

Melilite condensed from an ^{16}O -poor gaseous reservoir: Evidence from a fine-grained Ca-Al-rich inclusion of Northwest Africa 8613

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Abstract

Fine-grained Ca-Al-rich inclusions (FGIs) in CV chondrites are suggested to be condensates from the solar nebular gas and thus captured O-isotopes from the gas. We conducted a combined study of petrographic observations and *in situ* O-isotope analysis using secondary ion mass spectrometry for an FGI, named HKD01, from the reduced CV chondrite Northwest Africa 8613. HKD01 has an irregular shape and petrographically three-layered structures: a hibonite-rich core, a spinel-rich core, and a mantle. Each petrographic domain contains melilite, hibonite, and spinel with variable proportions of those minerals. The O-isotopic compositions of the constituent minerals plotted along the slope-1 line on an O three-isotope diagram ranged between $\Delta^{17}\text{O} \sim -23\text{‰}$ and 1‰ . Hibonite and spinel are uniformly ^{16}O -rich ($\Delta^{17}\text{O} = -23\text{‰}$) irrespective of their occurrences, while melilite crystals exhibit wide O-isotope variations ranging between $\Delta^{17}\text{O} \sim -23\text{‰}$ and 1‰ . The O-isotopic composition in a melilite crystal changes abruptly within $\sim 2\text{ }\mu\text{m}$, indicating that disturbances of O-isotopes in melilite after condensation are less than $\sim 2\text{ }\mu\text{m}$. Because the melilite in the FGI typically has grain sizes of 5–10 μm , the abrupt change of O-isotopic composition demonstrates that melilite crystals in the FGI preserve the O-isotopic composition of the nebular gas from which they condensed. In the mantle, aggregates of melilite crystals, having relatively large grain sizes (10–25 μm) and oscillatory chemical zoning, exhibit ^{16}O -poor compositions with small variations ranging between $\Delta^{17}\text{O} \sim -4$ and 1‰ . Among them, a large melilite crystal ($\sim 20\text{ }\mu\text{m}$) with homogeneously ^{16}O -poor composition ($\Delta^{17}\text{O} \sim 0\text{‰}$) across the single crystal was found. The coexistence of ^{16}O -poor and ^{16}O -rich melilite crystals without O-isotope disturbances in the FGI reveals that ^{16}O -poor ($\Delta^{17}\text{O} \sim 0\text{‰}$) nebular gas existed in the formation region of the FGI HKD01 in addition to ^{16}O -rich ($\Delta^{17}\text{O} \sim -23\text{‰}$) nebular gas.

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1. INTRODUCTION

Ca-Al-rich inclusions (CAIs) in meteorites are the oldest objects formed in the Solar System (Connelly et al., 2012)

and are composed of minerals that are predicted to be high-temperature equilibrium condensates from the solar nebular gas (e.g., Grossman, 1972). The O-isotopic compositions of minerals in CAIs are distributed along the carbonaceous chondrite anhydrous mineral (CCAM) line as a nearly slope-1 line on an O three-isotope diagram (Clayton et al., 1973; Clayton, 1993). The disequilibrium distributions of O-isotopes in CAIs exhibit a variation

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range mostly from $\Delta^{17}\text{O} \sim -24\text{‰}$ to 0‰ (e.g., Yurimoto et al., 2008; Krot, 2019 and references therein), with the exception of extremely ^{16}O -rich CAIs ($\Delta^{17}\text{O} < -28\text{‰}$, Gounelle et al., 2009; Krot et al., 2017; Kööp et al., 2020), although such an extremely ^{16}O -rich composition was also found for a chondrule from CH chondrite (Kobayashi et al., 2003). The origin of the O-isotope disequilibrium in coarse-grained CAIs in CV chondrites has been discussed on the basis of *in situ* O-isotope measurements by secondary ion mass spectrometry (SIMS) (e.g., Yurimoto et al., 1994). The disequilibrium origin has been interpreted to be (i) condensation from the solar nebular gas with variable O-isotopic compositions for condensate CAIs (Katayama et al., 2012; Kawasaki et al., 2012, 2017; Park et al., 2012); (ii) multiple partial melting and associated O-isotope exchange between the melt and solar nebular gas for igneous CAIs (Yurimoto et al., 1998; Ito et al., 2004; Yoshitake et al., 2005; Aléon et al., 2007; Krot et al., 2008, 2014; Wakaki et al., 2013; Kawasaki et al., 2015, 2018; Aléon, 2016); (iii) O-isotope exchange by solid-state diffusion at high temperatures in the solar nebular gas after solidification (Simon et al., 2011, 2016); or (iv) chemical exchange of O-isotopes on the parent body (Yoshitake et al., 2005; Krot et al., 2008, 2014, 2019; Park et al., 2012; Kawasaki et al., 2015, 2018). The O-isotope disequilibrium in coarse-grained CAIs could also have resulted from a combination of such processes (Kawasaki et al., 2018) with the most efficient processes depending on the formation process and petrography of each CAI.

On the other hand, fine-grained Ca-Al-rich inclusions (FGIs) from carbonaceous chondrites are suggested to be condensates directly from the solar nebular gas, based on their complex layered structure of constituent minerals (Wark and Lovering, 1977; Krot et al., 2004; Han et al., 2015, 2019; Han and Brearley, 2017) and volatility-fractionated trace-element patterns (Boynnton, 1975; Davis and Grossman, 1979). Since FGIs are direct nebular condensates, their O-isotopic compositions could be indicators of those for the solar nebular gas from which the FGIs condensed. Constituent minerals of FGIs exhibit disequilibrium distributions of O-isotopes. ^{16}O -rich minerals ($\Delta^{17}\text{O} \sim -20\text{‰}$) are commonly observed in FGIs, which suggests that they formed in an ^{16}O -rich gaseous reservoir (Wasson et al., 2001; Krot et al., 2002; Itoh et al., 2004; Aléon et al., 2005; Bodéan et al., 2014; Ushikubo et al., 2017; Han et al., 2019). Constituent minerals of FGIs in less primitive chondrites tend to exhibit more ^{16}O -poor compositions up to $\Delta^{17}\text{O} \sim 0\text{‰}$, and these ^{16}O -poor signatures have been suggested to originate from chemical exchange of O-isotopes in the nebular gas and/or on the parent body after their condensation (Wasson et al., 2001; Itoh et al., 2004; Aléon et al., 2005). So far, there has been no clear evidence for primarily ^{16}O -poor minerals in FGIs even though their presence could provide strong direct constraints on the O-isotope evolution of the solar nebular gas.

In this study, we conducted a coordinated study using *in situ* O-isotope measurements and detailed petrographic observations of an FGI named HKD01 from the reduced CV chondrite Northwest Africa 8613 (NWA 8613), which

is considered to be one of the most primitive CV chondrites (Hertwig et al., 2019). Here, we present an original ^{16}O -poor signature recorded in melilite in HKD01, which was acquired during condensation in the early Solar System. A previous study reported that the Al–Mg mineral isochron defined by spinel and melilite in HKD01 gives an initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of $(4.812 \pm 0.089) \times 10^{-5}$ (Kawasaki et al., 2020), suggesting that the Al–Mg system has not been disturbed since its formation. We also performed additional *in situ* Al–Mg isotope measurements for hibonite in HKD01 to give better constraints on its formation timescale and relative age.

2. EXPERIMENTAL TECHNIQUES

2.1. Electron microscopy and microanalysis

The FGI HKD01 was present in a polished section of NWA 8613. The polished section was coated with a carbon thin film (~ 20 nm) for electron microscopy and microanalysis. It was then coated with a gold thin film (~ 70 nm) for O and Al–Mg isotope measurements using SIMS. Backscattered electron (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 X-ray spectrometer (EDS; Oxford X-Max 150) installed on the FE-SEM. A 15 keV electron beam probe with currents of 1 nA (for quantitative analysis) and 10 nA (for mapping) were employed in our study. Crystal orientation mapping was conducted via an electron backscatter diffraction system (EBSD; Oxford AZtec HKL) on the FE-SEM using a 20 keV and 4 nA electron beam probe. The sample surface was polished using colloidal silica (Buehler Mastermet) on a Buehler VibroMet 2 for EBSD analysis. The bulk chemical composition of HKD01 was estimated as an average of multiple measurements covering the entire inclusion using a raster electron beam. Mg K α elemental maps were used to generate quantitative åkermanite content (Åk) maps of melilite by calibrating Mg X-ray intensities with quantitative elemental analyses. Other mineral phases (e.g., hibonite and spinel), polishing flaws, and melilite areas affected by X-ray signals from other phases in the quantitative Åk maps were masked in gray based on differences in the intensities of O K α , Mg K α , and Ca K α . The Åk content in O-isotope measurement locations by SIMS in melilite was obtained from the quantitative Åk maps. Statistical errors for the Åk content of melilite for the SIMS spots were less than 0.2 mol% (2σ).

