}O -rich compositions ($\Delta^{17}\text{O} \sim -23\text{‰}$) with $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.5 \pm 0.4) \times 10^{-5}$. The values of $(^{26}\text{Al}/^{27}\text{Al})_0$ are consistent with the formation sequence inferred from petrography. The formation period for the V2-01 CAI is estimated to be 0.18 ± 0.07 Myr from the difference in initial $^{26}\text{Al}/^{27}\text{Al}$ values. These data suggest that the oxygen isotopic composition of solar nebular gas surrounding the CAI changed from ^{16}O -rich to ^{16}O -poor and back to ^{16}O -rich during the first ~ 0.2 Myr of Solar System formation.

1. INTRODUCTION

1.1 ^{26}Al – ^{26}Mg systematics of fluffy Type A CAIs

Ca-Al-rich inclusions (CAIs) in meteorites are the oldest objects in the Solar System, with an average age of 4567 Ma according to U-corrected Pb–Pb absolute chronology (Connelly et al., 2012). Many CAIs contained live ^{26}Al , a short-lived radionuclide with a half-life of 0.705 Myr (Norris et al., 1983), at their formation (Lee et al., 1976; MacPherson et al., 1995). Whole-rock ^{26}Al – ^{26}Mg isochron studies indicate the initial $^{26}\text{Al}/^{27}\text{Al}$ ratio ($(^{26}\text{Al}/^{27}\text{Al})_0$) value of $(5.23 \pm 0.13) \times 10^{-5}$, called the canonical (Jacobsen et al., 2008; Larsen et al., 2011), which may reflect the $(^{26}\text{Al}/^{27}\text{Al})_0$ value at the time of Al–Mg fractionation of the CAIs or their precursors by evaporation and condensation processes (MacPherson et al., 2010, 2012). On the other hand, internal ^{26}Al – ^{26}Mg mineral isochrons for CAIs, estimated using secondary ion mass spectrometry (SIMS), show a range of $(^{26}\text{Al}/^{27}\text{Al})_0$ values (Kita et al., 2012; MacPherson et al., 2012; Mishra and Chaussidon, 2014; Kawasaki et al., 2015), possibly representing a range of formation ages. The data of MacPherson et al. (2012) show that melted CAIs tend to be younger than unmelted CAIs, suggesting the CAI melting events continued for at least 0.2 Myr after the formation of CAI with the canonical ratio. CAI-chondrule compound objects show lower $(^{26}\text{Al}/^{27}\text{Al})_0$ values than most CAIs, suggesting that they have younger melting ages than CAIs; the melting events continued for at least 2.0 Myr after the CAI formation (Krot et al., 2005, 2007; Wakaki et al., 2011; MacPherson et al., 2012; Kawasaki et al., 2015). These inferred ages for the melting events of CAIs and CAI-chondrule compound objects likely correspond to ages of transient heating events that occurred in the early Solar System. On the other hand, chronological studies of unmelted CAIs (i.e., condensate aggregates)

determine the ages of condensation of their constituent minerals and formation periods of the unmelted CAIs because their components may have been individually formed in the solar nebula and then aggregated together into unmelted CAIs. However, very few studies focus on the ages of individual components of condensate aggregates (e.g., Park et al., 2014).

Reversely zoned melilite crystals have been found in fluffy Type A CAIs (a type of unmelted CAI). These crystals have chemical compositions that become less åkermanitic from the core to rim (MacPherson and Grossman, 1984). MacPherson and Grossman (1984) suggested that the reversely zoned melilite crystals in fluffy Type A CAIs were formed by direct condensation from nebular gas with decreasing pressure; the fluffy Type A CAIs were never extensively melted. Therefore, the reversely zoned melilite crystals and other constituent minerals were individually formed and subsequently accreted together to form fluffy Type A CAIs. To determine the formation period of fluffy Type A CAIs, a comparative study of the formation ages of individual reversely zoned melilite crystals and other constituent minerals is conducted by their individual ^{26}Al – ^{26}Mg systematics using SIMS. Internal ^{26}Al – ^{26}Mg isochrons may be determined for individual reversely zoned melilite crystals because within the grains there are significant chemical variations in $^{27}\text{Al}/^{24}\text{Mg}$ ratios.

In contrast to the condensation formation model for reversely zoned melilite crystals in fluffy Type A CAIs, crystallization from incomplete melt with melt evaporation was also suggested (Grossman et al., 2002). Significant mass dependent fractionation of magnesium isotopes was expected for the melt evaporation processes by experimental studies (Davis et al., 1990; Richter et al., 2002, 2007; Mendybaev et al., 2013) and shown in Type B CAIs using SIMS (Bullock et al., 2013). Thus, the idea of crystallization from incomplete melt with melt evaporation could be tested by changes in the degree of magnesium isotopic fractionation along with the crystal growth of reversely zoned melilite.

1.2 Oxygen isotopes in fluffy Type A CAIs

Phases in CAIs from CV chondrites have unequilibrated oxygen isotopic compositions distributed along the carbonaceous chondrite anhydrous mineral (CCAM) line (Clayton et al. 1977; Clayton 1993). Disequilibrium distributions of oxygen isotopes among inter- and intra-crystals of CAIs have been observed through in situ analysis using SIMS (e.g., Yurimoto et al., 1994; Yurimoto et al., 1998). The distributions of oxygen

isotopic compositions of CAI minerals were suggested to be formed by thermal processes in the solar protoplanetary disk within different oxygen isotopic environments (Itoh and Yurimoto, 2003; Yurimoto and Kuramoto, 2004)—multiple melting (Yurimoto et al., 1998; Ito et al., 2004; Itoh et al., 2004; Yoshitake et al., 2005; Aléon et al., 2007; Krot et al., 2008; Yurimoto et al., 2008; Wakaki et al., 2013; Kawasaki et al., 2015), condensation (Katayama et al., 2012; Kawasaki et al., 2012; Park et al., 2012), and solid-state diffusion (Itoh and Yurimoto, 2003; Fagan et al., 2004)—as well as aqueous and thermal metamorphism/alteration on the parent body (Wasson et al., 2001; Itoh et al., 2004; Krot et al., 2008; Park et al., 2012; Kawasaki et al., 2015). A combination of such processes may have led to the disequilibrium oxygen isotopic distributions observed in CAIs, although most efficient processes are different for each mineral and each CAI.

Oxygen isotopic compositions in reversely zoned melilite crystals in a fluffy Type A CAI from Vigarano named V2-01 have been measured using SIMS with a line-profile technique (Katayama et al., 2012). The oxygen isotopic compositions tend to gradually become ^{16}O -rich from cores to rims, indicating that the oxygen isotopic compositions of surrounding nebular gas gradually changed from ^{16}O -poor to ^{16}O -rich during condensation. Such trends for oxygen isotope distributions of melilite have also been observed in other Type A CAIs from Allende and Efremovka (Kawasaki et al., 2012; Park et al., 2012). In addition to the melilite, oxygen isotope measurements for other minerals in fluffy Type A CAIs would assist in the understanding of the oxygen isotope change in surrounding nebular gas during fluffy Type A CAI formation. Moreover, a combined study of oxygen isotope and ^{26}Al – ^{26}Mg systematics in a fluffy Type A CAI would help determine the time scale of oxygen isotope change in the solar nebular gas.

In this study, we conducted oxygen isotope measurements and ^{26}Al – ^{26}Mg systematics using SIMS for V2-01, a fluffy Type A CAI from Vigarano (CV3). The chemical and oxygen isotopic zoning of melilite crystals in V2-01 has already been studied by Katayama et al. (2012). Preliminary measurements of the oxygen isotopic compositions for minerals other than melilite were reported by Harazono and Yurimoto (2003) and Yurimoto et al. (2008). The purposes of this study are (1) to determine the formation period of the V2-01 fluffy Type A CAI, (2) to test the formation process of reversely zoned melilite crystals in the fluffy Type A CAI, (3) to determine the oxygen isotope change during V2-01 CAI formation, and (4) to investigate time scale of oxygen isotope change in nebular gas.

2. EXPERIMENTAL

2.1 Sample preparation and elemental analysis

The fluffy Type A CAI, V2-01, is included in a polished thin section of the Vigarano CV3 carbonaceous chondrite. The polished thin section was coated with a thin (~20 nm) carbon coat for backscattered electron (BSE) imaging and an elemental analysis using an energy dispersive X-ray spectrometer (EDS), oxygen isotope measurements using SIMS, and Al-Mg isotope measurements using SIMS with a peak jumping mode. In addition, the carbon coated section was overlaid with a gold thin film (~70 nm) for Al-Mg isotope measurements using SIMS in multicollecion mode. The gold coating allows for a better stability for secondary ion emission for an intense primary beam than the carbon coating, which results in higher precision and accuracy in measurement results.

BSE images were obtained using a field emission type scanning electron microscope (FE-SEM; JEOL JSM-7000F) at Hokkaido University. Quantitative elemental analysis and X-ray elemental mapping were conducted using an energy dispersive spectrometer (EDS, Oxford X-Max 150) installed on the FE-SEM. A 15 keV electron beam probe with currents of 0.3 nA (for quantitative analysis) and 5 nA (for mapping) was employed in our study.

2.2 Oxygen isotope analysis

Oxygen isotopic compositions of the minerals in V2-01 were measured using a SIMS instrument (Cameca ims-1280HR) of Hokkaido University. A $^{133}\text{Cs}^+$ primary beam (20 keV, 200 pA) with a diameter of 10 μm was used for oxygen isotope measurements of diopside, fassaite, and spinel. Negative secondary ions ($^{16}\text{O}^-$, $^{17}\text{O}^-$, and $^{18}\text{O}^-$) were measured. A normal incident electron flood gun was used for the electrostatic charge compensation of the analyzing area during the measurements. $^{16}\text{O}^-$ was measured using a Faraday cup, while $^{17}\text{O}^-$ and $^{18}\text{O}^-$ were measured using an electron multiplier with the peak jumping mode of a sector magnet. The mass resolution of $M/\Delta M$ was set at ~6000 to ensure that the contribution of $^{16}\text{OH}^-$ to $^{17}\text{O}^-$ is negligible. The secondary ion intensity of $^{16}\text{O}^-$ was $\sim 1 \times 10^8$ cps. Each measurement was conducted for 30 cycles of a counting sequence with $^{16}\text{O}^-$ for 1 s, $^{17}\text{O}^-$ for 2 s, and $^{18}\text{O}^-$ for 1 s. Russian spinel ($\delta^{17}\text{O} = 4.42\text{‰}$, $\delta^{18}\text{O} = 8.50\text{‰}$; Yurimoto et al., 1994) was used as a standard to correct the instrumental mass fractionation.

2.3 Magnesium isotope analysis in multicollection mode

Magnesium isotopes and $^{27}\text{Al}/^{24}\text{Mg}$ isotope ratios of the minerals in V2-01 were measured using a SIMS instrument (Cameca ims-1280HR) of Hokkaido University. An $^{16}\text{O}^-$ primary beam accelerated to 23 keV was employed in the experiment. We used both the peak-jumping mode and the multicollection mode, depending on the secondary ion intensities of magnesium isotopes from the minerals. For diopside, fassaite, and spinel, the magnesium isotopes ($^{24}\text{Mg}^+$, $^{25}\text{Mg}^+$, and $^{26}\text{Mg}^+$) and $^{27}\text{Al}^+$ were measured simultaneously in the multicollection mode with four Faraday cups: $^{24}\text{Mg}^+$ for L2* ($10^{11} \Omega$), $^{25}\text{Mg}^+$ for L1 ($10^{11} \Omega$), $^{26}\text{Mg}^+$ for H1 ($10^{11} \Omega$), and $^{27}\text{Al}^+$ for H2* ($10^{10} \Omega$). The primary beam current was set to 7 nA with an elliptical shape of $6 \times 12 \mu\text{m}$ for the diopside and spinel measurements, while the primary beam current was set to 10 nA with an elliptical shape of $5 \times 9 \mu\text{m}$ for measurements of the fassaite measurements. The mass resolution of $M/\Delta M$ was set at ~ 2000 . The contributions of ion interferences (e.g., $^{48}\text{Ca}^{2+}$, $^{24}\text{MgH}^+$, $^{25}\text{MgH}^+$, and $^{52}\text{Cr}^{2+}$) were negligible under these conditions. The secondary ion intensities of $^{24}\text{Mg}^+$ were typically 1.1×10^8 , 7.5×10^7 , and 1.5×10^8 cps for diopside, fassaite, and spinel, respectively. Each measurement was conducted with 20 cycles of counting the secondary ions for 10 s.

The excess radiogenic ^{26}Mg , $\delta^{26}\text{Mg}^*$, was calculated using an exponential fractionation law with the coefficient $\alpha_{\text{natural}} = 0.5128$, because natural fractionation for magnesium isotopes is considered to be controlled by evaporation processes (Davis et al., 2015). However, the natural mass fractionation deviates from the instrumental mass fractionation of SIMS, which differs among target minerals under the measurement conditions (Itoh et al., 2008). Thus, we determined the instrumental mass fractionation, α_{SIMS} , through measurements of Takashima augite, synthetic fassaite glass, and Russian spinel for each mineral, to calculate the excess radiogenic ^{26}Mg . The α_{SIMS} for spinel was determined through the linear regression of the $\Phi^{25}\text{Mg}$ and $\Phi^{26}\text{Mg}$ values of Takashima augite and Russian spinel, while the α_{SIMS} for fassaite and diopside was determined through the linear regressions of the $\Phi^{25}\text{Mg}$ and $\Phi^{26}\text{Mg}$ values of Takashima augite and synthetic fassaite glass, where $\Phi^{25,26}\text{Mg} = 1000 \times \ln [(^{25,26}\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^{25,26}\text{Mg}/^{24}\text{Mg})_{\text{ref.}}]$. The terrestrial reference ratios of $(^{25}\text{Mg}/^{24}\text{Mg})_{\text{ref.}} = 0.12663$ and $(^{26}\text{Mg}/^{24}\text{Mg})_{\text{ref.}} = 0.13932$ (Catanzaro et al., 1966) were used, although the final corrected- $\delta^{26}\text{Mg}^*$ values are independent of reference ratios. The α_{SIMS} values are not only different among minerals but also different among measurement sessions for the same mineral. We therefore determined the α_{SIMS} values for each mineral in every measurement session. In this study, the α_{SIMS} for spinel was determined as $0.531 \pm$

0.004 and 0.515 ± 0.004 for two different sessions, the α_{SIMS} for diopside was determined as 0.493 ± 0.009 , and the α_{SIMS} for fassaite was determined as 0.488 ± 0.006 (2σ). From the results of the linear regressions, an instrumental offset for the $\delta^{26}\text{Mg}^*$ values, β , which ranged from +0.44 to +1.19 with 2σ errors of 0.02–0.08 depending on minerals and analytical sessions, was identified. The corrected $\delta^{26}\text{Mg}^*$ values were determined by the following equation

$$\begin{aligned} \delta^{26}\text{Mg}^* = & \delta^{26}\text{Mg}_{\text{sample}} - \left[\left(1 + \frac{\delta^{25}\text{Mg}_{\text{sample}}}{1000} \right)^{\frac{1}{\alpha_{\text{natural}}}} - 1 \right] \times 1000 \\ & - \beta + \left[\left(1 + \frac{\delta^{25}\text{Mg}_{\text{std}}}{1000} \right)^{\frac{1}{\alpha_{\text{natural}}}} - 1 \right] \times 1000 \\ & - \left[\left(1 + \frac{\delta^{25}\text{Mg}_{\text{std}}}{1000} \right)^{\frac{1}{\alpha_{SIMS}}} - 1 \right] \times 1000, \end{aligned} \quad (1)$$

where $\delta^{25,26}\text{Mg}_{\text{sample}} = [({}^{25,26}\text{Mg}/{}^{24}\text{Mg})_{\text{sample}}/({}^{25,26}\text{Mg}/{}^{24}\text{Mg})_{\text{ref.}} - 1] \times 1000$ and $\delta^{25}\text{Mg}_{\text{std}} = [({}^{25}\text{Mg}/{}^{24}\text{Mg})_{\text{std}}/({}^{25}\text{Mg}/{}^{24}\text{Mg})_{\text{ref.}} - 1] \times 1000$. The first and second terms on the right-hand side of the equation was transformed into $\delta^{26}\text{Mg}^*_{\text{sample}}$, and as a result, the equation would be finally expressed as

$$\begin{aligned} \delta^{26}\text{Mg}^* = & \delta^{26}\text{Mg}^*_{\text{sample}} - \beta + \left[\left(1 + \frac{\delta^{25}\text{Mg}_{\text{std}}}{1000} \right)^{\frac{1}{\alpha_{\text{natural}}}} - 1 \right] \times 1000 \\ & - \left[\left(1 + \frac{\delta^{25}\text{Mg}_{\text{std}}}{1000} \right)^{\frac{1}{\alpha_{SIMS}}} - 1 \right] \times 1000. \end{aligned} \quad (2)$$

A standard error of the mean of 20 cycles in a single analysis of $\delta^{26}\text{Mg}^*_{\text{sample}}$ was applied for estimating the analytical errors of final corrected- $\delta^{26}\text{Mg}^*$ values. If the standard errors of both $\delta^{25}\text{Mg}_{\text{sample}}$ and $\delta^{26}\text{Mg}_{\text{sample}}$ were independently used for estimating the final analytical error, the final analytical error would be overestimated because the standard errors of $\delta^{25}\text{Mg}_{\text{sample}}$ and $\delta^{26}\text{Mg}_{\text{sample}}$ are usually larger than statistical errors calculated from total ion counts in the measurement condition due to an instrumental mass fractionation during the 20 cycle measurement. In contrast, the standard error of $\delta^{26}\text{Mg}^*_{\text{sample}}$, which is much less affected by the instrumental mass fractionation during the measurement, is comparable to the statistical error. Thus, we use the standard error of $\delta^{26}\text{Mg}^*_{\text{sample}}$ instead of those of $\delta^{25}\text{Mg}_{\text{sample}}$ and $\delta^{26}\text{Mg}_{\text{sample}}$ for estimating the final analytical error. An analytical error of $\delta^{25}\text{Mg}_{\text{std}}$ was assigned as a

standard error of repetitive measurements of terrestrial standards. The errors of $\delta^{26}\text{Mg}^*_{\text{sample}}$, $\delta^{25}\text{Mg}_{\text{std}}$, α_{natural} , α_{SIMS} , and β were used for estimating the final analytical error for each spot through propagation of the errors. The error of α_{natural} was negligible for the measurement conditions used. The analytical errors (2 sigma) for $\delta^{26}\text{Mg}^*$ range from 0.09 to 0.16‰.

The relative sensitivity factor for aluminum and magnesium was determined for each mineral through Takashima augite, synthetic fassaite glass, and Russian spinel measurements for diopside, fassaite, and spinel, respectively. The instrumental mass fractionations for Takashima augite and synthetic fassaite glass were distinct from each other in our measurement conditions. The instrumental mass fractionations for diopside and fassaite in V2-01 may also have varied with the chemical compositions under the same measurement conditions. Thus, the $\delta^{25}\text{Mg}$ values for diopside and fassaite were not determined in this study. On the other hand, the systematic errors of $\delta^{25}\text{Mg}$ were negligible to determine the $\delta^{26}\text{Mg}^*$ because the statistical errors of $\delta^{26}\text{Mg}^*_{\text{sample}}$ on the measurements were dominant in the uncertainty of the calculated $\delta^{26}\text{Mg}^*$ values using Eq. (2). Therefore, the $\delta^{26}\text{Mg}^*$ values were correctly calculated within errors shown in Table 3. The $\delta^{25}\text{Mg}$ values for spinel in V2-01 were estimated assuming that $\delta^{25}\text{Mg}$ of Russian spinel is 0.

2.4 Magnesium isotope analysis in peak-jumping mode

For melilite, magnesium isotopes ($^{24}\text{Mg}^+$, $^{25}\text{Mg}^+$, and $^{26}\text{Mg}^+$) were measured using an electron multiplier, while $^{27}\text{Al}^+$ was measured using a Faraday cup with the peak jumping mode of a sector magnet. The $^{16}\text{O}^-$ primary beam accelerated to 23 keV was used and the secondary ion intensity of $^{24}\text{Mg}^+$ was set to 3×10^5 cps under a mass resolution of $M/\Delta M$ of ~ 3500 , which is sufficient to resolve Mg hydrate interferences at masses 25 and 26. Because melilite crystals in V2-01 exhibit chemical zonation, the primary beam current was adjusted to maintain constant $^{24}\text{Mg}^+$ intensity for each spot according to the chemical compositions in order to compensate dead time correction of the electron multiplier. Under this condition, the primary beam current was ranged from 0.2 to 1.0 nA with a diameter of 3 to 5 μm . Each measurement was conducted for 50 cycles of a counting sequence with $^{24}\text{Mg}^+$ for 3 s, $^{25}\text{Mg}^+$ for 10 s, $^{26}\text{Mg}^+$ for 10 s, and $^{27}\text{Al}^+$ for 1 s. The analytical errors for $\delta^{26}\text{Mg}^*$ were assigned as internal errors (2SE) and were typically $\sim 1.2\%$. An instrumental mass fractionation and the relative sensitivity factor for aluminum and magnesium were determined through measurements of synthetic melilite glass. The calculation methods were the same as those described in

Section 2.3.

3. RESULTS

3.1 Petrographic description

The CAI V2-01 is a fluffy Type A CAI from the Vigarano CV3 with a size of ~7 mm across (Fig. 1). A detailed petrographic description of V2-01 and chemical and oxygen isotopic distributions in reversely zoned melilite crystals have been presented by Katayama et al. (2012). The CAI is mainly composed of melilite in addition to spinel, fassaite, hibonite, perovskite, and Fe-metal as accessory minerals. Anorthite is present as a secondary alteration product replacing melilite. Melilite is abundant throughout the inclusion, with crystal sizes of ~50 to 600 μm . Some melilite crystals contain spinel crystals with sizes of a few micrometers to tens of micrometers; a few spinel crystals are attached to hibonite and/or perovskite. Two types of fassaite are present in V2-01: lath-shaped, <1 μm grains; and anhedral crystals from several microns to ~30 μm , within the melilite crystals. The rounded anhedral crystals are often attached to perovskite grains.

V2-01 has an irregular, “fluffy” shape and a Wark-Lovering (W-L) rim (Wark and Lovering, 1977) surrounding the entire CAI. A forsterite accretionary rim is also observed outside the W-L rim (Fig. 2), which has layers, from innermost to outermost, of melilite, spinel, anorthite, and diopside. Perovskite grains are often attached to spinel crystals in the W-L rim. The W-L rim minerals and the forsterite accretionary rim also occur in the CAI interior due to the highly indented, irregular rim shape of the CAI.

Spinel grains in both the CAI interior and W-L rim typically have FeO contents of less than 0.3 wt % and Fe/(Mg+Fe) ratios less than 0.01. Only spinels with such low FeO contents were measured by SIMS for the ^{26}Al – ^{26}Mg systematics in this study. In contrast, rims of spinel grains in the W-L rim and the small spinel grains in the W-L rim with sizes of less than ~5 μm show high FeO contents, up to ~5 wt %. Spinel grains with sizes of ~3 μm have Mg-rich cores and Fe-rich rims (Fig. 2c). In this study, spinels with higher FeO contents could not be analyzed for the ^{26}Al – ^{26}Mg systematics because the primary beam size used, 6 $\times$ 12 μm , was larger than the grains. Representative chemical compositions of minerals are shown in Table 1.

3.2 Chemical and oxygen isotopic zoning of reversely zoned melilite crystals

Katayama et al. (2012) determined the oxygen isotopic compositions of nine reversely zoned melilite crystals from V2-01. In the present study, we determined the ^{26}Al – ^{26}Mg systematics for six (grains 1, 3, 8, 9, 15, and 21) of those nine grains. Four (grains 1, 9, 15, and 21) were adjacent to the W-L rim and the other two grains (grains 3 and 8) were not. We resummmary the descriptions of the chemical and oxygen isotopic zoning of six reversely zoned melilite crystals below. Data of chemical and oxygen isotopic distributions for Figures 3 and 4 were obtained by Katayama et al. (2012).

Grain 1 (Fig. 3a) is $200 \times 400 \mu\text{m}$ and is adjacent to the W-L rim. It exhibited reverse zoning from the core ($\sim\text{Åk}30$) to the rim ($\sim\text{Åk}4$), although highly gehlenitic compositions ($< \sim\text{Åk}6$) are only present at the W-L rim side. The chemical zoning pattern appears to be continuous with an adjacent grain, suggesting parallel growth (Fig. 3a). A variation in oxygen isotopic composition is observed in a zone with the chemical composition ranging from $\sim\text{Åk}6$ to $\sim\text{Åk}5$ (Fig. 4a). The oxygen isotopic composition is homogeneously distributed in the grain interior ($\Delta^{17}\text{O} \sim -6\text{‰}$) despite reverse zoning, but changes gradually towards ^{16}O -rich from $\sim\text{Åk}6$ and reaches $\Delta^{17}\text{O} \sim -25\text{‰}$ near the rim ($\sim\text{Åk}5$).

Grain 3 (Fig. 3b) is $250 \times 300 \mu\text{m}$ and is not attached to the W-L rim. It exhibits reverse zoning from the core ($\sim\text{Åk}21$) to the rim ($\sim\text{Åk}5$), and its isotopic composition is homogeneous ($\Delta^{17}\text{O} \sim -5\text{‰}$).

Grain 8 is $150 \times 200 \mu\text{m}$ and is not attached to the W-L rim. Half of the crystal is shown in Fig. 3c. The grain is reversely zoned from the core ($\sim\text{Åk}15$) to the rim ($\sim\text{Åk}5$). The line profiles of oxygen isotopic compositions along the inferred direction of crystal growth (reverse zoning in chemical composition) (Fig. 4b) show that the oxygen isotopic composition is homogeneous in the grain interior ($\Delta^{17}\text{O} \sim -13\text{‰}$) despite reverse chemical zoning. The composition changes gradually towards ^{16}O -rich from $\sim\text{Åk}7$ and reaches $\Delta^{17}\text{O} \sim -20\text{‰}$ near the rim ($\sim\text{Åk}4$).

Grain 9 is $300 \times 600 \mu\text{m}$ and is adjacent to the W-L rim. Half of the crystal is shown in Fig. 3d. It exhibits reverse zoning from the core ($\sim\text{Åk}18$) to the rim ($\sim\text{Åk}5$). A variation in the oxygen isotopic composition is observed in a zone with the chemical composition ranging from $\sim\text{Åk}8$ to $\sim\text{Åk}5$. The compositions ranged from $\Delta^{17}\text{O} = -5$ to -28‰ and change from ^{16}O -poor to ^{16}O -rich composition along the inferred direction of crystal growth.

Grain 15 (Fig. 3e) is $80 \times 150 \mu\text{m}$ and is adjacent to the W-L rim. It exhibits reverse zoning from the core ($\sim\text{\AA}k20$) to the rim ($\sim\text{\AA}k3$), although highly gehlenitic compositions ($< \sim\text{\AA}k8$) are only present near the W-L rim. A variation in the oxygen isotopic composition is observed in a zone with chemical composition ranging from $\sim\text{\AA}k6$ to $\sim\text{\AA}k3$. The oxygen isotopic composition is homogeneously ^{16}O -poor in the grain interior ($\Delta^{17}\text{O} \sim -7\text{‰}$) despite reverse zoning, but it changes gradually towards ^{16}O -rich from $\sim\text{\AA}k6$ and reaches $\Delta^{17}\text{O} \sim -16\text{‰}$ near the rim ($\sim\text{\AA}k3$).

Grain 21 (Fig. 3f) is $80 \times 120 \mu\text{m}$ and is adjacent to the W-L rim. It exhibits reverse zoning from the core ($\sim\text{\AA}k24$) to the rim ($\sim\text{\AA}k2$), although highly gehlenitic compositions ($< \sim\text{\AA}k6$) are only present at the W-L rim side of the grain. A variation in oxygen isotopic composition is observed in a zone with chemical composition ranging from $\sim\text{\AA}k5$ to $\sim\text{\AA}k2$. The isotopic composition is homogeneously ^{16}O -poor at the grain interior ($\Delta^{17}\text{O} \sim -8\text{‰}$) despite reverse chemical zoning, but it changes gradually towards ^{16}O -rich from $\sim\text{\AA}k5$ and reaches $\Delta^{17}\text{O} \sim -20\text{‰}$ near the rim ($\sim\text{\AA}k2$).

3.3 Oxygen and Al–Mg isotopic compositions of diopside, fassaite, and spinel

The oxygen and magnesium isotopic compositions and $^{27}\text{Al}/^{24}\text{Mg}$ ratios for diopside, fassaite, and spinel in V2-01 are summarized in Tables 2 and 3. The oxygen isotopic compositions of spinel in the CAI interior enclosed by melilite crystals, fassaite enclosed by melilite crystals, and diopside and spinel in the W-L rim are plotted on the CCAM line in Fig. 5. The spinel in CAI interior has ^{16}O -rich compositions of $\Delta^{17}\text{O} \sim -24\text{‰}$, while the minerals in the W-L rim has homogeneously ^{16}O -rich compositions of $\Delta^{17}\text{O} \sim -23\text{‰}$. On the other hand, the fassaite grains enclosed by melilite showed two distinct oxygen isotopic compositions, one grain with $\Delta^{17}\text{O} \sim -17\text{‰}$, while other three grains have $\Delta^{17}\text{O} \sim -12\text{‰}$.