The chemical composition of Madagascar hibonite was studied with a field emission electron probe microanalyzer (FE-EPMA; JEOL JXA-8530F) at Korea Polar Research Institute using a 15 keV accelerating voltage, a 50 nA beam current, and a 3 μm beam size with five wavelength dispersive X-ray spectrometers (WDS). Natural and synthetic minerals were used as standards. Counting times were 40 s on the peak and 20 s on high and low off-peak backgrounds, respectively. We used the Phi-Rho-Z algorithm

for the matrix correction method by Armstrong/Love Scott (Armstrong, 1995), implemented within the Probe for EPMA (Pfe) software package. The detection limits for oxides calculated by the Pfe software were as follows (in wt% with a confidence of 99%): SiO₂ (0.01), TiO₂ (0.03), ZrO₂ (0.03), ThO₂ (0.02), Al₂O₃ (0.01), La₂O₃ (0.04), Ce₂O₃ (0.07), Pr₂O₃ (0.06), Nd₂O₃ (0.06), Sm₂O₃ (0.06), FeO (0.02), MgO (0.01), CaO (0.005), ZnO (0.04), and SrO (0.02).

2.2. O-isotope analysis

O-isotopic compositions of the minerals in HKD01 were measured using SIMS instruments (Cameca ims-1270e7 and ims-1280HR) at Hokkaido University, following the analytical procedures reported in Kawasaki et al. (2018). A ¹³³Cs⁺ primary beam (20 keV, 20–40 pA) with a diameter of 1.5–3.5 μm was used in the experiment. Negative secondary ions (¹⁶O[−], ¹⁷O[−], and ¹⁸O[−]) were measured simultaneously in multicollection mode using a multicollector Faraday cup (10¹¹ Ω, L1), an axial electron multiplier, and a multicollector electron multiplier (H2), respectively. A normal-incidence electron flood gun was used for electrostatic charge compensation of the analyzed area during the measurements. The mass resolution $M/\Delta M$ for ¹⁷O[−] was set at ~6000 to ensure that the contribution of ¹⁶OH[−] to ¹⁷O[−] was negligible, while that for ¹⁶O[−] and ¹⁸O[−] was ~2000. The secondary ion intensity of ¹⁶O[−] was 1.1–2.5 × 10⁷ cps. Each measurement was conducted with 40–60 cycles of counting the secondary ions for 4 s. Obtained count rates were corrected for FC background, EM dead time, and relative yield for each detector. Synthetic åkermanite (δ¹⁸O = 6.0‰) and synthetic gehlenite (δ¹⁸O = 7.4‰) were used to correct the instrumental mass fractionation for melilite, and Russian spinel (δ¹⁸O = 8.5‰) was used to correct those for spinel and hibonite. Analytical errors include an internal error for individual analysis and uncertainty of the instrumental mass fractionation (assigned as 2SE of repetitive analyses of the standards). Typical errors for δ¹⁷O, δ¹⁸O, and Δ¹⁷O were 2.0‰, 0.9‰, and 2.1‰ (2σ), respectively. Higher precision analyses were also conducted for several spots (#769–774) by applying extended counting times to 120 cycles with a slightly larger, ~4 μm primary beam. The resulting errors for δ¹⁷O, δ¹⁸O, and Δ¹⁷O were 1.2‰, 0.5‰, and 1.2‰, respectively.

2.3. Mg-isotope analysis

Mg-isotopes and ²⁷Al/²⁴Mg ratios for hibonite in HKD01 were measured using a SIMS instrument (Cameca ims-1280HR) at Hokkaido University, following the analytical procedures reported in Kawasaki et al. (2019, 2020). An ¹⁶O[−]-primary beam (23 keV, 60–100 pA) with a diameter of 5–7 μm was used in the experiment. Mg-isotopes (²⁴Mg⁺, ²⁵Mg⁺, and ²⁶Mg⁺) were measured using an axial electron multiplier, while ²⁷Al⁺ was measured using a multicollector Faraday cup (10¹⁰ Ω, H2*) simultaneously with ²⁵Mg⁺, in peak-jumping mode. The mass resolution $M/\Delta M$ was set at ~4000, which is sufficient to resolve ion interferences (e.g., ⁴⁸Ca²⁺, ²⁴MgH⁺, and

²⁵MgH⁺) from ²⁴Mg⁺, ²⁵Mg⁺, and ²⁶Mg⁺. The secondary ion intensities for ²⁴Mg⁺ were 0.08–2.2 × 10⁵ cps. Each measurement was conducted for 100 cycles with a counting sequence with ²⁴Mg⁺ for 2 s, ²⁵Mg⁺ for 2 s, ²⁵Mg⁺ and ²⁷Al⁺ for 4 s, and ²⁶Mg⁺ for 6 s. Obtained count rates were corrected for the FC background and EM deadtime. The relative sensitivity factors (RSFs) for Al and Mg were determined through measurements of Madagascar hibonite. The excess radiogenic ²⁶Mg, δ²⁶Mg*, was calculated via an exponential fractionation law with a coefficient $\alpha_{natural} = 0.5128$ because natural fractionation for Mg-isotopes is considered to be controlled by evaporation processes (Davis et al., 2015). The analytical errors for δ²⁶Mg* were assigned as internal errors (2SE) and were 0.9–4.1‰ depending on the secondary ion intensities of Mg-isotopes. The δ²⁵Mg values for hibonite were calculated after corrections of instrumental mass fractionation by assuming that the δ²⁵Mg of the Madagascar hibonite was zero.

3. RESULTS

3.1. Mineralogy and petrology

HKD01 has an irregular shape with a size of approximately 10 × 12 mm and is composed mainly of hibonite, spinel and melilite, with little perovskite or diopside (Fig. 1). HKD01 has a core-mantle structure. The core is subdivided into hibonite-rich and spinel-rich regions. Representative mineral chemistry of hibonite, spinel, melilite, and perovskite is summarized in Table 1. The EBSD data to determine grain boundaries are shown in Figs. S1–S4.

The hibonite-rich core consists mainly of euhedral, lath-shaped hibonite crystals with sizes of typically 5–15 μm, and melilite crystals with sizes of typically less than 10 μm, in addition to a smaller amount of spinel with sizes of less than 10 μm (Fig. 2). The spinel exhibits an anhedral shape and occurs adjacent to hibonite crystals. Melilite crystals exhibit chemical zoning with increasing Åk content from the core (typically ~Åk₁) to the rim (~Åk₂) (Fig. 2d).

The spinel-rich core entirely surrounds the hibonite-rich core, consisting mainly of spinel and melilite crystals with sizes of typically less than 10 μm, and rare perovskite (5–15 μm in size) and lath-shaped hibonite crystals (5–15 μm in size) (Fig. 3). Melilite crystals exhibit chemical zoning with increasing Åk content from the core (typically ~Åk₂) to the rim (~Åk₅) (Fig. 3d).

The mantle surrounds the spinel-rich core and consists mainly of spinel and melilite crystals (typically 5–15 μm) and lath-shaped hibonite crystals (typically 5–20 μm) and rare perovskite. Melilite crystals generally exhibit chemical zoning with increasing Åk content from the core (typically ~Åk₁) to the rim (~Åk₄). Some melilite crystals in the mantle have Åk-rich cores (~Åk₄), which correspond to oscillatory chemical zoning changing from reverse zoning to normal zoning from the core to the rim (Fig. 4d). In the mantle, aggregates of melilite crystals having complex chemical zoning are rarely observed (Fig. 5). These melilite aggregates contain relatively large melilite crystals with

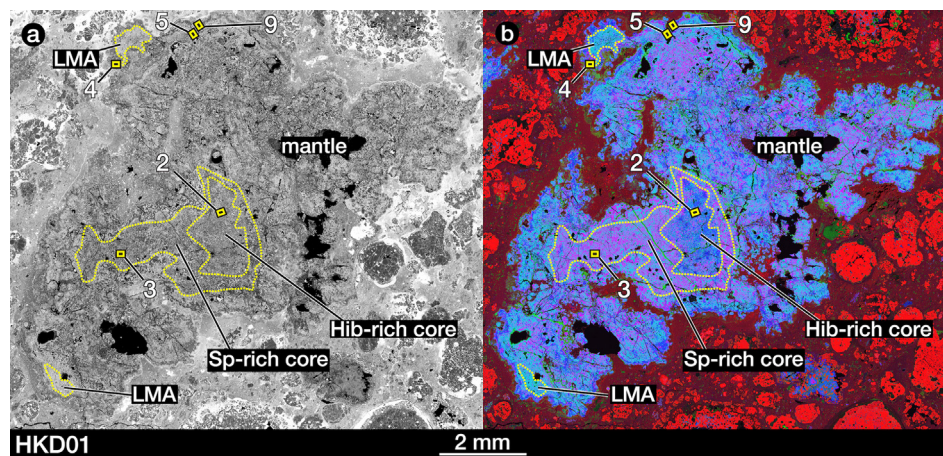


Fig. 1. (a) Backscattered electron (BSE) image of HKD01. (b) Composite X-ray elemental map of HKD01 with Mg (red), Ca (green), and Al (blue). Centers of yellow boxes numbered 2, 3, 4, 5 and 9 correspond to the areas shown in Figs. 2, 3, 4, 5 and 9, respectively. Yellow broken lines indicate boundaries of each petrographic domain. LMA, large melilite aggregate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Representative chemical compositions of hibonite, spinel, and melilite in HKD01.