Figure 6 shows the magnesium isotopic compositions and $^{27}\text{Al}/^{24}\text{Mg}$ ratios of minerals plotted on the ^{26}Al – ^{26}Mg isochron diagram. The spinel measured in CAI interior has an excess ^{26}Mg , with $\delta^{26}\text{Mg}^* \sim 0.98 \pm 0.09\text{‰}$ (2SD, $n = 12$). On the other hand, the spinel measured in the W-L rim shows a $\delta^{26}\text{Mg}^*$ of $\sim 0.77 \pm 0.07\text{‰}$ (2SD, $n = 9$), which is clearly smaller than that for the CAI interior. If we define a model isochron of the spinel in the CAI interior assuming initial $(\delta^{26}\text{Mg}^*)_0 = -0.0159 \pm 0.0014\text{‰}$ (Larsen et al., 2011), the spinel in the CAI interior would have $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$.

The minerals of the W-L rim have the same oxygen isotopic compositions, indicating sequential formation in the same gaseous reservoir, which satisfies a condition to generate an internal mineral isochron. The mineral isochron gives $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.5 \pm 0.4) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = -0.05 \pm 0.05\%$ for diopside and spinel in the W-L rim. Chronological validities of these isochrons are discussed in later sections. The Al–Mg isotopic compositions for fassaite plot on the model isochron for spinel in the CAI interior and are resolved from the isochron for minerals in the W-L rim (Fig. 6).

3.4 Al–Mg isotopic compositions of reversely zoned melilite crystals

The magnesium isotopic compositions and $^{27}\text{Al}/^{24}\text{Mg}$ ratios for the reversely zoned melilite crystals in V2-01 are summarized in Table 4. Figure 7 shows the magnesium isotopic compositions and $^{27}\text{Al}/^{24}\text{Mg}$ ratios of each grain plotted on ^{26}Al – ^{26}Mg isochron diagrams. As described earlier, the oxygen isotopic compositions changed during crystal growth. Nevertheless, all data for a given crystal plot on a straight line, suggesting contemporaneous formation. The isochron of grain 1 gave an initial value of $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.6 \pm 0.3) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = 0.5 \pm 0.7\%$ (Fig. 7a), grain 3 gave $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.7 \pm 0.6) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = 0.1 \pm 1.0\%$ (Fig. 7b), grain 8 gave $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.6 \pm 0.4) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = 0.6 \pm 1.0\%$ (Fig. 7c), grain 9 gave $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.9 \pm 0.4) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = 0.0 \pm 0.8\%$ (Fig. 7d), grain 15 gave $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.8 \pm 0.3) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = -0.6 \pm 0.6\%$ (Fig. 7e), and grain 21 gave $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.5 \pm 0.2) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = 0.5 \pm 0.6\%$ (Fig. 7f). Validities of these isochrons are discussed in a later section.

3.5 Magnesium isotopic fractionations of reversely zoned melilite crystals

Variations of mass-dependent magnesium isotopic fractionations within the reversely zoned melilite crystals along inferred directions of crystal growth are observed (Fig. 8). The fractionations range between $\sim 0\%$ and $\sim 9\%$ in $\delta^{25}\text{Mg}$. Three patterns for magnesium isotopic fractionation are recognized. The $\delta^{25}\text{Mg}$ values of grains 1 and 15 tend to decrease with increasing $^{27}\text{Al}/^{24}\text{Mg}$ ratios (Figs. 8a and 8e). Grains 3 and 21 show constant $\delta^{25}\text{Mg}$ values (Figs. 8b and 8f). The $\delta^{25}\text{Mg}$ values of grains 8 and 9 tend to increase with increasing $^{27}\text{Al}/^{24}\text{Mg}$ ratios (Figs. 8c and 8d).

The magnesium isotopic fractionation of grain 1 ranges from ~ 0 to $\sim 6\%$ in $\delta^{25}\text{Mg}$ (Fig. 8a). The $\delta^{25}\text{Mg}$ values gradually decreased with crystal growth. The ^{16}O -rich zone ($\sim \text{Åk6}$) grew with a constant $\delta^{25}\text{Mg}$ value of $\sim 0\%$ (Fig. 4a).

Grain 15 shows magnesium isotopic fractionation ranging from ~1 to ~5‰ in $\delta^{25}\text{Mg}$ (Fig. 8e). The $\delta^{25}\text{Mg}$ values appear to gradually decrease with crystal growth, which is similar to the case for grain 1. The ^{16}O -rich zone ($< \sim \text{\AA}6$) has a constant $\delta^{25}\text{Mg}$ value of ~1‰.

Grains 3 and 21 have uniform $\delta^{25}\text{Mg}$ values of ~2‰ and ~1‰, respectively (Figs. 8b and 8f).

Grain 8 shows magnesium isotopic fractionation ranging from ~1 to ~4‰ in $\delta^{25}\text{Mg}$ (Fig. 8c). A zone with $> \sim \text{\AA}8$ shows a constant $\delta^{25}\text{Mg}$ value of ~1‰, while the ^{16}O -rich zone ($< \sim \text{\AA}8$) has variable $\delta^{25}\text{Mg}$ values, from ~1 to ~4‰ according to crystal growth (Fig. 4b).

Grain 9 shows magnesium isotopic fractionation ranging from ~4 to ~9‰ in $\delta^{25}\text{Mg}$ (Fig. 8d), which gradually increased with crystal growth. A zone with $> \sim \text{\AA}10$ shows a constant $\delta^{25}\text{Mg}$ value of ~4‰.

4. DISCUSSION

4.1 Formation processes of reversely zoned melilite crystals

4.1.1 Grains in which $\delta^{25}\text{Mg}$ values decrease with crystal growth

The oxygen isotopic compositions of grains 1 and 15 changed from ^{16}O -poor to ^{16}O -rich and the $\delta^{25}\text{Mg}$ values decreased with reversely zoned crystal growths. Redistribution of oxygen and magnesium within and/or among CAI minerals by solid-state diffusion in the solar nebula or on the parent body has been suggested (Itoh and Yurimoto, 2003; Fagan et al., 2004; Itoh et al., 2004; Ito and Messenger, 2010; Simon et al., 2011; Kawasaki et al., 2015). Thus, solid-state diffusion of oxygen and magnesium isotopes in reversely zoned melilite crystals should be considered as a possibility for the cause of oxygen and magnesium isotopic variations. Katayama et al. (2012) showed that the oxygen isotopic zoning in grain 1 is not related to the distance from the crystal rim but only to crystal composition, indicating that oxygen self-diffusion in melilite was not responsible for the oxygen isotopic variations in grain 1. Grain 15 showed the same characteristics as grain 1. Magnesium self-diffusion in gehlenite is slower than oxygen self-diffusion at temperatures below ~1500 K (Yurimoto et al., 1989; Ito and Ganguly, 2009). The ambient temperature for the formation of grains 1 and 15 could also be below ~1500 K, because the equilibrium condensation temperatures for grains 1 and 15

were ~1390 to ~1420 K at $P_{\text{total}} = 10^{-4}$ atm or ~1470 to ~1490 K at $P_{\text{total}} = 10^{-3}$ atm, from a solar composition gas, according to the phase diagram of Yoneda and Grossman (1995). This suggests that the magnesium isotopic variations in grains 1 and 15 cannot be explained by solid-state diffusion in reversely zoned melilite crystals. The well-correlated $\delta^{26}\text{Mg}^*$ values and $^{27}\text{Al}/^{24}\text{Mg}$ ratios of grains 1 and 15 (Figs. 7a and 7e) were also inconsistent with the redistribution of magnesium isotopes after the solidification. Therefore, these grains likely preserve their original magnesium isotopic fractionation patterns obtained during crystal growths.

MacPherson and Grossman (1984) showed that the occurrence of reversely zoned melilite crystals found in fluffy Type A CAIs could be explained by condensation from a solar nebular gas during a period of decreasing pressure. This condensation can also explain the reversely zoned melilite crystals in V2-01 fluffy Type A CAI (Katayama et al., 2012). In contrast, Grossman et al. (2002) suggested that the reversely zoned melilite crystals could also be formed by crystallization from incomplete melts with melt evaporation. They predicted that the magnesium isotopes of reversely zoned melilite formed by such a process would have significantly enriched $\delta^{25}\text{Mg}$ at the gehlenitic side of the crystal. However, grains 1 and 15 showed depleted $\delta^{25}\text{Mg}$ at the gehlenitic side of the crystal (Figs 8a and 8e), which is inconsistent with the above-mentioned prediction. Therefore, the magnesium isotopic fractionation patterns in grains 1 and 15 are strong evidence for a condensation origin of the reversely zoned melilite crystals, as proposed by Katayama et al. (2012).

The magnesium isotopic variations in grains 1 and 15 may represent responses to changes in magnesium isotopic compositions of the surrounding nebular gas from which the grains were condensed. At this time, the pressure of surrounding nebular gas may have decreased during condensation (MacPherson and Grossman, 1984). In summary, the oxygen isotopic compositions of the surrounding nebular gas changed from ^{16}O -poor to ^{16}O -rich, the $\delta^{25}\text{Mg}$ values decreased, and the pressure decreased, during the condensation of grains 1 and 15. The ^{16}O -rich gehlenitic zone of grain 1 showed a homogeneous $\delta^{25}\text{Mg}$ of ~0‰ (Fig. 4a), indicating that the ^{16}O -rich nebular gaseous reservoir had nearly solar $\delta^{25}\text{Mg}$ value. The magnesium isotopic variations support a model describing that the ^{16}O -rich nebular gaseous reservoir for the fluffy Type A CAI originated from a solar coronal gas (Katayama et al., 2012).

4.1.2 Grains with constant $\delta^{25}\text{Mg}$ values

Grains 3 and 21 showed constant $\delta^{25}\text{Mg}$ values of $\sim 2\text{‰}$ and $\sim 1\text{‰}$, respectively (Figs. 8b and 8f). Because there were no significant enrichments of $\delta^{25}\text{Mg}$ at the gehlenitic zone of the crystal, the formation of grains 1 and 15 by crystallization from incomplete melts with melt evaporation is unlikely, but formation by condensation from the solar nebular gas is possible. It is noted that we cannot prove a condensation origin of grains 3 and 21, because a significant magnesium isotopic fractionation is not always necessary during melt evaporation processes, as will be discussed in Section 4.1.3.

The oxygen isotopic compositions of grain 3 are homogeneously ^{16}O -poor ($\Delta^{17}\text{O} \sim -5\text{‰}$), while those of grain 21 show variations ranging from $\Delta^{17}\text{O} \sim -8$ to -20‰ and changing from ^{16}O -poor to ^{16}O -rich with crystal growth. Given that grains 3 and 21 formed by condensation from nebular gas, the oxygen and magnesium isotopic variations suggest that grain 3 formed in a homogeneous, ^{16}O -poor, nebular gaseous reservoir with a nearly solar $\delta^{25}\text{Mg}$ value, while grain 21 formed in a nebular gas that changed from ^{16}O -poor to ^{16}O -rich, with nearly solar $\delta^{25}\text{Mg}$ value.

4.1.3 Grains in which $\delta^{25}\text{Mg}$ values increase with crystal growth

The $\delta^{25}\text{Mg}$ values for grains 8 and 9 increase with decreasing Åk content (Figs 8c and 8d). The trends of magnesium isotopic fractionations observed in these grains are consistent with the formation of reversely zoned melilite crystals by crystallization from evaporating melts (Grossman et al., 2002). Melt evaporation causes loss of magnesium and silicon relative to more refractory aluminum and calcium, and results in heavier magnesium and silicon isotopic compositions for the residual melt than for the precursor (e.g., Richter et al., 2002). Laboratory evaporation experiments show that the isotopic fractionation of evaporating melts follows the Rayleigh law (Richter et al., 2007; Mendybaev et al., 2013). The equation is given as $R/R_0 = f^{(\alpha-1)}$, where R is $^{25}\text{Mg}/^{24}\text{Mg}$ in the residual melt, R_0 is $^{25}\text{Mg}/^{24}\text{Mg}$ in the melt before evaporation, f is the fraction of ^{24}Mg remaining in the residual melt, and α is the kinetic isotopic fractionation factor. Richter et al. (2007) determined the kinetic isotopic fractionation factor, α , for magnesium from a CAI-composition melt in vacuum at various temperature conditions. The relationship between the magnesium isotopic fractionation and the fraction of ^{24}Mg remaining in the residual melt at a given temperature can be calculated.

The chemical compositions of grains 8 and 9 are in the range Åk5–20. According to the phase diagram for melilite (Osborn and Schairer, 1941), the temperature of melting

would be higher than ~1750 K and lower than ~1830 K, because these are the solidus temperatures of Åk20 and Åk5, respectively. We used the kinetic isotopic fractionation factor of $\alpha = 0.98822$ at 1873 K (Richter et al., 2007), which was the lowest temperature in their experiment. Because the observed magnesium isotopic fractionation for grains 8 and 9 were ~3‰ and ~5‰, respectively, in $\delta^{25}\text{Mg}$, (Figs 8c and 8d), the fraction of ^{24}Mg remaining in the residual evaporating melt could be calculated using the kinetic isotope fractionation factor of $\alpha = 0.98822$. The fractions of ^{24}Mg remaining in the residual melt for grains 8 and 9 were calculated to be ~78% and ~65%, respectively (Fig. 9).

Richter et al. (2007) found a slight temperature dependence for the kinetic isotopic fractionation factor. An extrapolation from their data gave a kinetic isotopic fractionation factor of $\alpha \sim 0.9898$ at 1750 K, which is the lower limit of melting temperature for grains 8 and 9. If use consider this kinetic isotopic fractionation factor, the fractions of ^{24}Mg remaining in the residual melt for grains 8 and 9 would be ~75% and ~61%, respectively (Fig. 9). The difference of temperature between 1873 K and 1750 K corresponds to the difference of $f = 4\%$, which is negligible for the discussion here. Thus, we used $\alpha = 0.98822$.

The residual melt composition of $f = 78\%$ with ~3‰ of mass-dependent isotope fractionation in $\delta^{25}\text{Mg}$ for grain 8 corresponds to $^{27}\text{Al}/^{24}\text{Mg} \sim 40$ (Figs. 8c). The residual melt composition of $f = 65\%$ with ~5‰ of mass dependent isotope fractionation in $\delta^{25}\text{Mg}$ for grain 9 corresponds to $^{27}\text{Al}/^{24}\text{Mg} \sim 44$ (Figs. 8d). Therefore, the melt composition before evaporation would be calculated to be $^{27}\text{Al}/^{24}\text{Mg} \sim 31$ for grain 8 and $^{27}\text{Al}/^{24}\text{Mg} \sim 29$ for grain 9. For grain 8, the $^{27}\text{Al}/^{24}\text{Mg}$ ratio of ~31 corresponds to the boundary between ^{16}O -poor and ^{16}O -rich zones, where the $\delta^{25}\text{Mg}$ value increases (Fig. 4b), which apparently supports crystallization from incomplete melts with simultaneous evaporation. This formation process, however, is not in agreement with the result that grain 8 already had reverse zoning before evaporative melting. Because this process involves the incomplete melting of pre-existing melilite, with melt evaporation and subsequent overgrowth of melilite with reverse zoning on the relict core, a preferential melting of relatively gehlenitic rim of reversely zoned pre-existing melilite crystal is necessary. However, the liquidus temperature is lower in the interior, åkermanitic zone than in the outer, gehlenitic zone of reversely zoned grain 8 (Osborn and Schairar, 1941). The melting relationship implies that it is difficult for the interior zone to be unmelted at the melting temperature of the outer zone of grain 8. Therefore,

the melt evaporation process is not possible for the formation of reverse zoning in grain 8. On the other hand, the $^{27}\text{Al}/^{24}\text{Mg}$ of the melt before evaporation was calculated to be ~ 29 for grain 9, corresponding to $\delta^{25}\text{Mg} \sim 6\text{‰}$ (Fig. 8d). However, according to the calculation, the $\delta^{25}\text{Mg}$ at $^{27}\text{Al}/^{24}\text{Mg} \sim 29$ should be 5‰ lower than $\delta^{25}\text{Mg} \sim 9\text{‰}$ at $^{27}\text{Al}/^{24}\text{Mg} \sim 44$, while the observed difference of $\delta^{25}\text{Mg}$ was $\sim 3\text{‰}$. These disagreements between observations and calculations suggest that the melt evaporation process did not play a main role in the formation of reverse zoning for grains 8 and 9.

It is noted that the kinetic isotopic fractionation factor, α , depends on the chemical composition of the starting melt (Mendybaev et al. 2013). In evaporation experiments by Richter et al. (2007), the starting composition had ~ 11 wt % MgO, although reversely zoned melilite crystals in fluffy Type A CAIs have $\text{MgO} < 5$ wt %. However, there are no evaporation experiments using the chemical composition of melilite, which is necessary to accurately discuss the formation processes of reversely zoned melilite crystals.

We assumed Rayleigh fractionation for the discussion of the formation of reversely zoned melilite crystals, but isotope exchange between evaporated species and the melt should also be taken into account. Evaporation with back reaction of evaporated species can reduce net isotopic fractionation, and as a result, elemental fractionation can be decoupled from isotopic fractionation (Ozawa and Nagahara, 2001). In fact, chondrules lack the isotopic fractionation of evaporated elements predicted by Rayleigh fractionation (e.g., Alexander et al., 2000; Galy et al., 2000). Given that the kinetic isotopic fractionation of magnesium during evaporation is decreased by isotope exchange, the $^{27}\text{Al}/^{24}\text{Mg}$ for melts before evaporation could be lower. Therefore, the formation of reversely zoned grains 8 and 9 could possibly be explained by the crystallization from evaporating melts depending on evaporation conditions.

In contrast to the formation of reversely zoned melilite crystals by melt evaporation, condensation from a solar nebular gas during a period of decreasing pressure (MacPherson and Grossman, 1984) can readily explain their formation, similar to other reversely zoned grains (1, 3, 15, and 21 discussed in Sections 4.1.1 and 4.1.2). Considering a consistency with other grains, the condensation formation of grains 8 and 9 appear to be highly plausible. If these grains formed by condensation from solar nebular gas, it is implied that the oxygen isotopic compositions of the surrounding nebular gas changed from ^{16}O -poor to ^{16}O -rich and the $\delta^{25}\text{Mg}$ values increased as

condensation progressed.

4.2 Formation sequence and oxygen isotope change in the surrounding environment for fluffy Type A CAI V2-01

The spinel crystals in the CAI interior were enclosed by melilite crystals. This relationship clearly shows that the spinel was formed prior to the melilite. In contrast, thermodynamic calculations predict condensation of melilite from the solar nebular gas before spinel (e.g., Grossman et al., 1972; Wood and Hashimoto, 1993). Spinel-hibonite aggregates in CM2 chondrites show textural evidence for direct condensation of spinel after hibonite (MacPherson et al., 1984), which has been supported by additional multiple evidences of textures and isotopic and trace elemental compositions (MacPherson and Davis, 1994; Simon et al., 2006). In addition, Han et al. (2015) conducted crystallographic observations of the spinel-hibonite inclusions in the ALH77037 CO3 chondrite, showing epitaxial nucleation and growth of spinel on hibonite. These studies suggest that hibonite reacted with gas to form spinel and melilite condensation could be kinetically hindered relative to spinel. In this model, spinel could be formed before melilite. Spinel-hibonite-perovskite assemblages, of which spinel replaces hibonite, were also observed in melilite-rich region of a Type A CAI from the Allende CV3 chondrite (Park et al., 2012). On the other hand, the formation of spinel and melilite in distinct reservoirs could be considered because of the different oxygen isotopic compositions of spinel and melilite. Given that the condensation of melilite occurred in a distinct reservoir from the one in which spinel formed, the formation of spinel prior to the melilite can readily be explained.

Katayama et al. (2012) suggested that the reversely zoned melilite crystals formed at the inner edge region of the solar nebula, where coronal and nebular gases are encountered and mixed (Yurimoto et al., 2008). In this case, the mixing of coronal gas with nebular gas may result in a change in chemical composition of the nebular gas, which implies that the condensation of melilite occurred in a gaseous reservoir different from that of spinel formation. Thus, the formation sequence may not necessarily follow the predicted equilibrium condensation sequence in a closed system. In V2-01, spinel in the interior and the melilite crystals have distinct $(^{26}\text{Al}/^{27}\text{Al})_0$ values, as discussed in Section 4.3.5. The difference in initial values supports the interpretation that the CAI was not formed by single heating event. Therefore, the observed textural relationship between the spinel in the CAI interior and the melilite crystals in V2-01 can be understood by the formation of spinel prior to melilite. The fassaite grains in CAI interior enclosed by

melilite crystals were also likely formed prior to the melilite crystals as shown by the textural relationships. Oxygen self-diffusion in spinel and that in clinopyroxene are much slower than oxygen self-diffusion in melilite at temperatures below ~1500 K (Yurimoto et al., 1989; Ryerson and McKeegan, 1994), which suggests that the oxygen isotopic compositions of spinel and fassaite in V2-01 represent the original compositions at their formation. Thus, the spinel in the CAI interior formed in an ^{16}O -rich reservoir in the solar nebula, as indicated by its ^{16}O -rich composition (Fig. 5). On the other hand, the variations of oxygen isotopic compositions for fassaite grains (Fig. 5) suggest that they formed in a variable oxygen isotope reservoir. These imply that the oxygen isotopic compositions of nebular gas for fluffy Type A CAI formation were already variable before melilite formation.

The reversely zoned melilite grains 1 and 15 have variations in $\delta^{25}\text{Mg}$, where the $\delta^{25}\text{Mg}$ values decrease with decreasing åkermanite content, while the $\delta^{25}\text{Mg}$ values increase with decreasing åkermanite content in the grains 8 and 9 (Fig. 8). In contrast, the $\delta^{25}\text{Mg}$ values for grains 3 and 21 are constant despite variations in åkermanite content (Figs. 8b and 8f). The observed variations of magnesium isotopic fractionations in the reversely zoned melilite crystals indicate the presence of variable magnesium isotope gaseous reservoirs in the fluffy Type A CAI-forming region of the solar nebula. These melilite grains had grown individually in distinct environments of the solar nebula, and subsequently accumulated into the CAI. A Type A CAI from the Efremovka CV3, HKE 01, is composed of two domains, which grew in nebular reservoirs with distinct oxygen isotopic compositions, temperature and/or pressure (Kawasaki et al., 2012). Therefore, crystals or domains forming separately in the solar nebula and then accumulating to form each CAI may be common in the formation of fluffy Type A CAI.

The formation process of the W-L rims on coarse-grained CAIs remains controversial. There are two major models describing W-L rim formation: as subsolidus evaporation residues (Wark, 2005); and condensation products (Simon et al., 2005). It was revealed that the W-L rims on Types A and B CAIs are enriched in rare earth elements (REEs) relative to the underlying CAI interiors (Wark and Boynton, 2001; Wark, 2005). Differences in the chondrite-normalized REE patterns between the W-L rims and the host CAIs could be explained by the evaporation of host CAI interiors to form the W-L rims. Wark and Boynton (2001) suggested that the W-L rims formed by flash heating at a high temperature (~3000 K for a few seconds), although Wark (2005) excluded flash heating, based on observations of melilite adjacent to the W-L rim of a fluffy Type A

CAI from Allende, which showed no sign of melting. Alternatively, subsolidus evaporation was suggested as the formation process of W-L rims (Wark, 2005). In contrast, Simon et al. (2005) suggested a condensation origin for W-L rims. They examined magnesium isotopic compositions of both W-L rims and melilite in the CAI interior, and showed that the W-L rims have a constant $\delta^{25}\text{Mg}$ of ~ 0 while adjacent melilites have variable $\delta^{25}\text{Mg}$ values in each CAI. These relationships suggest that the W-L rims are not the derivatives of the CAI interiors but are condensation products (Simon et al., 2005). Although not all the W-L rims on all CAIs might have formed through the same process, the W-L rims at least would have formed at the last stages of each CAI formation. Therefore, after the condensation of ^{16}O -rich melilite, formation of the V2-01 W-L rim might have occurred continuously in an ^{16}O -rich reservoir in the solar nebula, as suggested by its ^{16}O -rich compositions (Fig. 5).

The formation sequence and oxygen isotope change in the surrounding environment of the V2-01 fluffy Type A CAI can be summarized as follows (Fig. 10): (1) The spinel crystals formed in an ^{16}O -rich reservoir ($\Delta^{17}\text{O} \sim -24\text{‰}$), while the fassaite crystals formed in a variable oxygen isotope reservoir ($\Delta^{17}\text{O} \sim -12$ and -17‰). (2) The reversely zoned melilite crystals started to form in various ^{16}O -poor nebular gaseous reservoirs ($\Delta^{17}\text{O}$ values larger than -10‰) with variable magnesium isotopic compositions. A portion of melilite crystals enclosed the spinel and fassaite crystals formed during stage (1). The melilite crystals were overgrown in a variable oxygen isotope reservoir changing from ^{16}O -poor to ^{16}O -rich ($\Delta^{17}\text{O} \sim -25\text{‰}$). (3) The melilite crystals accumulated to form the V2-01 CAI precursor. (4) W-L rim minerals were formed in an ^{16}O -rich reservoir ($\Delta^{17}\text{O} \sim -23\text{‰}$). The formation sequence above indicates that the V2-01 CAI was formed in variable oxygen isotope reservoirs that changed from ^{16}O -rich to ^{16}O -poor and back to ^{16}O -rich. The trend of cyclic oxygen isotope change in the surrounding environment is also suggested on the basis of oxygen isotope distributions in other CAIs, including a Type B2 CAI from Vigarano and compact Type A CAIs from the Allende CV3 (Yoshitake et al., 2005; Simon et al., 2011; Park et al., 2012).

4.3 Formation period of the V2-01 fluffy Type A CAI

4.3.1 Al–Mg systematics of spinel in the CAI interior

Spinel in the CAI interior probably formed before the start of melilite condensation, as discussed in Section 4.2, suggesting that the formation age of the spinel should be estimated independently from other constituent minerals of V2-01. The spinel showed a

constant $\delta^{26}\text{Mg}^*$ value of $\sim 0.98\%$ (Fig. 6). Given that we defined the isochron of the spinel in the CAI interior assuming an initial $(\delta^{26}\text{Mg}^*)_0$ of $-0.0159 \pm 0.0014\%$ for the Solar System (Larsen et al., 2011), the initial value of the spinel was $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$. On the other hand, using the initial $(\delta^{26}\text{Mg}^*)_0$ value of $-0.040 \pm 0.029\%$, obtained in a different laboratory (Jacobsen et al., 2008), gave $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.7 \pm 0.3) \times 10^{-5}$, which is indistinguishable from our value because of our measurement errors of the $\delta^{26}\text{Mg}^*$. Therefore, the selection of initial values was not a significant issue for our ^{26}Al – ^{26}Mg chronological study.

The inferred initial value of $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$ might be slightly larger than the canonical $(^{26}\text{Al}/^{27}\text{Al})_0$ value of $(5.23 \pm 0.13) \times 10^{-5}$ (Jacobsen et al., 2008) or $(5.252 \pm 0.019) \times 10^{-5}$ (Larsen et al., 2011), although they are within 3 sigma errors of each other. The initial value of the interior spinel may have been disturbed through melting events or solid-state diffusion during late thermal events, resulting in magnesium isotope exchange with surrounding minerals. In order for the $^{26}\text{Mg}^*$ of spinel to have been disturbed by resetting due to either the melting event or the solid-state diffusion, surrounding minerals should have different $^{27}\text{Al}/^{24}\text{Mg}$ ratios than the spinel ($^{27}\text{Al}/^{24}\text{Mg} \sim 2.5$). Melilite in V2-01 showed an $^{27}\text{Al}/^{24}\text{Mg}$ ratio of at least ~ 10 (Fig. 7), which meets this requirement. However, the spinel is a liquidus mineral in the bulk composition of the V2-01 fluffy Type A CAI (Stolper, 1982), indicating that a complete melting of the CAI is required for complete resetting of the Al–Mg system. Because the V2-01 CAI has never been extensively melted, the resetting of Al–Mg system due to melting event is implausible.