wt.%	<i>Hibonite-rich core</i>			<i>Spinel-rich core</i>				<i>Mantle</i>				<i>Large melilite aggregate</i>	
	Hib	Sp	Mel	Hib	Sp	Mel	Pv	Hib	Sp	Mel	Pv	Mel	Mel
MgO	2.7	28.2	0.2	4.3	28.5	0.4	–	3.5	27.9	0.4	–	0.3	2.1
Al ₂ O ₃	83.5	70.5	36.5	78.2	70.5	36.1	–	81.0	69.8	36.2	–	35.9	31.0
SiO ₂	–	–	22.0	0.4	–	22.2	–	–	–	22.2	–	21.9	24.8
CaO	8.5	–	40.8	8.6	–	41.4	40.4	8.5	–	41.1	40.7	41.1	41.1
TiO ₂	5.2	0.3	–	8.1	1.0	–	59.4	7.1	0.4	–	59.3	–	–
FeO	–	0.5	–	–	–	–	–	–	1.2	–	–	–	–
Total	100.0	99.5	99.5	99.6	100.0	100.1	99.7	100.0	99.3	99.8	100.0	99.2	99.1
<i>Cations</i>													
Mg	0.46	1.00	0.01	0.73	1.01	0.03	–	0.59	1.00	0.03	–	0.02	0.15
Al	11.09	1.98	1.98	10.49	1.97	1.94	–	10.79	1.98	1.95	–	1.95	1.69
Si	–	–	1.01	0.05	–	1.01	–	–	–	1.02	–	1.01	1.15
Ca	1.03	–	2.01	1.05	–	2.03	0.98	1.03	–	2.01	0.99	2.03	2.03
Ti	0.44	0.01	–	0.69	0.02	–	1.01	0.60	0.01	–	1.01	–	–
Fe	–	0.01	–	–	–	–	–	–	0.02	–	–	–	–
Total	13.02	3.00	5.00	13.01	3.00	5.01	1.99	13.00	3.00	5.01	1.99	5.01	5.01
Per oxygen	19	4	7	19	4	7	3	19	4	7	3	7	7

Hib: hibonite, Mel: melilite, Pv: perovskite, Sp: spinel.

sizes of 10–25 μm and minor spinel and hibonite crystals (<10 μm). We call this region a “large melilite aggregate”. The large melilite crystals exhibit complex chemical zoning with repetitive oscillation from the crystal core to the rim (typically $\sim\text{Ak}_5 \rightarrow \sim\text{Ak}_2 \rightarrow \sim\text{Ak}_{12} \rightarrow \sim\text{Ak}_6$, Fig. 5d), although not all crystals in the region show such oscillations on the surface of the polished section, probably due to off-center sectioning of crystals and differences in nucleation time.

The entire inclusion is rimmed by thin ($\sim 10 \mu\text{m}$) mineral layers of spinel ($\pm$ hibonite) and diopside (Fig. 4a and b). Spinel and hibonite crystals near the rim tend to be larger (typically 20–50 μm in size) than those in the interior (Fig. 4a and b).

Bulk chemical compositions of the entire FGI HKD01, hibonite-rich core, spinel-rich core, and mantle are listed in Table 2 and plotted on the cosmochemical phase diagram presented by MacPherson and Huss (2005) (Fig. 6). The bulk compositions of the entire HKD01, spinel-rich core, and mantle plot on the melilite + spinel field, while that of the hibonite-rich core plots on the grossite + spinel field. Spinel coordinates for the entire HKD01, hibonite-rich core, spinel-rich core, and mantle are 28, 24, 40, and 16, respectively; they are all plotted above the spinel-saturated surface (0–10). The bulk chemical composition of HKD01 is significantly different from those for previously reported spinel-rich FGIs (Krot et al., 2004; Kawasaki et al., 2020) because of its unique mineral assemblages.

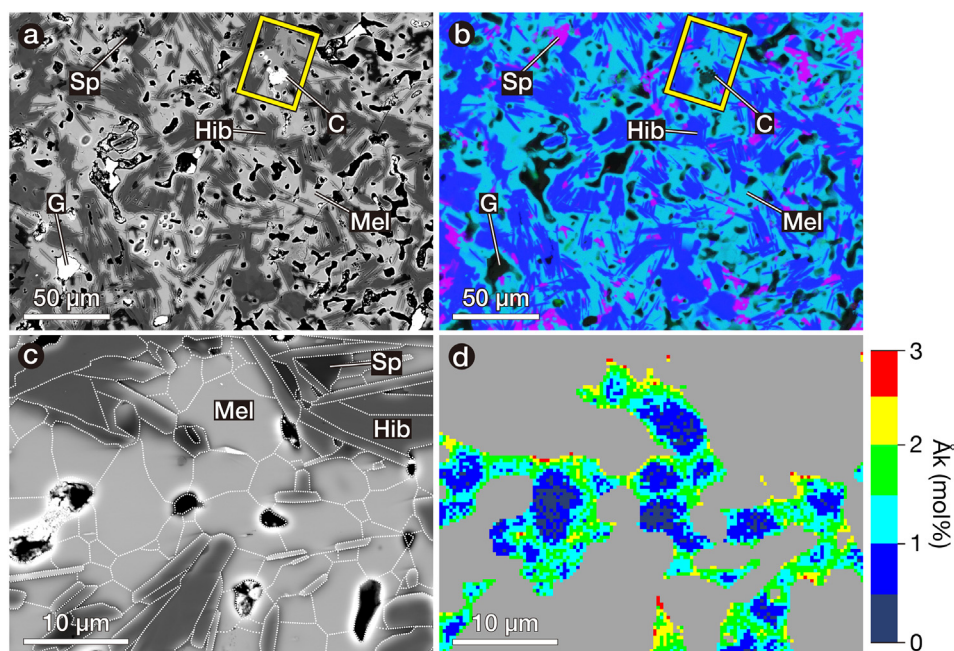


Fig. 2. (a) BSE image of a representative area of the hibonite-rich core part. (b) Composite X-ray elemental map of the same area shown in (a), with Mg (red), Ca (green), and Al (blue). (c) Magnified BSE image of the area indicated by yellow boxes in (a) and (b). White dotted lines indicate grain boundaries determined through EBSD analysis. (d) Quantitative map of åkermanite content ($\text{\AA k}$) in melilite from the same area displayed in (c). Other mineral phases and melilite areas affected by X-ray signals from other phases are masked in gray. C, sputtering crater; G, gold coating residues; Hib, hibonite; Mel, melilite; Sp, spinel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

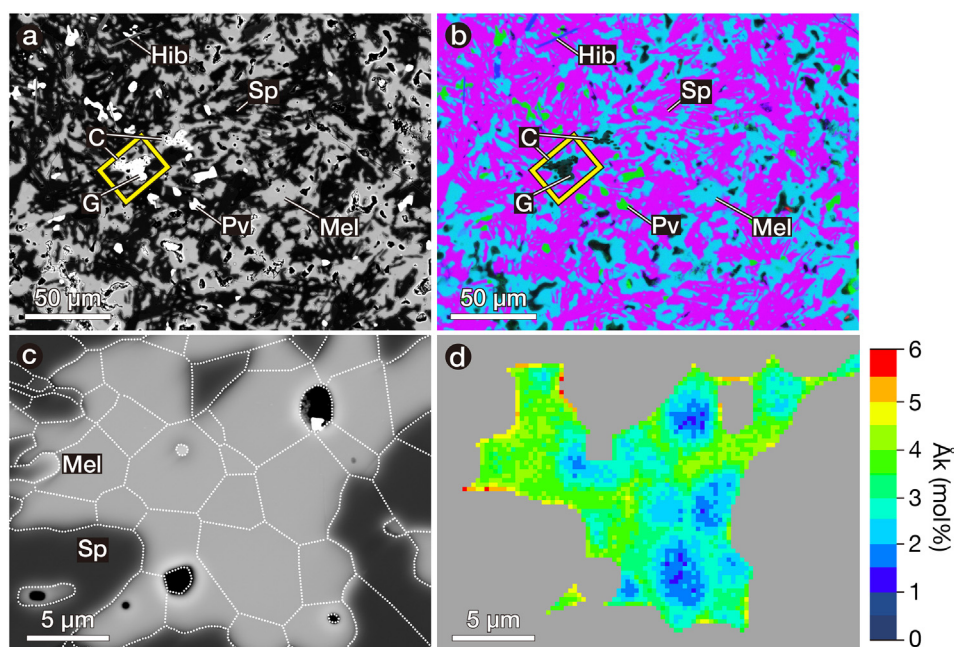


Fig. 3. (a) BSE image of a representative area of the spinel-rich core part. (b) Composite X-ray elemental map of the same area shown in (a), with Mg (red), Ca (green), and Al (blue). (c) Magnified BSE image of the area indicated by yellow boxes in (a) and (b). White dotted lines indicate grain boundaries determined through EBSD analysis. (d) Quantitative map of åkermanite content ($\text{\AA k}$) in melilite from the same area displayed in (c). Other mineral phases and melilite areas affected by X-ray signals from other phases are masked in gray. C, sputtering crater; G, gold coating residues; Hib, hibonite; Mel, melilite; Pv, perovskite; Sp, spinel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