Another possibility is the resetting of the Al–Mg system due to magnesium isotope exchange between the spinel and the surrounding melilite by solid-state diffusion of magnesium isotopes during metamorphism in the asteroidal parent body of the Vigarano meteorite. Magnesium isotope exchange between spinel and anorthite resulting in resetting of the Al–Mg system was demonstrated in a Type C CAI from Allende, although it depended on the grain sizes (Kawasaki et al., 2015). The observed Mg–Fe zoning in the W-L rim spinel, with sizes of $\sim 3 \mu\text{m}$ (Fig. 2c), suggests that the diffusion distance of Fe^{2+} in the spinel in V2-01 was less than a few micrometers. An incorporation of Fe^{2+} might have occurred during the metamorphism. Diffusivity of magnesium isotopes in spinel is almost the same as or slower than Fe^{2+} (Liermann and Ganguly, 2002), indicating that the diffusion distance of magnesium isotopes in the spinel in V2-01 should have been less than a few micrometers. This further suggests that

the exchange of magnesium isotopes by solid-state diffusion during metamorphism was probably insufficient to disturb the $^{26}\text{Mg}^*$ of spinel in the CAI interior, which have sizes of a few tens of micrometers, that were measured for ^{26}Al – ^{26}Mg systematics. Therefore, the resetting of the Al–Mg system to disturb the $^{26}\text{Mg}^*$ for the spinel in the CAI interior probably did not occur, and the spinel might preserve a closed system from its formation.

4.3.2 Al–Mg systematics of the diopside and spinel in W-L rim

The Al–Mg isotopic compositions of diopside and spinel in the W-L rim were measured and a mineral isochron for the W-L rim could be defined (Fig. 6). The initial values inferred for the isochron of W-L rim were $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.5 \pm 0.4) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = -0.05 \pm 0.05\text{‰}$. The $(^{26}\text{Al}/^{27}\text{Al})_0$ value is significantly lower than that of the spinel in the CAI interior or the canonical initial value, which is mainly due to the low $\delta^{26}\text{Mg}^*$ value for spinel in the W-L rim ($\sim 0.79\text{‰}$). For a chronological interpretation of the deviation of $(^{26}\text{Al}/^{27}\text{Al})_0$ values, studying the exchange of the magnesium isotope with the surrounding minerals by solid-state diffusion was also considered important. For a decrease in the concentration of $^{26}\text{Mg}^*$ in the W-L rim spinel through the exchange of magnesium isotope with other minerals, the presence of adjacent minerals having lower $^{27}\text{Al}/^{24}\text{Mg}$ ratios than that in the spinel ($^{27}\text{Al}/^{24}\text{Mg} \sim 2.5$) is necessary. However, the mineral adjacent to the spinel, i.e., melilite, has an $^{27}\text{Al}/^{24}\text{Mg}$ ratio of >20 , suggesting that exchange of the magnesium isotope with other minerals by solid-state diffusion to be unlikely. The possibility of the exchange of the magnesium isotope with the Vigarano matrix minerals should also be cared, however, the exchange could be disregarded since, based on the discussion in Section 4.3.1, the distance of diffusion of the magnesium isotope in the V2-01 spinel was estimated to be less than a few micrometers. Therefore, the spinel in the W-L rim may have preserved a closed system starting from its formation and the inferred $(^{26}\text{Al}/^{27}\text{Al})_0$ value has a chronological significance.

4.3.3 Al–Mg systematics of the reversely zoned melilite crystals

As discussed in Sections 4.1.1 and 4.1.2, the grains 1, 3, 15 and 21 likely formed by condensation from solar nebular gas. If the crystal growth of these grains was slow enough, the gehlenitic sides would have depleted $\delta^{26}\text{Mg}^*$ relative to the isochron lines in the ^{26}Al – ^{26}Mg isochron diagrams, owing to the evolution of the Al–Mg system of solar nebular gas. However, the data show that $\delta^{26}\text{Mg}^*$ of the gehlenitic sides of these grains are not systematically depleted relative to the isochron slopes (Fig. 7), which

indicates that they formed in the gas with a homogeneous distribution of $(^{26}\text{Al}/^{27}\text{Al})_0$ within the time durations corresponding to the errors of $(^{26}\text{Al}/^{27}\text{Al})_0$ value for each isochron although the oxygen isotopic compositions in the gas were variable. The time durations for the formation of the grains were estimated to be within 0.15 Myr for grain 1, 0.27 Myr for grain 3, 0.12 Myr for grain 15, and 0.09 Myr for grain 21. The condensation of the reversely zoned melilite crystals (grains 1, 3, 15 and 21) from solar nebular gas occurred within the time duration of 0.09–0.27 Myr.

As discussed in Section 4.1.3, grains 8 and 9 could have been formed by either the crystallization from the evaporating melt with a back reaction of the evaporated species or the condensation from the solar nebular gas. Given that these grains formed by crystallization from evaporating melt, the $(^{26}\text{Al}/^{27}\text{Al})_0$ values for the overgrown melilite from the evaporating melt and for the relic melilite may be distinct. However, according to our data, grains 8 and 9 seem to have well-resolved single isochrons, implying their formations to have included evaporative melting that occurred within time durations of 0.20 Myr for grain 8 and 0.15 Myr for grain 9. On the other hand, if they were formed by condensation, the time durations for the condensation were calculated to be 0.20 Myr for grain 8 and 0.15 Myr for grain 9 using the same method described for grains 1, 3, 15, and 21.

The $(^{26}\text{Al}/^{27}\text{Al})_0$ values for the reversely zoned melilite crystals in V2-01 were smaller than the canonical $(^{26}\text{Al}/^{27}\text{Al})_0$ value (Jacobsen et al., 2008; Larsen et al., 2011) (Fig. 11). A possible explanation for this discrepancy might be the systematic shift in the $(^{26}\text{Al}/^{27}\text{Al})_0$ values resulting from the analytical artifacts for the determination of the $^{27}\text{Al}/^{24}\text{Mg}$ ratio. We used synthetic melilite glass with $^{27}\text{Al}/^{24}\text{Mg} = 3.82$ as the standard in terms of the relative sensitivity factor (RSF) for aluminium and magnesium. If the RSF was shifted by ~11%, the discrepancy of $(^{26}\text{Al}/^{27}\text{Al})_0$ value observed in this study can be accounted for. However, we measured the $^{27}\text{Al}/^{24}\text{Mg}$ ratios of the melilite using FE-SEM equipped with EDS to confirm the $^{27}\text{Al}/^{24}\text{Mg}$ ratios determined by the SIMS measurements; and as a result of which, a systematic shift of the level of ~11% in the $^{27}\text{Al}/^{24}\text{Mg}$ ratios was never observed, suggesting that the discrepancy between the $(^{26}\text{Al}/^{27}\text{Al})_0$ values for the melilite and the canonical $(^{26}\text{Al}/^{27}\text{Al})_0$ value would not have resulted from the analytical artifacts for the determination of the $^{27}\text{Al}/^{24}\text{Mg}$ ratio. The well-correlated isochrons among the wide range of $^{27}\text{Al}/^{24}\text{Mg}$ ratios (Fig. 7) support this inference. Therefore, it can be said that the inferred $(^{26}\text{Al}/^{27}\text{Al})_0$ values for the melilite have chronological significance.

4.3.4 Al–Mg systematics of the fassaite enclosed by melilite

If we draw a regression line for the Al–Mg isotopic compositions for fassaite, the line seems to give values of $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.1 \pm 1.8) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = 0.1 \pm 0.4\text{‰}$. However, two problems were encountered while defining the fassaite isochron: (1) the oxygen isotopic compositions for fassaite were variable (Fig. 5); and (2) the regression would essentially be based on two points. The variable oxygen isotopic compositions of the fassaite grains argue against the possibility of them being formed from a single reservoir. On the other hand, the ^{26}Al – ^{26}Mg isochron should be defined for minerals that formed from a single reservoir under equilibrium (e.g., Kawasaki et al., 2015). Thus, the isochron for fassaite cannot be defined readily. However, in spite of their variable oxygen isotopic compositions, we defined the isochrons for the reversely zoned melilite crystals in Section 4.3.3. The isochrons of the reversely zoned melilite crystals could be tested by using data with various $^{27}\text{Al}/^{24}\text{Mg}$ ratios, and as a result, no systematic shifts in the data plots were observed. However, in the case of fassaite, the regression line was drawn basically using two points; thus, any systematic shifts in the data plots could not be determined. Therefore, the fassaite isochron has not been provided in this paper. Nevertheless, the Al–Mg isotopic compositions for the fassaite grains seem to plot on the model isochron for the spinel in the CAI interior and not on the mineral isochron of the W–L rim (Fig. 6), implying that the fassaite grains formed simultaneously with the spinel in the CAI interior before the formation of the W–L rim, which is in agreement with the formation sequences estimated through the petrographic observations.

4.3.5 Formation period of the V2-01 fluffy Type A CAI

The $(^{26}\text{Al}/^{27}\text{Al})_0$ values are identical among the six reversely zoned melilite crystals and the W–L rim within the analytical errors (Fig. 11), and show an average value of $(4.7 \pm 0.3) \times 10^{-5}$ (2SD). The time duration for their formation was calculated to be within 0.13 Myr. Thus, it can be inferred that the formation and accumulation of the reversely zoned melilite crystals and the formation of the W–L rim occurred over a period of less than 0.13 Myr in the variable oxygen isotope gaseous reservoir that changed from ^{16}O -poor to ^{16}O -rich (Fig. 10). On the other hand, the spinel in CAI interior shows $(^{26}\text{Al}/^{27}\text{Al})_0$ value of $(5.6 \pm 0.2) \times 10^{-5}$, which is larger than the value of $(4.7 \pm 0.3) \times 10^{-5}$ for the melilite crystals and the W–L rim (Fig. 11). The difference in the $(^{26}\text{Al}/^{27}\text{Al})_0$ values corresponds to an age difference of 0.18 ± 0.07 Myr, indicating that the V2-01 fluffy Type A CAI formed over a period of 0.18 ± 0.07 Myr in oxygen isotope reservoirs that varied from ^{16}O -rich to ^{16}O -poor and back to ^{16}O -rich (Fig. 10).

4.4 Implications for astrophysical setting of Type A CAI-forming region

Katayama et al. (2012) proposed that the change in the oxygen isotopic composition of the surrounding nebular gas from ^{16}O -poor to ^{16}O -rich during the growth of the reversely zoned melilite crystals in the V2-01 fluffy Type A CAI corresponds to the inner edge region of the solar nebula, where ^{16}O -rich solar and ^{16}O -poor planetary gases are encountered and mixed (Yurimoto et al., 2008). The environmental change around the melilite crystals might have occurred due to radial excursion of inner edge of solar protoplanetary disk (Shu et al., 1997; Itoh and Yurimoto, 2003) or the radial transportation of grains (Ciesla, 2007, 2009). Similar nebular environments were suggested based on the measurements of oxygen isotopic and chemical zoning for intra- and inter- melilite crystals in Type A CAIs from Efremovka and Allende (Kawasaki et al., 2012; Park et al., 2012). As discussed in Section 4.3.5, our additional oxygen isotope data and the ^{26}Al – ^{26}Mg systematics for V2-01 indicated that the oxygen isotopic composition of solar nebular gas surrounding the CAI changed from ^{16}O -rich to ^{16}O -poor and back to ^{16}O -rich over a period of 0.18 ± 0.07 Myr, which suggests that the solar nebular gas from which V2-01 formed changed in oxygen isotopic composition from ^{16}O -rich to ^{16}O -poor and back to ^{16}O -rich during the first 0.18 ± 0.07 Myr of the Solar System. These findings imply that the radial excursion of the inner edge of the solar nebula, or radial transportation resulting in changes in the oxygen isotopic composition of the gas from which CAIs formed continued for at least 0.18 ± 0.07 Myr.

5. CONCLUSIONS

Oxygen isotopic distributions and petrography of the V2-01 fluffy Type A CAI revealed the formation sequence and oxygen isotope change in the surrounding environment. The sequence is described as follows: (1) Spinel in the CAI interior formed in a ^{16}O -rich reservoir ($\Delta^{17}\text{O} \sim -24\text{‰}$), while fassaite formed in a variable oxygen isotope reservoir ($\Delta^{17}\text{O} \sim -12$ and -17‰). (2) Reversely zoned melilite crystals formed in a variable oxygen isotope reservoir changing from ^{16}O -poor ($\Delta^{17}\text{O}$ values larger than -10‰) to ^{16}O -rich ($\Delta^{17}\text{O} \sim -25\text{‰}$) and accumulated to form the V2-01 CAI precursor. A portion of melilite crystals enclosed pre-existing spinel and fassaite crystals. (3) W-L rim minerals formed in a ^{16}O -rich reservoir ($\Delta^{17}\text{O} \sim -23\text{‰}$). Variations of mass dependent magnesium isotopic fractionation observed in the reversely zoned melilite crystals that formed by condensation indicate a presence of a variable magnesium isotope gaseous reservoir in the solar nebula.

The ^{26}Al – ^{26}Mg systematics are consistent with the inferred formation sequence. Spinel in the CAI interior, six reversely zoned melilite crystals, and W-L rim minerals showed $(^{26}\text{Al}/^{27}\text{Al})_0$ values of $(5.6 \pm 0.2) \times 10^{-5}$, $(4.7 \pm 0.3) \times 10^{-5}$, and $(4.5 \pm 0.4) \times 10^{-5}$, respectively. The oxygen isotope distributions and the ^{26}Al – ^{26}Mg systematics indicated that V2-01 formed over a period of 0.18 ± 0.07 Myr in a variable oxygen isotope reservoir that changed from ^{16}O -rich to ^{16}O -poor and back to ^{16}O -rich. The region of the formation of V2-01 fluffy Type A CAI is suggested to correspond to the inner edge region of the solar nebula where ^{16}O -rich solar and ^{16}O -poor planetary gases are encountered and mixed (Yurimoto et al., 2008; Katayama et al., 2012). Our findings imply that the radial excursion of the inner edge of the solar nebula or radial transportation, resulting in changes in the oxygen isotopic composition of the gas from which CAIs formed continued for at least 0.18 ± 0.07 Myr.

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1110 Washington, D. C.: Mineralogical Society of America. pp. 141–186.
- 1111

1112 Table 1. Representative compositions of diopside, fassaite, and spinel in V2-01.

wt%	CAI interior				W-L rim			
	Fas	Fas	Sp	Sp	Di	Di	Sp	Sp
MgO	5.9	8.1	27.9	27.4	17.9	14.8	27.8	27.4
Al ₂ O ₃	20.8	17.4	71.2	70.0	0.3	8.6	71.0	71.1
SiO ₂	31.9	36.7	n.d.	n.d.	55.3	49.6	n.d.	n.d.
CaO	24.5	24.7	n.d.	n.d.	26.1	25.8	n.d.	n.d.
TiO ₂	15.1	11.9	0.3	0.2	n.d.	1.4	0.4	0.3
V ₂ O ₅	1.7	1.1	1.0	1.2	n.d.	n.d.	0.4	0.5
FeO	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	0.2	0.8
Total	99.9	100.0	100.4	99.0	99.6	100.1	99.8	100.0
Cations								
Mg	0.33	0.45	0.98	0.98	0.97	0.80	0.98	0.97
Al	0.91	0.76	1.98	1.97	0.01	0.36	1.99	1.99
Si	1.19	1.36	n.d.	n.d.	2.00	1.79	n.d.	n.d.
Ca	0.98	0.98	n.d.	n.d.	1.01	1.00	n.d.	n.d.
Ti	0.42	0.33	0.01	0.00	n.d.	0.04	0.01	0.00
V	0.04	0.03	0.02	0.02	n.d.	n.d.	0.01	0.01
Fe	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.00	0.02
Total	3.87	3.89	2.98	2.98	3.99	3.99	2.99	2.99
per oxygen	6	6	4	4	6	6	4	4

Di: diopside, Fas: fassaite, Sp: spinel, n.d. = not detected

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1116 Table 2. Oxygen isotopic compositions (‰) of diopside, fassaite, and spinel in V2-01.

Mineral	$\delta^{17}\text{O}$	2σ	$\delta^{18}\text{O}$	2σ	$\Delta^{17}\text{O}$	2σ
CAI interior						
Fas	-32.1	2.2	-29.5	1.8	-16.8	2.0
Fas	-19.1	2.0	-17.1	2.1	-10.2	2.1
Fas	-20.8	2.2	-16.3	1.7	-12.3	2.1
Fas	-20.4	2.2	-15.7	2.1	-12.2	2.0
Sp	-47.8	2.1	-44.7	1.6	-24.5	2.1
Sp	-46.1	1.8	-44.0	1.4	-23.3	1.6
Sp	-47.4	2.3	-45.9	2.0	-23.5	2.0
W-L rim						
Di	-44.0	2.3	-42.3	1.4	-22.0	2.4
Di	-45.5	1.8	-42.0	1.4	-23.7	1.8
Sp	-45.8	2.1	-44.0	1.3	-22.9	2.0
Sp	-45.2	1.9	-42.9	1.7	-22.9	1.6

1117 Di: diopside, Fas: fassaite Sp: spinel

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1120 Table 3. Magnesium isotopic compositions (‰) and $^{27}\text{Al}/^{24}\text{Mg}$ ratios of diopside,
1121 fassaite, and spinel in V2-01.

Mineral	$^{27}\text{Al}/^{24}\text{Mg}$	2σ	$\delta^{26}\text{Mg}^*$	2σ	$\delta^{25}\text{Mg}$	2σ
CAI interior						
Fas	3.45	0.02	1.39	0.14	-	-
Fas	2.49	0.04	1.01	0.13	-	-
Fas	3.77	0.05	1.44	0.13	-	-
Fas	3.66	0.03	1.48	0.15	-	-
Sp	2.48	0.00	0.98	0.14	-0.62	0.06
Sp	2.48	0.00	0.97	0.14	-0.61	0.06
Sp	2.47	0.00	0.95	0.14	-0.64	0.05
Sp	2.48	0.00	1.03	0.13	-0.08	0.05
Sp	2.50	0.00	1.05	0.16	-0.53	0.05
Sp	2.47	0.00	0.97	0.13	-0.66	0.05
Sp	2.48	0.00	1.03	0.14	-0.68	0.06
Sp	2.47	0.00	0.92	0.11	0.30	0.08
Sp	2.48	0.00	1.01	0.11	0.61	0.08
Sp	2.49	0.00	0.98	0.13	0.69	0.07
Sp	2.48	0.00	0.99	0.11	0.30	0.06
Sp	2.49	0.00	0.91	0.13	0.02	0.05
W-L rim						
Di	0.02	0.00	-0.02	0.13	-	-
Di	0.42	0.03	0.08	0.10	-	-
Di	0.49	0.02	0.04	0.11	-	-
Di	0.04	0.00	-0.02	0.12	-	-
Di	0.04	0.00	0.00	0.09	-	-
Sp	2.49	0.00	0.76	0.13	0.02	0.04
Sp	2.51	0.00	0.70	0.11	0.94	0.07
Sp	2.51	0.00	0.79	0.11	0.92	0.08
Sp	2.53	0.00	0.81	0.11	1.04	0.08
Sp	2.49	0.00	0.75	0.13	0.76	0.06
Sp	2.49	0.00	0.77	0.14	0.62	0.07
Sp	2.51	0.00	0.75	0.12	0.67	0.07
Sp	2.50	0.00	0.81	0.12	0.80	0.10
Sp	2.51	0.00	0.80	0.11	0.84	0.07

1122 Di: diopside, Fas: fassaite, Sp: spinel, -: not determined (see text in detail)

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1125 Table 4. Magnesium isotopic compositions (‰) and $^{27}\text{Al}/^{24}\text{Mg}$ ratios of melilite
1126 crystals in V2-01.

Grain	#	$^{27}\text{Al}/^{24}\text{Mg}$	2σ	$\delta^{26}\text{Mg}^*$	2σ	$\delta^{25}\text{Mg}$	2σ	Grain	#	$^{27}\text{Al}/^{24}\text{Mg}$	2σ	$\delta^{26}\text{Mg}^*$	2σ	$\delta^{25}\text{Mg}$	2σ
1	87	18.91	0.07	6.1	1.2	2.2	1.0	9	182	35.34	0.15	12.8	1.2	7.9	0.9
1	89	47.36	0.18	16.4	1.1	0.7	1.0	9	183	44.89	0.13	15.5	1.0	9.7	0.9
1	90	44.00	0.49	15.2	1.7	0.1	1.2	9	184	43.79	0.13	15.3	1.0	8.5	0.8
1	91	28.56	0.07	9.4	1.0	0.2	1.0	9	186	30.20	0.09	10.6	1.4	6.1	1.0
1	95	24.87	0.27	8.7	1.7	1.1	1.1	9	187	27.45	0.05	8.7	1.2	5.7	0.9
1	96	32.28	0.37	10.9	1.0	1.1	0.9	9	191	14.39	0.04	5.3	1.1	3.0	0.9
1	97	13.67	0.15	5.0	1.2	3.5	0.9	9	192	14.58	0.08	4.7	1.0	3.3	0.8
1	99	8.16	0.08	2.5	1.5	6.4	0.9	9	227	35.68	0.23	12.9	1.0	7.5	0.9
1	100	30.66	0.35	10.0	1.1	2.4	0.8	9	229	20.60	0.11	8.3	1.2	4.0	1.0
1	116	6.89	0.01	3.2	1.2	5.6	0.8	9	230	15.68	0.08	5.2	0.9	4.2	1.0
1	117	50.04	0.27	17.4	1.1	0.1	0.8	9	232	10.48	0.05	3.7	1.0	4.0	0.9
1	118	11.24	0.04	5.0	1.1	4.8	0.8	15	269	11.05	0.03	3.9	1.1	4.8	0.7
3	67	33.34	0.08	11.5	1.3	1.7	0.7	15	270	16.96	0.08	5.4	0.9	4.2	0.7
3	86	16.32	0.06	6.2	1.1	2.1	1.0	15	271	132.44	4.26	45.8	2.5	1.1	1.5
3	277	10.29	0.03	3.1	1.1	2.4	0.7	15	272	17.23	0.10	4.9	0.9	4.2	0.6
3	278	26.97	0.11	8.7	0.9	2.0	0.7	15	273	13.97	0.05	4.2	1.1	5.6	0.8
3	285	22.42	0.31	7.7	1.4	1.6	0.9	15	274	21.37	0.10	7.3	0.8	2.2	0.6
3	286	28.73	0.27	10.0	0.9	1.6	0.8	15	275	84.68	0.97	28.3	2.3	1.5	1.6
3	289	13.31	0.12	4.7	0.9	1.7	0.8	15	276	21.10	0.09	6.1	0.9	4.3	0.7
3	290	10.19	0.10	3.6	1.4	2.1	0.9	21	233	11.83	0.05	4.9	1.3	1.2	1.0
8	101	27.86	0.31	10.5	1.4	1.8	0.9	21	234	17.32	0.07	6.1	1.3	1.5	1.0
8	102	22.95	0.24	8.8	1.2	1.2	0.9	21	235	23.93	0.09	8.3	1.0	0.9	0.9
8	103	39.81	0.44	13.8	1.0	3.6	0.8	21	236	36.44	0.51	12.4	1.6	0.6	1.1
8	104	19.06	0.21	5.9	1.1	0.6	0.8	21	237	46.98	3.17	17.0	1.9	0.9	1.1
8	119	34.02	0.17	12.2	1.2	1.2	0.9	21	238	24.89	0.14	9.2	1.2	1.7	0.9
8	120	40.19	0.33	13.7	1.1	4.6	0.9	21	264	18.01	0.06	5.5	1.2	2.4	0.7
8	121	24.37	0.09	8.1	1.3	1.8	0.8	21	265	27.43	0.09	8.9	0.9	0.8	0.7
8	122	15.01	0.10	5.4	1.1	0.9	0.9	21	266	44.25	0.16	15.1	1.3	1.3	0.8
8	123	33.17	0.13	11.1	1.3	3.0	0.9	21	267	146.14	1.20	47.7	1.9	2.1	1.1
8	125	52.96	0.38	18.0	1.3	3.8	0.8	21	268	41.28	0.43	13.1	1.4	1.5	0.8
8	126	40.19	0.25	13.6	1.2	2.5	0.7								
8	181	21.92	0.05	8.6	1.2	0.8	0.9								

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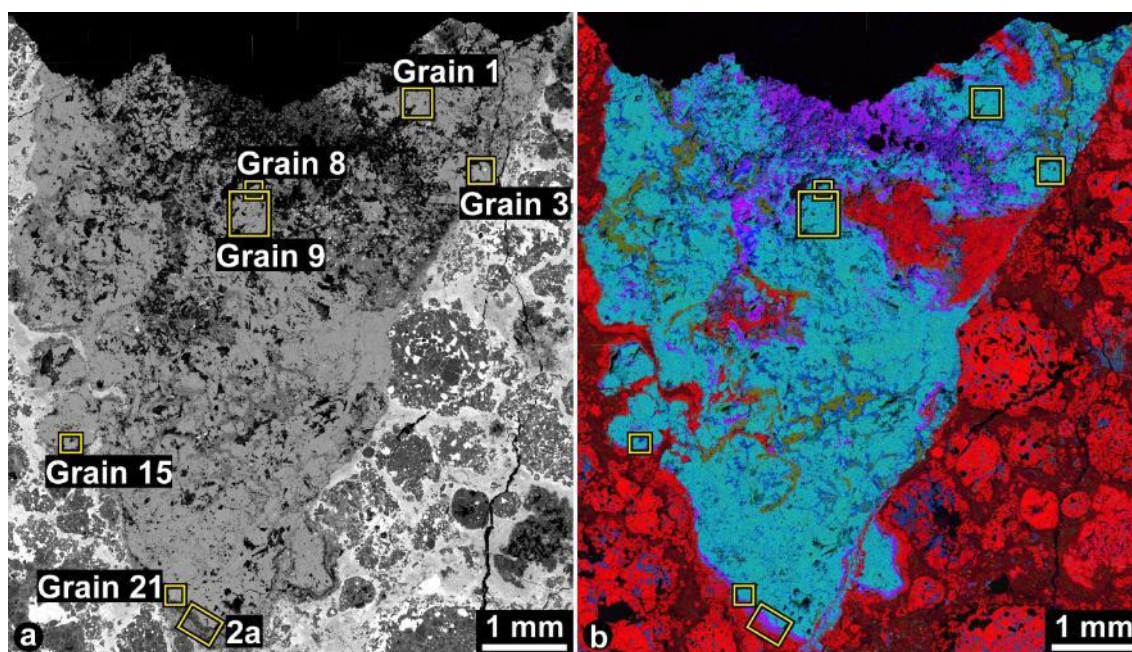


Figure 1. (a) Backscattered electron (BSE) image of the fluffy Type A CAI, V2-01, from the Vigarano CV3 chondrite. Yellow boxes indicate areas containing grains 1, 3, 8, 9, 15, and 21 (Fig. 3); one box, labeled “2a”, is shown in Fig 2a. (b) Combined X-ray elemental map of V2-01 with Mg (red), Ca (green), and Al (blue).

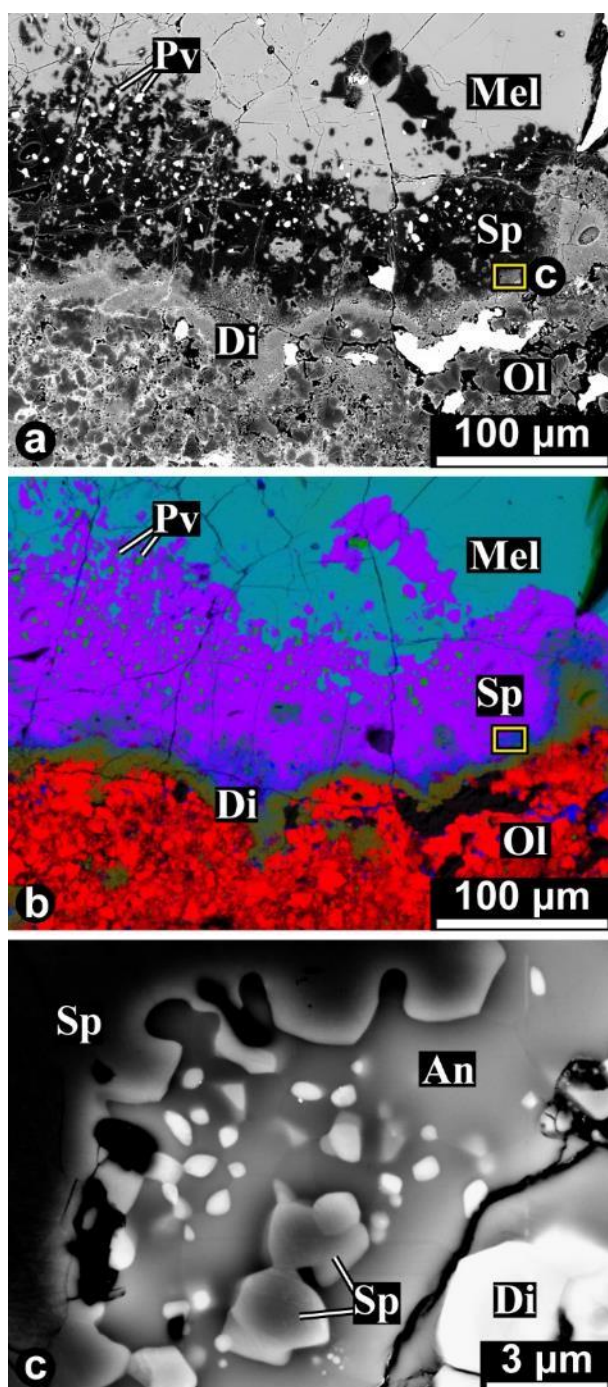


Figure 2. (a) BSE image of the Wark-Lovering rim (W-L rim) in the area of V2-01 indicated by box 2a in Fig. 1a. (b) Combined X-ray elemental map of the area in (a) with Mg (red), Ca (green), and Al (blue). (c) Magnified BSE image of the area indicated by box (c) in (a). An, anorthite; Di, diopside; Mel, melilite; Ol, olivine; Pv, perovskite; Sp, spinel.