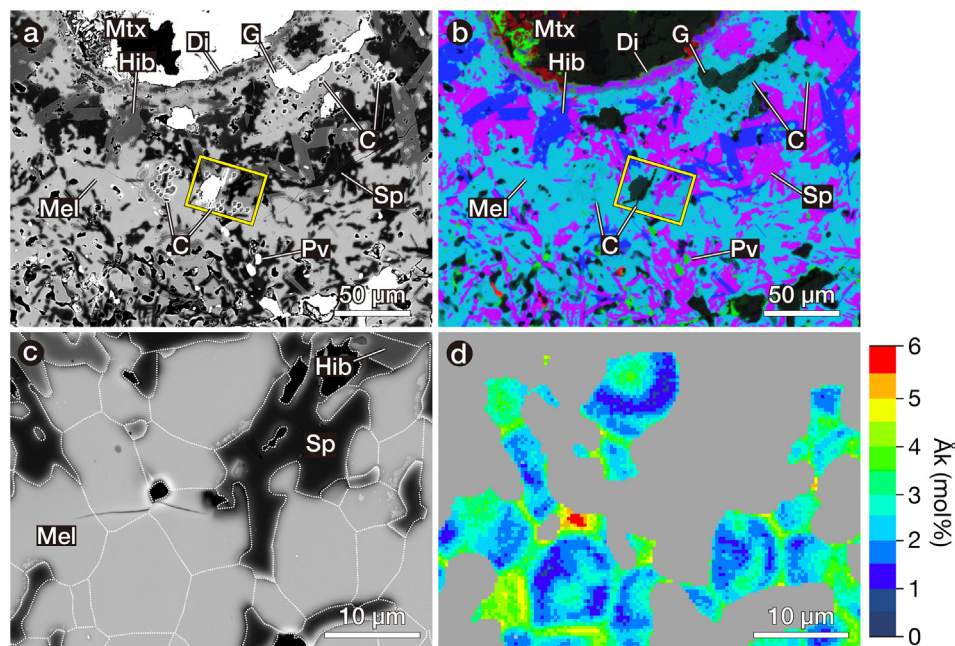


Fig. 4. (a) BSE image of a representative area of the mantle part. (b) Composite X-ray elemental map of the same area shown in (a), with Mg (red), Ca (green), and Al (blue). (c) Magnified BSE image of the area indicated by yellow boxes in (a) and (b). White dotted lines indicate grain boundaries determined through EBSD analysis. (d) Quantitative map of åkermanite content (Åk) in melilite from the same area displayed in (c). Other mineral phases and melilite areas affected by X-ray signals from other phases are masked in gray. C, sputtering crater; Di, diopside; G, gold coating residues; Hib, hibonite; Mel, melilite; Pv, perovskite; Sp, spinel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

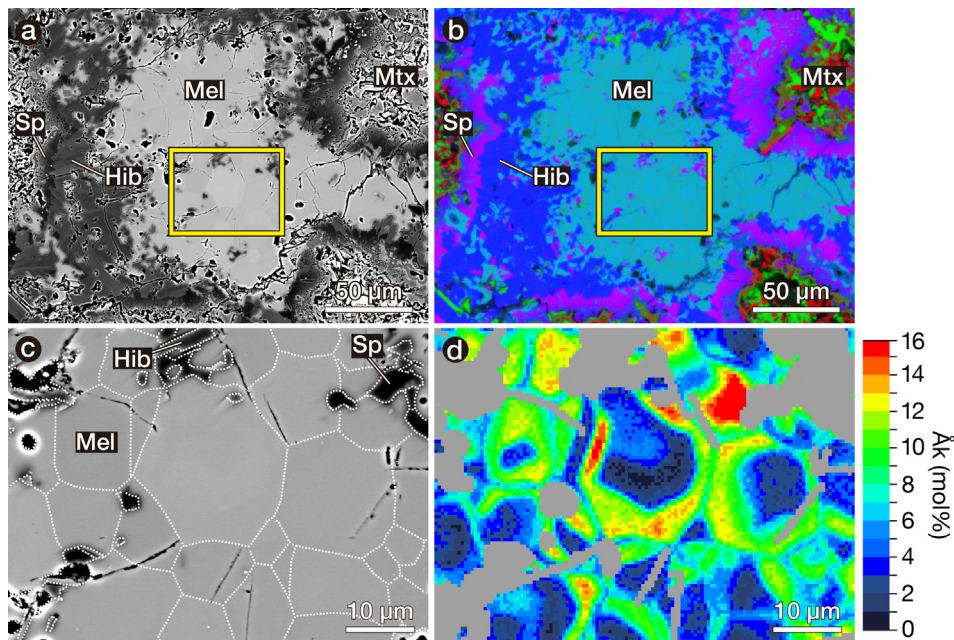


Fig. 5. (a) BSE image of a representative area of a large melilite aggregate. (b) Composite X-ray elemental map of the same area shown in (a), with Mg (red), Ca (green), and Al (blue). (c) Magnified BSE image of the area indicated by yellow boxes in (a) and (b). White dotted lines indicate grain boundaries determined through EBSD analysis. (d) Quantitative map of åkermanite content (Åk) in melilite from the same area displayed in (c). Other mineral phases and melilite areas affected by X-ray signals from other phases are masked in gray. Hib, hibonite; Mel, melilite; Sp, spinel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Bulk compositions (wt.%) of HKD01 normalized to 100%.

Location	No. an.	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO
Bulk	187	14.4	1.4	48.9	1.8	10.0	23.5
Hibonite-rich core	18	11.5	1.7	57.0	2.0	7.2	20.6
Spinel-rich core	86	13.4	1.3	48.7	1.7	13.2	21.7
Mantle	83	16.0	1.3	47.5	1.8	7.4	25.9

No. an. = Number of analysis.

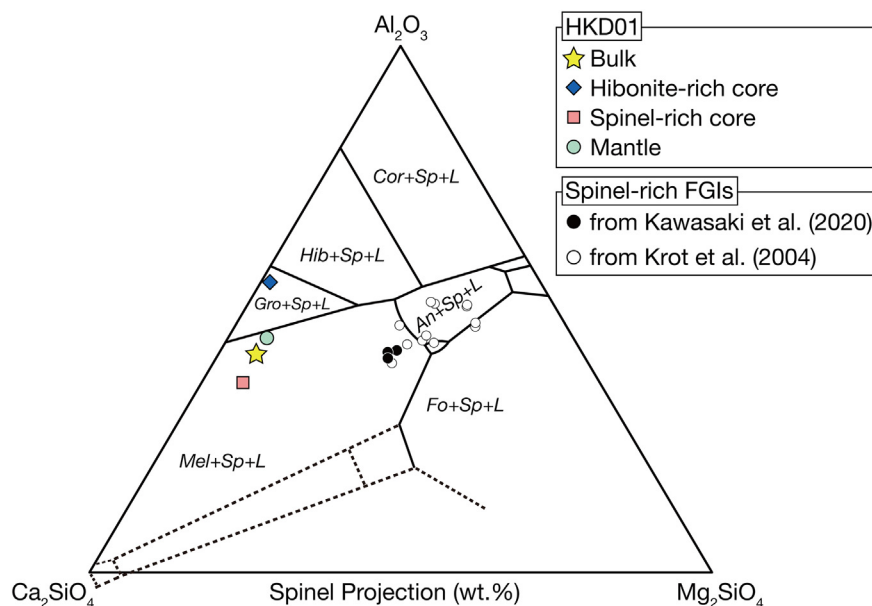


Fig. 6. Bulk chemical compositions (wt.%) of FGI HKD01 and spinel-rich FGIs projected from spinel (MgAl_2O_4) onto the plane of Ca_2SiO_4 –forsterite (Mg_2SiO_4)–corundum (Al_2O_3) (MacPherson and Huss, 2005). Literature data for spinel-rich FGIs (Krot et al., 2004; Kawasaki et al., 2020) are plotted for comparison. An, anorthite; Cor, corundum; Fo, forsterite; Gro, grossite; Hib, hibonite; L, liquid; Mel, melilite; Sp, spinel.