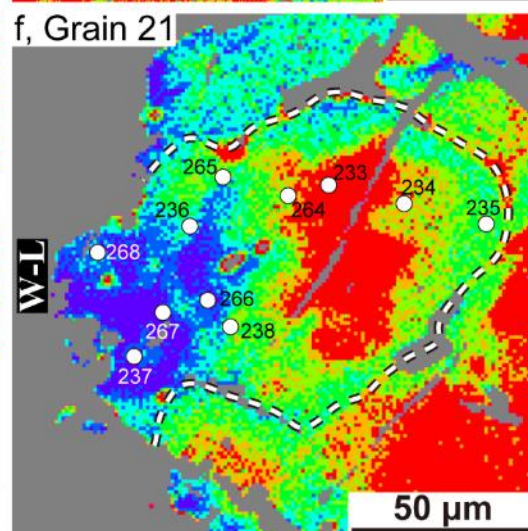
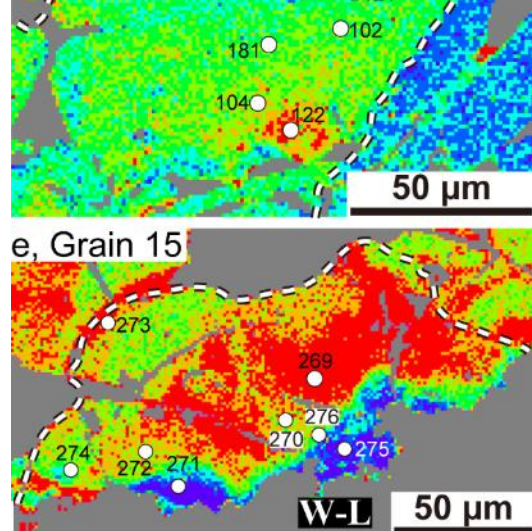
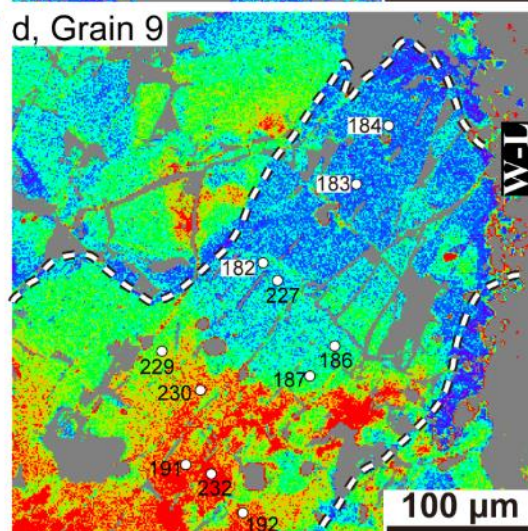
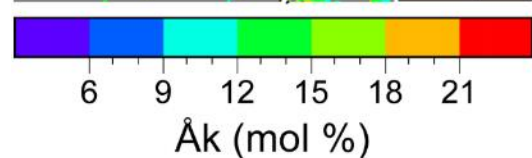
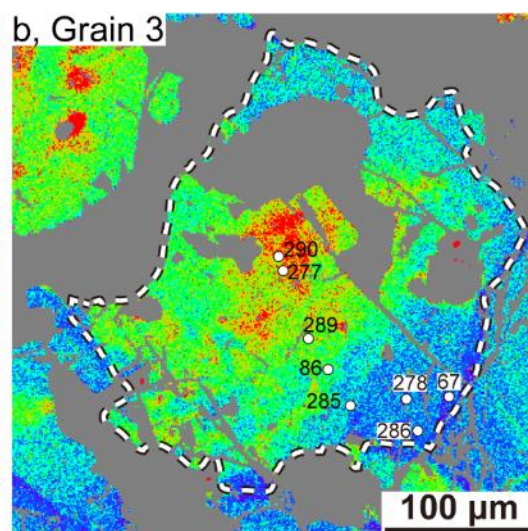
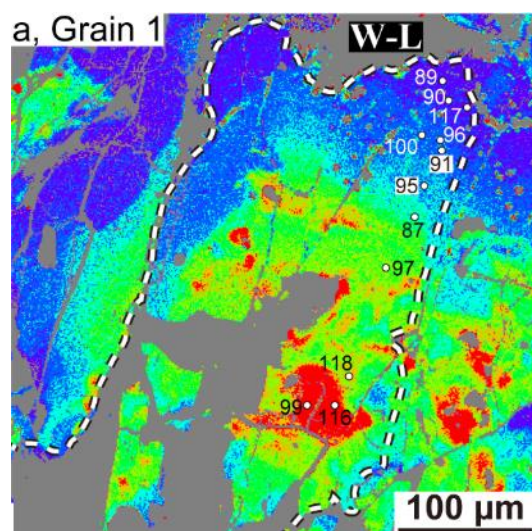


Figure 3. X-ray elemental maps corresponding to åkermanite contents of reversely zoned melilite crystals and measurement positions for magnesium isotopic compositions and $^{27}\text{Al}/^{24}\text{Mg}$ ratios. Color bars indicate åkermanite contents. Other mineral phases and polishing flaws are masked by grey color. Circles indicate measurement positions for Al-Mg isotopes. Numbers of each point correspond to the entries listed in Table 4. Data for X-ray elemental maps were obtained from literature (after Katayama et al., 2012). Dashed lines indicate grain boundaries determined through electron backscattered diffraction (EBSD) analysis. W-L is the Wark-Lovering rim.

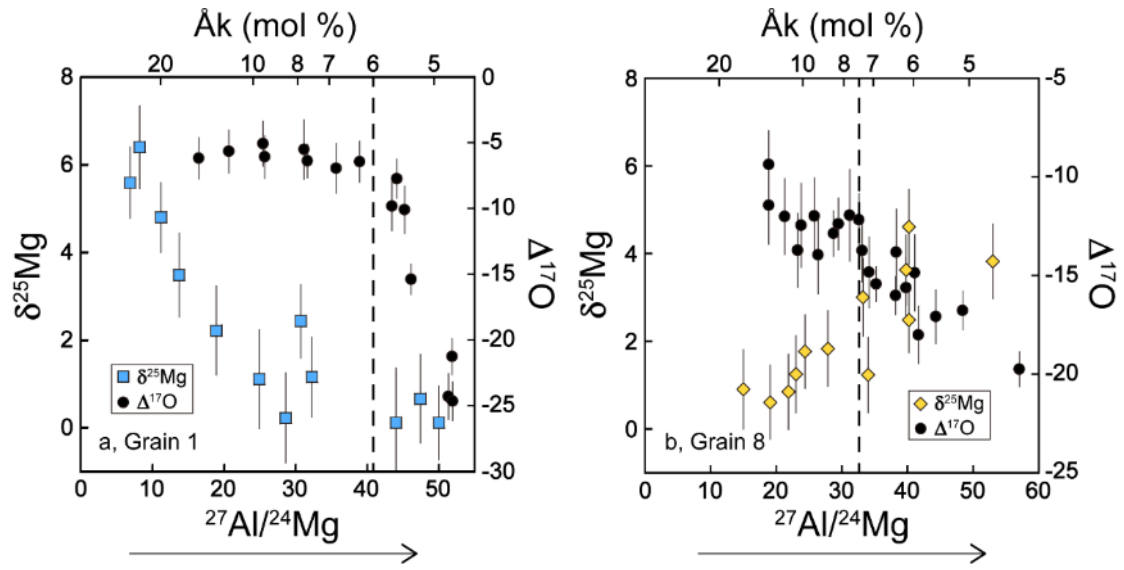


Figure 4. Relationships between the oxygen isotopic composition, the $\delta^{25}\text{Mg}$ values, and the chemical composition of reversely zoned melilite crystals. (a) grain 1; (b) grain 8. Dashed lines indicate the chemical compositions at which the oxygen isotopic compositions started to change. Arrows correspond to directions of compositional change with the growth of reversely zoned melilite crystals. Oxygen isotopic compositions are from Katayama et al. (2012).

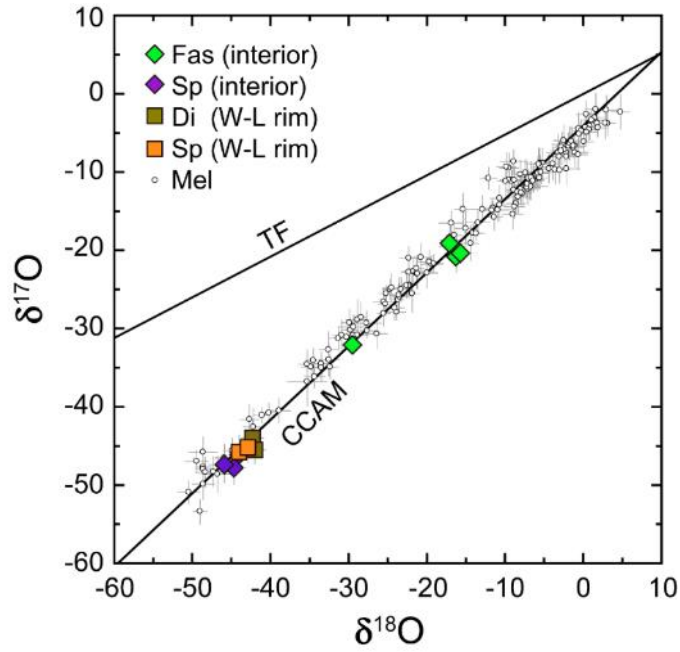


Figure 5. Oxygen isotopic compositions of diopside, fassaite, and spinel in V2-01. The oxygen isotopic compositions of melilite (Katayama et al., 2012) are plotted for comparison. Error bars are 2σ . TF, terrestrial fractionation line; CCAM, carbonaceous chondrite anhydrous mineral line; W-L, the Wark-Lovering rim; Di, diopside; Fas, fassaite; Mel, melilite; Sp, spinel.

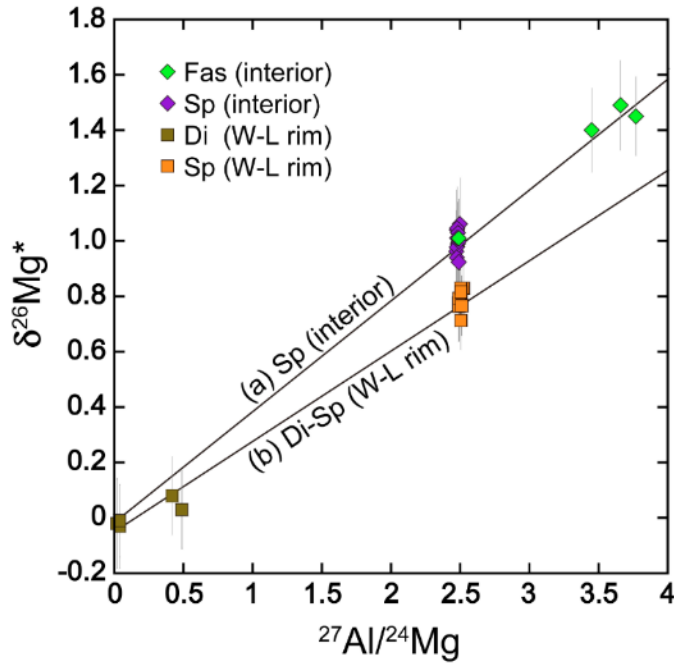


Figure 6. ^{26}Al – ^{26}Mg isochrons of V2-01. (a) Model isochron, $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$, of spinel in the CAI interior assuming a solar initial $(\delta^{26}\text{Mg}^*)_0 = -0.0159 \pm 0.0014\text{‰}$ (Larsen et al., 2011). (b) Internal mineral isochron of the W-L rim, $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.5 \pm 0.4) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = -0.05 \pm 0.05\text{‰}$. Errors are 2σ . W-L, the Wark-Lovering rim; Di, diopside; Fas, fassaite; Mel, melilite; Sp, spinel.