3.2. O-isotopic compositions

The measured O-isotopic compositions for minerals in HKD01 are summarized in Table S2 and plotted on the O three-isotope diagram (Fig. 7). Locations of SIMS measurements are shown in Figs. S5–S32. The O-isotopic compositions of all minerals are distributed along the CCAM line ranging between $\Delta^{17}\text{O} \sim -23\text{‰}$ and 1‰ , which shows O-isotope disequilibrium in HKD01.

The hibonite ($n = 9$) and spinel ($n = 16$) exhibit homogeneously ^{16}O -rich compositions ($\Delta^{17}\text{O} = -22.9 \pm 1.7\text{‰}$, 2SD), despite their occurrences (Table S2). In contrast to the hibonite and spinel, significant variations in O-isotopic compositions are observed for the melilite in HKD01, ranging from $\Delta^{17}\text{O} \sim -23$ to 1‰ (Fig. 7). The O-isotopic compositions of melilites in each petrographic region of HKD01 are shown in Fig. 8. The melilite in the hibonite-rich core shows large variations in O-isotopic composition ranging between $\Delta^{17}\text{O} \sim -23$ and -15‰ . The melilite in the spinel-rich core exhibits a homogeneous O-isotopic composition ($\Delta^{17}\text{O} = -19.5 \pm 1.9\text{‰}$, 2SD, $n = 45$). The O-isotopic compositions of melilite in the mantle show significant variations ranging between $\Delta^{17}\text{O} \sim -15$ and 0‰ . The melilite in the large melilite

aggregates exhibits ^{16}O -poor compositions with small variations ranging between $\Delta^{17}\text{O} \sim -4$ and 1‰ .

We obtained O-isotopic composition profiles for melilite crystals from the mantle (Fig. 9) and the large melilite aggregates (Fig. 10). The O-isotopic composition of the melilite crystals for the line profiles are listed in Table 3. Spatial resolutions (shown as horizontal bars) for each data point correspond to the probe sizes of SIMS analysis. The O-isotopic compositions on the traverse across melilite crystals in the mantle show a wide variation ranging between $\Delta^{17}\text{O} \sim -7$ and -1‰ (Fig. 9). The O-isotopic composition of melilite changes abruptly within $\sim 2\text{ }\mu\text{m}$ in a single crystal. On the other hand, a single melilite crystal with a size of $\sim 20\text{ }\mu\text{m}$ in the large melilite aggregates exhibits almost constant $\Delta^{17}\text{O}$ values of $-0.3 \pm 1.4\text{‰}$ across the crystal, despite its complex chemical zoning (Fig. 10). The variation curve for $\Delta^{17}\text{O}$ values may correspond to that for chemical zoning, but the $\Delta^{17}\text{O}$ variations are within analytical uncertainties.

3.3. Al–Mg isotopic compositions

The Mg-isotopic compositions and $^{27}\text{Al}/^{24}\text{Mg}$ ratios measured for minerals in HKD01 are summarized in

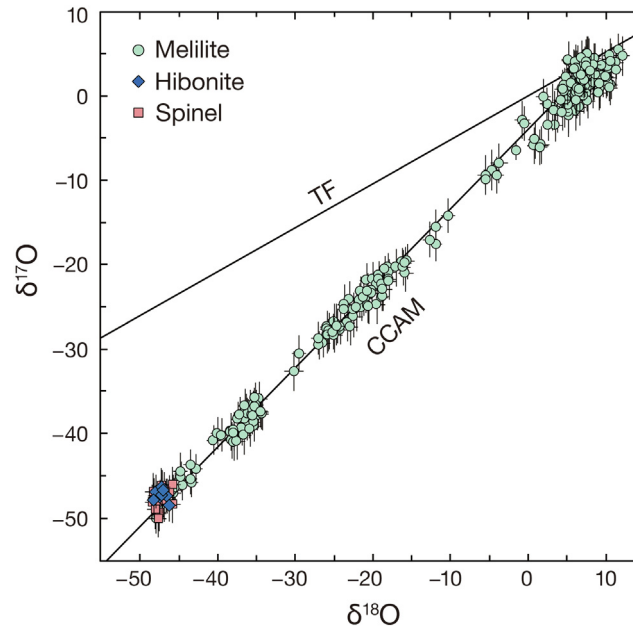


Fig. 7. O-isotope distributions of hibonite, spinel, and melilite in HKD01. Errors are 2σ . CCAM, carbonaceous chondrite anhydrous mineral line; TF, terrestrial fractionation line.

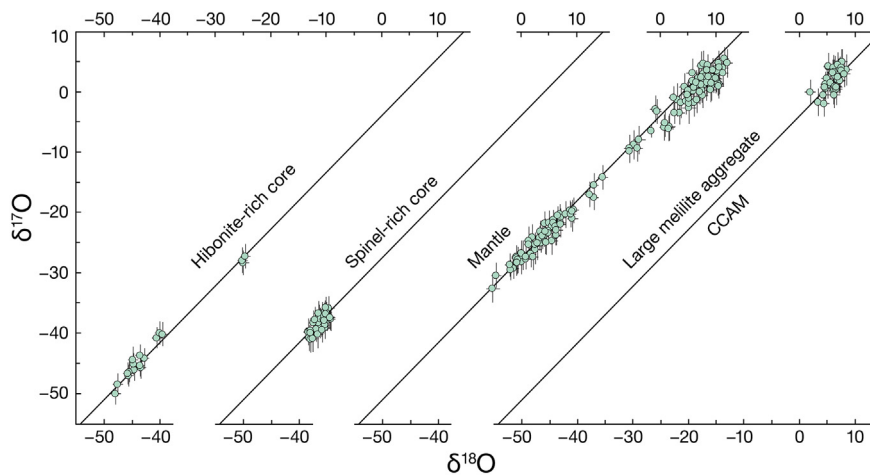


Fig. 8. O-isotope distributions for melilite in HKD01. Errors are 2σ . CCAM, carbonaceous chondrite anhydrous mineral line.

Table 4 and plotted on the ^{26}Al – ^{26}Mg evolution diagram in Fig. 11. Locations of SIMS measurements are shown in Figs. S5–S32. The Al–Mg isotope data for spinel and melilite are obtained from Kawasaki et al. (2020) and yield well-correlated ^{26}Al – ^{26}Mg mineral isochron, which gives $(^{26}\text{Al}/^{27}\text{Al})_0$ of $(4.812 \pm 0.089) \times 10^{-5}$ and initial $\delta^{26}\text{Mg}^*$, $(\delta^{26}\text{Mg}^*)_0$, of $-0.060 \pm 0.063\%$ (errors 2σ). The Al–Mg isotope data for the hibonite with $^{27}\text{Al}/^{24}\text{Mg} > \sim 320$ systematically deviate from the mineral isochrons for spinel and melilite (Fig. 11a). If we draw a regression line for the hibonite data on the diagram, it gives apparent initial values of $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.547 \pm 0.054) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = 0.42 \pm 0.37\%$. The validity of the Al–Mg isotope data for hibonite is discussed in Section 4.2.

We measured chemical compositions for the areas of several SIMS spots of the Mg-rich hibonite in HKD01 ($^{27}\text{Al}/^{24}\text{Mg} < \sim 40$) using the FE-SEM-EDS with a raster electron beam ($5 \times 5 \mu\text{m}$ in size) before SIMS analysis (Table S4). The Mg-poor hibonite ($^{27}\text{Al}/^{24}\text{Mg} > \sim 320$) could not be determined accurately because of its low Mg concentration and strong microscale chemical zoning (Fig. S33). Using the EDS data, we calculated $^{27}\text{Al}/^{24}\text{Mg}$ ratios, $(^{27}\text{Al}/^{24}\text{Mg})_{\text{true}}$, assuming terrestrial reference ratios of $^{25}\text{Mg}/^{24}\text{Mg} = 0.12663$ and $^{26}\text{Mg}/^{24}\text{Mg} = 0.13932$ (Catanzaro et al., 1966). The determined RSF, $(^{27}\text{Al}^{+}/^{24}\text{Mg}^{+})_{\text{SIMS}}/(^{27}\text{Al}/^{24}\text{Mg})_{\text{true}}$, for the HKD01 hibonite with $^{27}\text{Al}/^{24}\text{Mg}$ ratios between 20 and 41 was 0.787 ± 0.011 . The RSF for the Madagascar hibonite ($^{27}\text{Al}/^{24}\text{Mg} = 28.18$