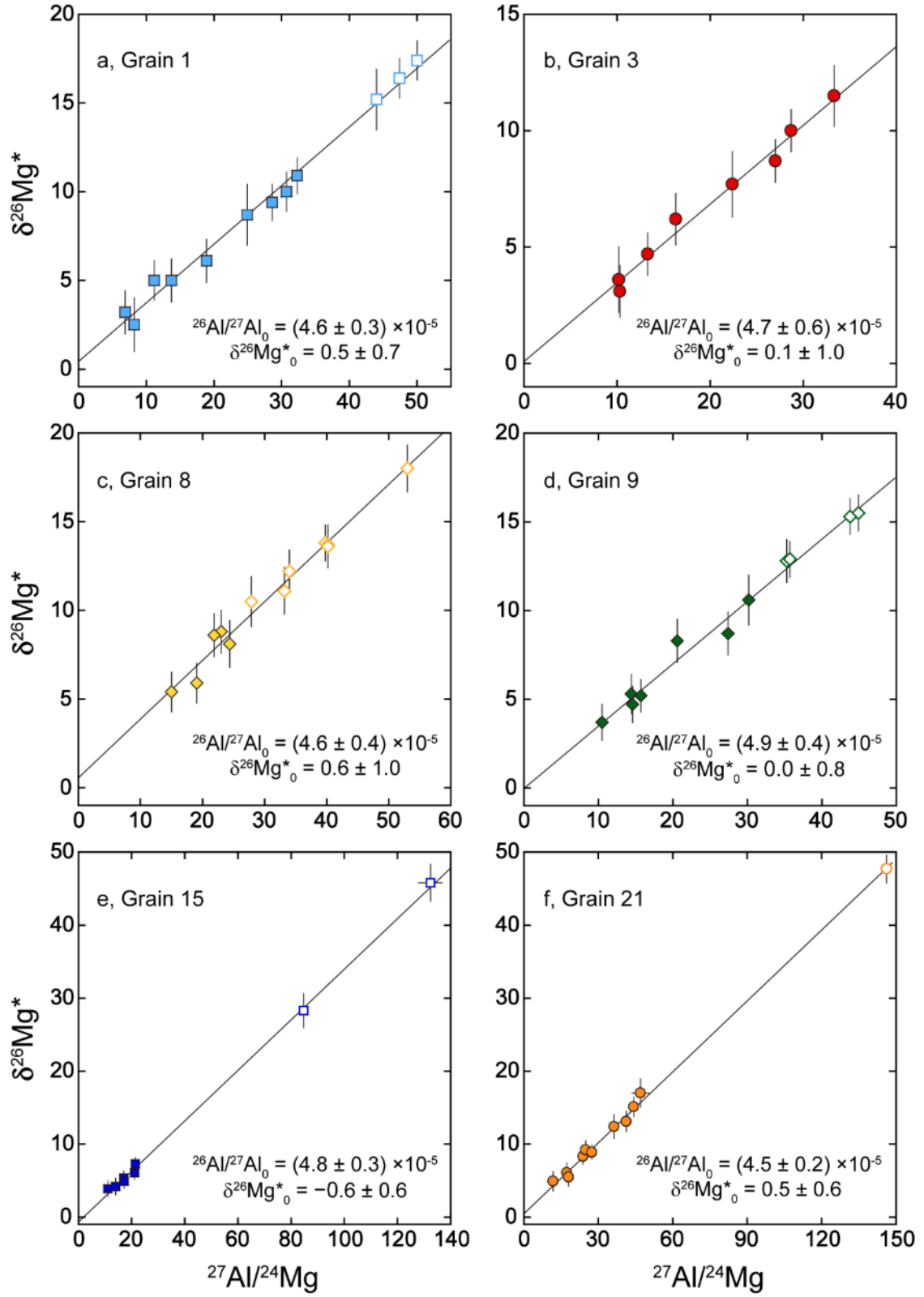
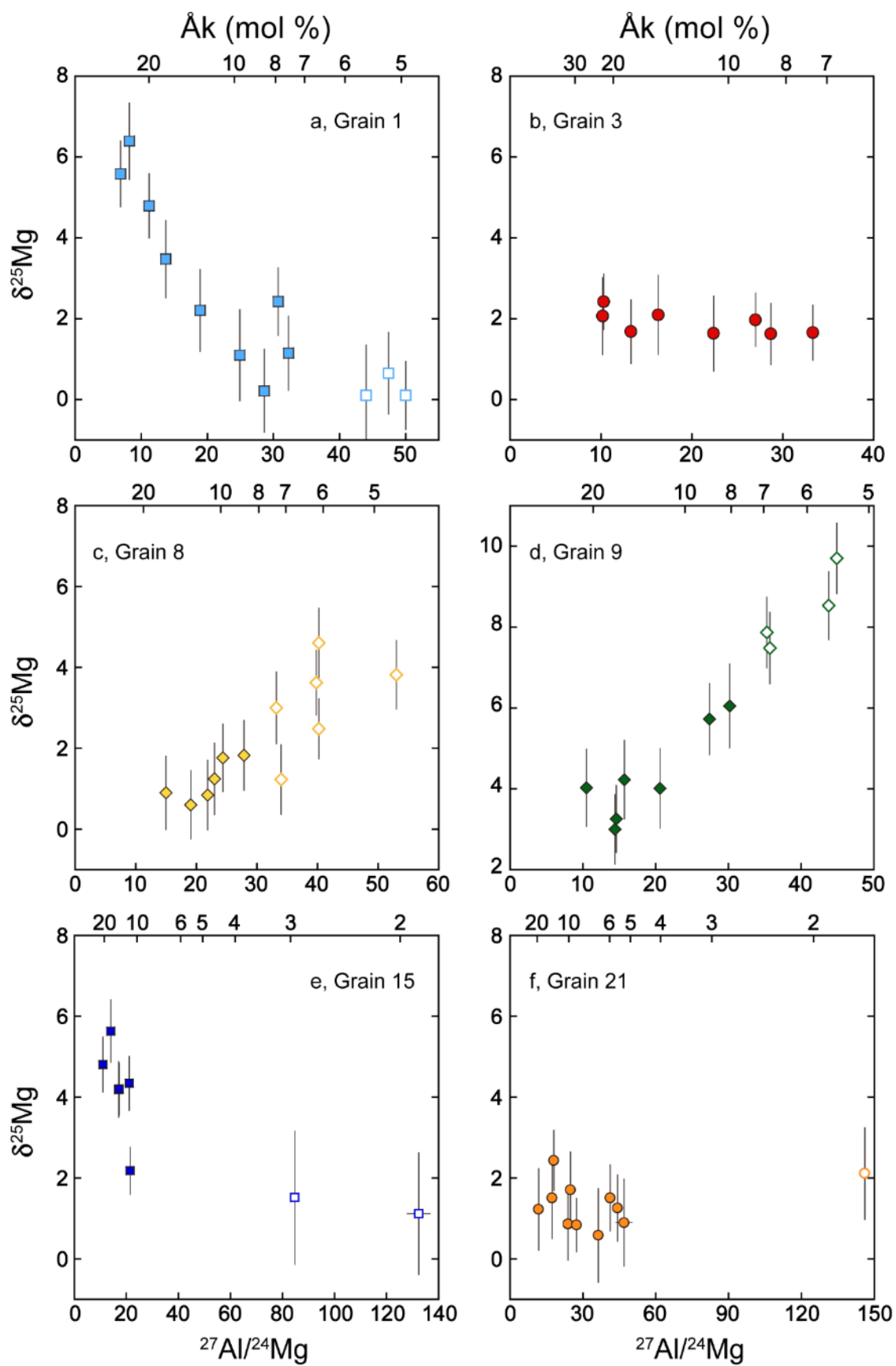


Figure 7. ^{26}Al – ^{26}Mg isochrons for individual reversely zoned melilite crystals in V2-01. Solid symbols correspond to inner zones having ^{16}O -poor compositions and

1179 open symbols correspond to outer zones with increasingly ^{16}O -rich compositions with
1180 decreasing $\text{\AA k}$ contents. Errors are 2σ .
1181



1183 Figure 8. Relationships between the $\delta^{25}\text{Mg}$ values and chemical compositions for each
1184 melilite crystal. Solid symbols correspond to inner zones having ^{16}O -poor
1185 compositions and open symbols correspond to outer zones with increasingly ^{16}O -rich
1186 compositions with decreasing Åk contents. Errors are 2σ .
1187

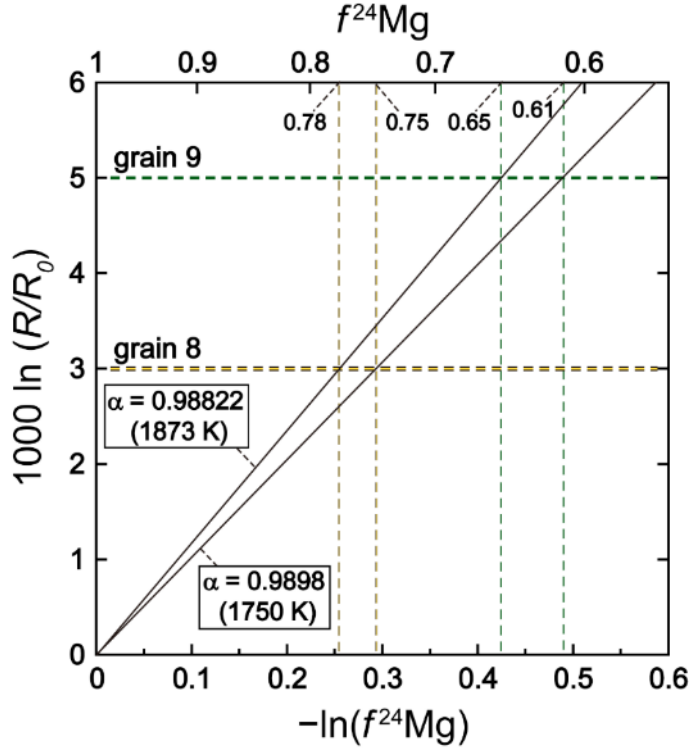


Figure 9. Relationships between elemental and isotopic fractionation during evaporation following the Rayleigh law plotted as $1000 \times \ln (R/R_0)$ versus $-\ln f^{24}\text{Mg}$ and $f^{24}\text{Mg}$, where R is $^{25}\text{Mg}/^{24}\text{Mg}$ in the residual melt, R_0 is $^{25}\text{Mg}/^{24}\text{Mg}$ in the melt before evaporation, and f is the fraction of ^{24}Mg remaining in the residual melt. The kinetic isotopic fractionation factor, α , is from Richter et al. (2007). Observed magnesium isotopic fractionation for grain 8 of $\ln (R/R_0) \sim 3\text{‰}$ and that for grain 9 of $\ln (R/R_0) \sim 5\text{‰}$ are indicated by horizontal dashed lines.

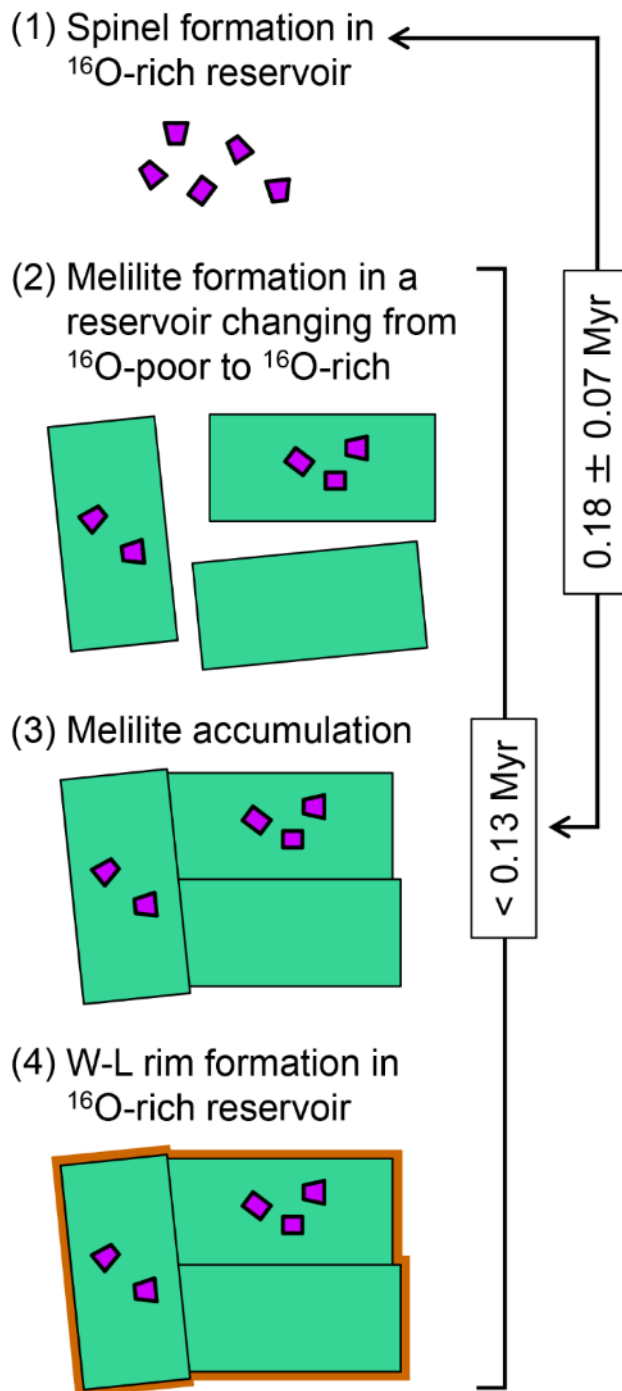


Figure 10. Schematic scenario for the formation of V2-01. The formation sequence of the CAI is described as follows: (1) Spinel crystals formed in a ^{16}O -rich reservoir. Fassaite crystals might also form at this stage. (2) Reversely zoned melilite crystals (green rectangles) formed in a variable oxygen isotope reservoir that changed from ^{16}O -poor to ^{16}O -rich. Some of melilite crystals enclose pre-existing spinel crystals (purple). (3) Melilite crystals accumulated to form a fluffy CAI. (4) W-L rim minerals

1204 formed in a ^{16}O -rich reservoir. Age differences among stages are shown in Fig. 11.
1205

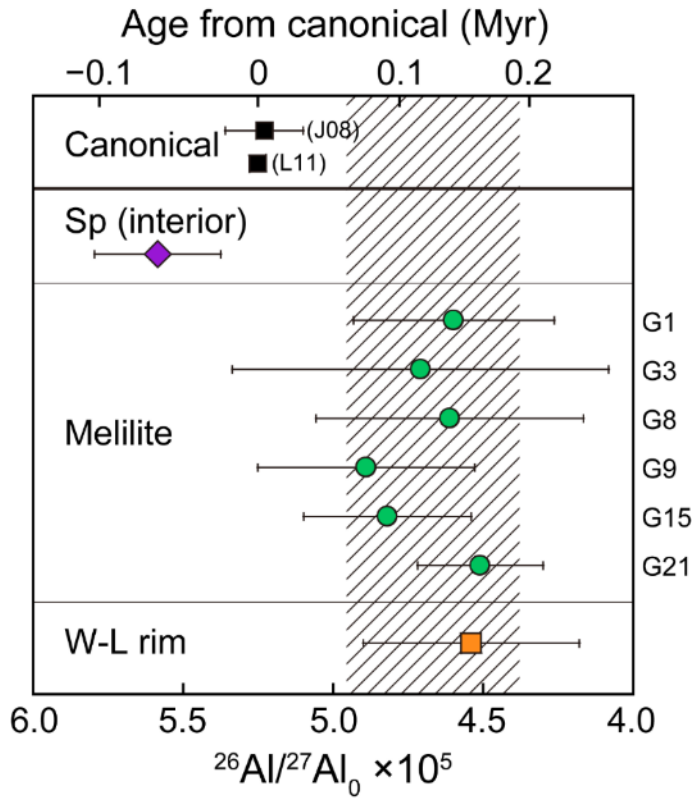


Figure 11. Comparisons of $(^{26}\text{Al}/^{27}\text{Al})_0$ values among spinel in the CAI interior, six reversely zoned melilite crystals, and the W-L rim. Canonical values are from Jacobsen et al. (2008), shown as J08 and Larsen et al. (2011), shown as L11. The age from canonical, upper x axis, was calculated using the $(^{26}\text{Al}/^{27}\text{Al})_0$ value by Larsen et al. (2011). Errors are 2σ . The width of the shaded area covers $\pm 2\text{SD}$ of $(^{26}\text{Al}/^{27}\text{Al})_0$ values for the six melilite crystals and for the W-L rim.