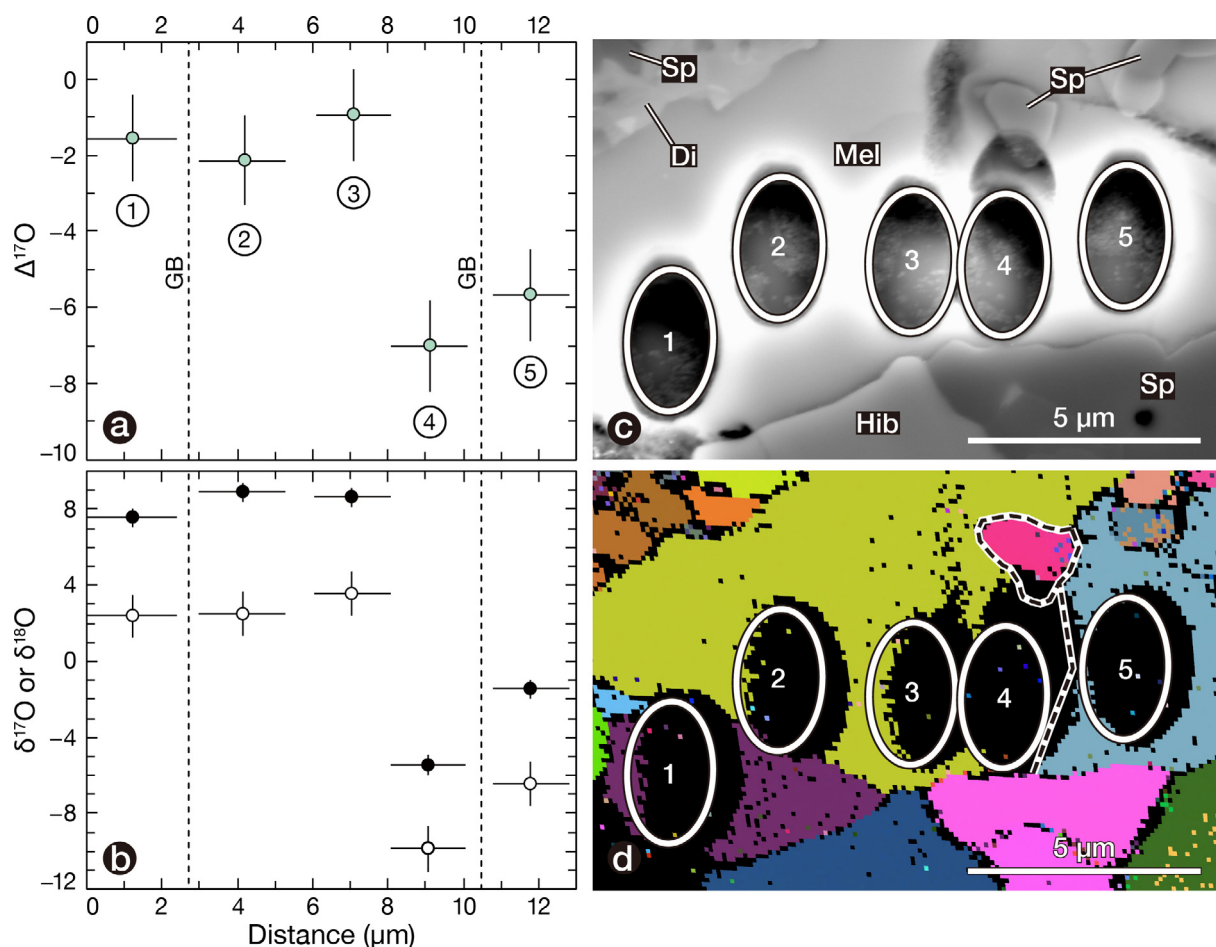


Fig. 9. Line profile for (a) $\Delta^{17}\text{O}$, (b) $\delta^{17}\text{O}$ (open circles) and $\delta^{18}\text{O}$ (filled circles) in melilite crystals in the mantle. Numbers 1–5 attached to each plot in (a) correspond to numbers of sputtering craters shown in (c) and (d). (c) BSE image of the analyzed area. (d) EBSD map of the same area displayed in (c). White ellipses correspond to positions of SIMS spots. Broken lines indicate grain boundaries that were manually drawn based on EBSD patterns. Kikuchi patterns in the SIMS spots were observed independently and the SIMS spots are confirmed to be positioned within the single crystal. Errors in O-isotopic compositions are 2σ and errors in distance correspond to the probe size. Di, diopside; GB, grain boundary; Hib, hibonite; Mel, melilite; Sp, spinel.

± 0.09 , Table S5), determined in the same analytical session, was 0.773 ± 0.008 . The data used to obtain RSF values for the HKD01 hibonite and Madagascar hibonite are summarized in Fig. S34 and Table S6.

4. DISCUSSION

4.1. Formation processes

According to the cosmochemical phase diagram (Fig. 6, MacPherson and Huss, 2005), the first and second crystallization phases from melts with bulk chemical compositions for the entire HKD01, the spinel-rich core, and the mantle are expected to be spinel and melilite, while those for the hibonite-rich core are spinel and grossite, respectively. In contrast, textural relationships for the HKD01 minerals indicate that hibonite formed prior to spinel and melilite for every occurrence (Figs. 2–5). Additionally, grossite was never observed in the hibonite-rich core nor anywhere

else in HKD01. These observations imply that the minerals in HKD01 could not have formed by melt crystallization. On the other hand, thermodynamic calculations predict that hibonite condenses before melilite, perovskite and spinel from a solar composition gas with decreasing temperatures (Yoneda and Grossman, 1995). The predicted condensation sequence is consistent with the textural relationships between hibonite and other constituent minerals in HKD01 (Figs. 2–5). These observations strongly support the condensation origin of the FGI HKD01.

Assuming a total pressure of $P^{\text{tot}} = 10^{-3}$ atm, condensation of hibonite begins at 1743 K, perovskite begins at 1688 K, melilite begins at 1628 K, and spinel begins at 1501 K from a solar composition gas, according to the calculations by Yoneda and Grossman (1995). Since highly gehlenitic melilite with an Åk content of less than 1 is rare in HKD01 (Figs. 2–5 and S35), condensation of most of the melilite could have occurred at < 1498 K (condensation temperature of melilite with Åk_1 at $P^{\text{tot}} = 10^{-3}$ atm),

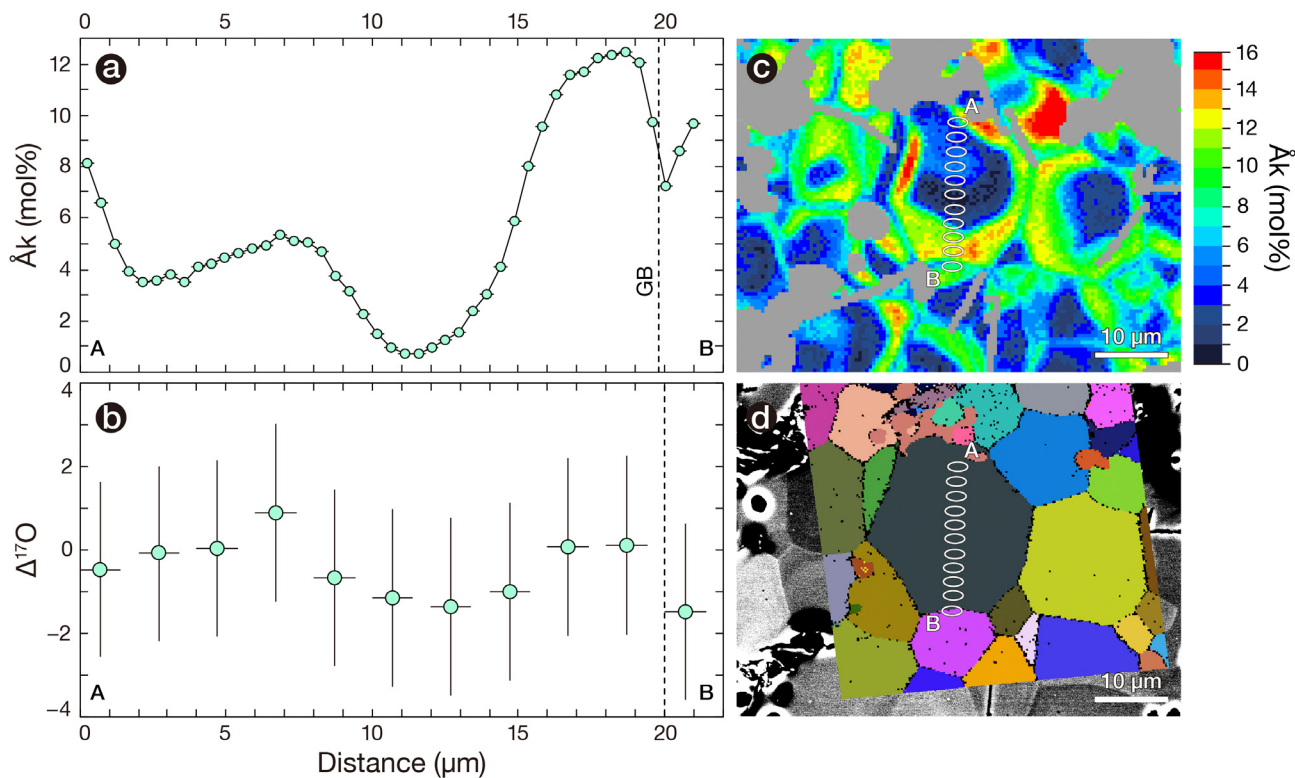


Fig. 10. Line profile for (a) åkermanite (Åk) content and (b) $\Delta^{17}\text{O}$ in melilite crystals in a large melilite aggregate along traverse A–B in (c) and (d). (c) Quantitative map of åkermanite content in melilite for the analyzed area taken from Fig. 5d. (d) EBSD map overlaid on BSE image of the same area displayed in (c). White ellipses correspond to positions of SIMS spots. Errors in O-isotopic compositions are 2σ and errors in distance correspond to the probe size. GB, grain boundary.

Table 3
Data for line profiles of O-isotopic compositions (‰) of melilite in the mantle and in large melilite aggregate.

Spot#	$\delta^{17}\text{O}$	2σ	$\delta^{18}\text{O}$	2σ	$\Delta^{17}\text{O}$	2σ	Distance (μm)	Φ (μm)
<i>across melilite polycrystals from the mantle (Fig. 9)</i>								
#774	2.4	1.1	7.6	0.5	−1.5	1.2	1.2	2.4
#771	2.5	1.2	8.9	0.5	−2.1	1.2	4.2	2.4
#770	3.6	1.2	8.6	0.5	−0.9	1.2	7.1	2.0
#772	−9.9	1.2	−5.4	0.5	−7.0	1.2	9.1	2.0
#769	−6.4	1.2	−1.5	0.5	−5.7	1.2	11.8	2.0
<i>across a single melilite crystal from the large melilite aggregate (Fig. 10)</i>								
#1273	3.1	2.0	6.8	0.9	−0.5	2.1	0.7	1.4
#1274	3.9	2.0	7.6	0.9	−0.1	2.1	2.7	1.4
#1275	3.9	2.1	7.4	0.9	0.0	2.1	4.7	1.4
#1276	4.6	2.1	7.0	0.9	0.9	2.1	6.7	1.4
#1277	2.7	2.1	6.6	0.9	−0.7	2.1	8.7	1.4
#1278	1.3	2.1	4.8	0.9	−1.1	2.1	10.7	1.4
#1286	1.6	2.1	5.7	0.9	−1.4	2.1	12.7	1.4
#1280	2.6	2.1	7.0	0.9	−1.0	2.1	14.7	1.4
#1281	3.4	2.1	6.4	0.9	0.1	2.1	16.7	1.4
#1282	3.3	2.1	6.2	1.0	0.1	2.1	18.7	1.4
#1285	0.9	2.1	4.6	0.9	−1.5	2.1	20.7	1.4

although there are no clear textural signatures to constrain the crystallization sequences among spinel, perovskite and melilite. Chemical zoning patterns observed in melilite crystals from each petrographic region (Figs. 2–5) cannot be readily explained by condensation from the solar nebular

gas with simply decreasing temperatures. Given the chemical composition of condensed melilite is sensitive to a change in the total pressure and temperature of the gas (Yoneda and Grossman, 1995), the chemical zoning patterns can be formed by pressure and/or temperature

Table 4
Magnesium isotopic compositions (‰) and $^{27}\text{Al}/^{24}\text{Mg}$ ratios of minerals in HKD01.

Minerals	Spot#	$^{27}\text{Al}/^{24}\text{Mg}$	2 σ	$\delta^{26}\text{Mg}^*$	2 σ	$\delta^{25}\text{Mg}$	2 σ
<i>Hibonite-rich core</i>							
Hib	7	28.7	0.1	10.1	0.9	1.2	0.6
Hib	43	34.8	0.8	12.2	1.0	−0.7	1.2
Hib	44	33.7	0.8	11.3	1.2	0.1	1.2
Hib	45	21.9	0.6	7.6	0.9	−1.1	1.2
Hib	727	20.9	0.2	7.2	1.3	0.9	0.9
Hib	729	321.9	5.3	104.7	2.3	−5.0	2.0
Hib	730	40.0	0.4	13.1	1.4	−0.2	1.0
Hib	734	19.8	0.2	6.9	1.3	0.9	0.9
Hib	735	23.9	0.2	8.3	1.3	1.3	0.9
Hib	736	25.3	0.3	8.1	1.3	2.4	0.9
Hib	738	41.7	0.4	13.9	1.4	−0.1	0.9
Mel	676	225.1	3.9	76.5	3.2	1.2	1.6
Mel	695	272.7	0.7	95.9	3.8	3.0	2.2
<i>Spinel-rich core</i>							
Mel	679	152.6	0.4	52.7	2.5	−0.5	1.2
Mel	694	139.7	1.2	47.7	2.9	3.0	2.0
Sp	710	2.52	0.00	0.82	0.11	0.45	0.15
Sp	713	2.52	0.00	0.81	0.14	0.09	0.14
<i>Mantle</i>							
Hib	6	517.2	3.3	170.4	4.1	−4.3	1.8
Hib	8	399.6	2.1	131.5	4.0	−2.9	1.9
Hib	11	46.1	0.1	15.1	1.1	2.4	0.7
Hib	731	383.6	6.1	124.5	2.9	−5.3	2.0
Hib	732	550.4	6.2	180.4	2.7	−8.6	2.4
Hib	733	28.8	0.3	9.9	1.3	3.2	0.9
Mel	677	145.6	2.4	51.0	2.5	0.9	1.3
Mel	678	120.2	0.5	41.7	2.4	1.3	1.2
Mel	698	85.3	0.2	27.9	2.5	0.8	1.9
Sp	716	2.51	0.00	0.75	0.12	2.55	0.15
Sp	717	2.51	0.00	0.85	0.11	2.62	0.15
<i>Large melilite aggregate</i>							
Mel	691	59.5	0.6	19.8	1.7	−0.9	1.7
Mel	693	61.4	0.2	21.6	1.9	−0.5	1.7

Hib: hibonite, Mel: melilite, Sp: spinel.

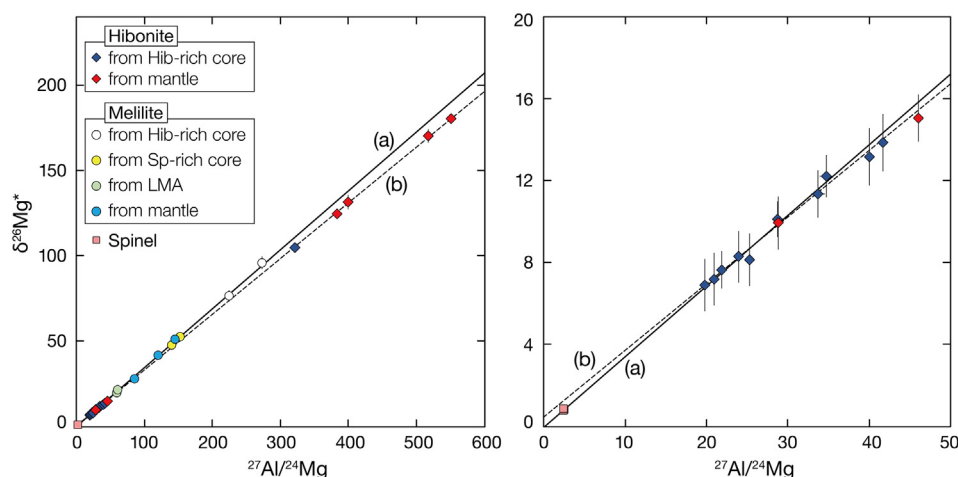


Fig. 11. Al–Mg isotope data for melilite, spinel, and hibonite in HKD01 plotted on the ^{26}Al – ^{26}Mg evolutionary diagrams. Each shows different ranges of the $^{27}\text{Al}/^{24}\text{Mg}$ ratio. Solid line (a) indicates a mineral isochron defined using melilite and spinel data giving initial values of $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.812 \pm 0.089) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = -0.060 \pm 0.063\text{‰}$ (Kawasaki et al., 2020). Broken line (b) indicates a regression line of hibonite data. Errors are 2 σ . Symbols without error bars exhibit errors smaller than their symbol sizes. LMA, large melilite aggregate.

changes during melilite condensation. We show one of possible condensation conditions for HKD01 melilite as an example, assuming a constant temperature of 1498 K. In that case, gaseous pressures during melilite condensation can be determined as follows: (1) Normally-zoned melilite crystals in the hibonite-rich core part condensed with increasing pressure from $\sim 1.0 \times 10^{-3}$ ($\sim \text{\AA}k_1$) to $\sim 1.2 \times 10^{-3}$ atm ($\sim \text{\AA}k_2$). (2) Normally-zoned melilite crystals in the spinel-rich core part condensed with increasing pressure from $\sim 1.2 \times 10^{-3}$ ($\sim \text{\AA}k_2$) to $\sim 1.6 \times 10^{-3}$ atm ($\sim \text{\AA}k_5$). (3) Normally-zoned melilite crystals in the mantle part condensed with increasing pressure from $\sim 1.0 \times 10^{-3}$ ($\sim \text{\AA}k_1$) to $\sim 1.5 \times 10^{-3}$ atm ($\sim \text{\AA}k_4$), while the $\text{\AA}k$ -rich cores ($\sim \text{\AA}k_4$) of the oscillatory-zoned crystals condensed at $P^{\text{tot}} \sim 1.5 \times 10^{-3}$ atm before the condensation of the surrounding normally-zoned melilites. (4) Complex chemical zoning patterns from the core to the rim of melilite crystals in the large melilite aggregates condensed with pressure changing repetitively. Thus, the crystal cores ($\text{\AA}k_5$) began to condense at $P^{\text{tot}} \sim 1.6 \times 10^{-3}$ atm, and then the pressure decreased to $\sim 1.2 \times 10^{-3}$ atm ($\text{\AA}k_2$). Subsequently the pressure increased again to $\sim 2.3 \times 10^{-3}$ atm ($\text{\AA}k_{12}$), and finally decreased to $\sim 1.7 \times 10^{-3}$ atm to condense the crystal rims ($\text{\AA}k_6$). Thus, the condensation of melilite crystals with chemical zoning could have formed from the solar nebular gas with pressure changing by a factor of two or three.

4.2. ^{26}Al – ^{26}Mg systematics

The $(^{26}\text{Al}/^{27}\text{Al})_0$ obtained from the regression line for the Al–Mg isotope data for the hibonite in HKD01, $(4.547 \pm 0.054) \times 10^{-5}$, is slightly but clearly lower than the $(^{26}\text{Al}/^{27}\text{Al})_0$ of $(4.812 \pm 0.089) \times 10^{-5}$ for the mineral isochron for melilite and spinel (Fig. 11). If the difference in $(^{26}\text{Al}/^{27}\text{Al})_0$ directly corresponds to a relative age difference, the hibonite can be calculated to have formed 0.06 ± 0.02 Myr after the formation of melilite and spinel. However, the textural relationships and thermodynamic calculations indicate the hibonite is most likely to have formed prior to the melilite and spinel as discussed in Section 4.1. This inconsistency between the $(^{26}\text{Al}/^{27}\text{Al})_0$ and the inferred formation sequences may imply heterogeneous distributions of ^{26}Al in the forming region.

On the other hand, Kööp et al. (2016) pointed out a possibility that the RSF for Al and Mg for meteoritic hibonite differs from that for the Madagascar hibonite. Because Madagascar hibonite contains significantly more FeO and rare earth elements (REEs) than hibonites in HKD01 (Tables S4 and S5), such a matrix effect may result in the RSF change in the SIMS measurements. The determined RSF of 0.787 ± 0.011 for the HKD01 hibonite, with $^{27}\text{Al}/^{24}\text{Mg}$ ratios between 20 and 41, is identical within the error to the RSF for 0.773 ± 0.008 for the Madagascar hibonite (Fig. S34). This indicates that there are no significant matrix effects on the RSFs for Al and Mg between the Madagascar hibonite and the HKD01 hibonite with those $^{27}\text{Al}/^{24}\text{Mg}$ ratios in our SIMS measurement conditions. Indeed, the Al–Mg data for hibonite, with $^{27}\text{Al}/^{24}\text{Mg}$ ratios

of less than 46 perfectly plot on the mineral isochron for melilite and spinel (Fig. 11), although this also could be due to a very small deviation between the two lines in the range of these low $^{27}\text{Al}/^{24}\text{Mg}$ ratios. Nevertheless, the Al–Mg data for Mg-poor hibonite ($^{27}\text{Al}/^{24}\text{Mg} > \sim 320$), for which RSFs could not be determined due to low the Mg concentration and microscale strong chemical zoning (Fig. S33), clearly deviate from the mineral isochron for melilite and spinel (Fig. 11). If the RSF for hibonite is 0.818, the plots of $^{27}\text{Al}/^{24}\text{Mg} > \sim 320$ move to the isochron. Although the value of 0.818 is just 4% different, it corresponds to a 5.7σ deviation in analytical uncertainty from the 0.787 ± 0.011 determined by the HKD01 hibonites for $^{27}\text{Al}/^{24}\text{Mg} < 41$. Accordingly, there may be small matrix effects on the RSFs depending on the $^{27}\text{Al}/^{24}\text{Mg}$ ratios of hibonite, and therefore we conclude that the Al–Mg data for Mg-poor hibonite ($^{27}\text{Al}/^{24}\text{Mg} > \sim 320$) should not be used for interpretation of the ^{26}Al – ^{26}Mg systematics. Instead, the mineral isochron for HKD01 can be defined using the data for melilite, spinel, and Mg-rich hibonite ($^{27}\text{Al}/^{24}\text{Mg} < \sim 46$) where the initial values are calculated to be $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.795 \pm 0.078) \times 10^{-5}$ and $(\delta^{26}\text{Mg}^*)_0 = -0.058 \pm 0.063\text{‰}$ (Fig. 12). The well-defined isochron including minerals from both the core and rim suggest that condensation of the HKD01 minerals occurred within a short period of time. The inferred $(^{26}\text{Al}/^{27}\text{Al})_0$ is clearly lower than the whole-rock CV CAI values $(^{26}\text{Al}/^{27}\text{Al})_0$ of $(5.23 \pm 0.13) \times 10^{-5}$ (Jacobsen et al., 2008) and $(5.252 \pm 0.019) \times 10^{-5}$ (Larsen et al., 2011). The relative age of HKD01 is calculated to be 0.09 ± 0.02 Myr from the formation of canonical CAIs, if we apply the value from Larsen et al. (2011).

4.3. Evidence for an ^{16}O -poor nebular gas during formation

The melilite crystals in HKD01 exhibit O-isotopic variations ranging from $\Delta^{17}\text{O} \sim -23\text{‰}$ to $\sim 1\text{‰}$, while the hibonite and spinel exhibit uniformly ^{16}O -rich compositions ($\Delta^{17}\text{O} \sim -23\text{‰}$) (Fig. 7). ^{16}O -rich signatures for minerals in FGIs have been suggested to reflect ^{16}O -rich compositions of the solar nebular gas from which they condensed (Wasson et al., 2001; Krot et al., 2002; Itoh et al., 2004; Aléon et al., 2005; Bodéan et al., 2014; Ushikubo et al., 2017; Han et al., 2019). The observed ^{16}O -rich signatures for the HKD01 minerals also indicate the presence of ^{16}O -rich nebular gas in the forming region.

On the other hand, variations in O-isotopic compositions (i.e., ^{16}O -poor signatures) of minerals in FGIs have been suggested to originate from O-isotope exchange in the nebular gas and/or on the parent body after condensation (Wasson et al., 2001; Itoh et al., 2004; Aléon et al., 2005). In HKD01, O-isotopic compositions of melilite crystals in the mantle change abruptly within $\sim 2\text{ }\mu\text{m}$ (Fig. 9), indicating that the O self-diffusion distance in the HKD01 melilite, in the nebular gas and/or on the parent body, is less than $\sim 2\text{ }\mu\text{m}$ after they condensed from the nebular gas. Therefore, the O-isotopic compositions of the HKD01 melilite are unlikely to have been significantly disturbed by diffusion-controlled isotope exchange, and the melilite crystals preserve the O-isotopic compositions of

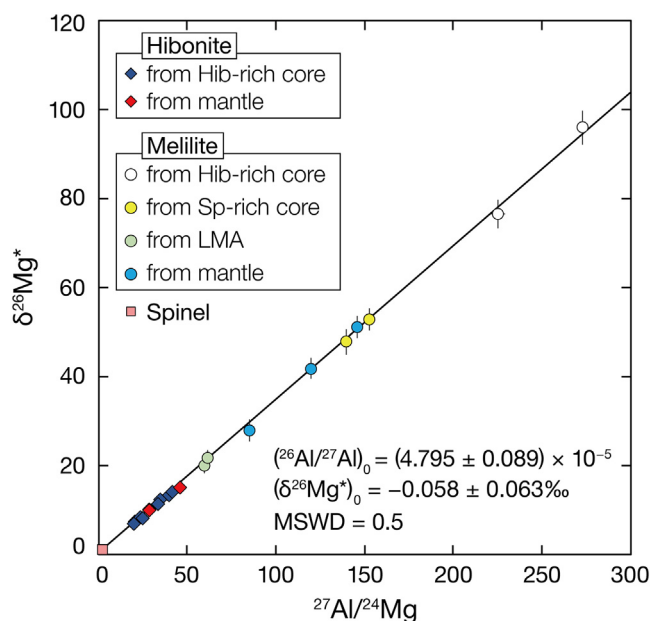


Fig. 12. ^{26}Al – ^{26}Mg mineral isochron for HKD01 defined by data for Mg-rich hibonite, melilite, and spinel. Isoplot Model 1 (Ludwig, 2003) was used to fit an isochron. Errors are 2σ . Symbols without error bars exhibit errors smaller than their symbol sizes. LMA, large melilite aggregate.

the nebular gas from which they condensed. Additionally, Wasson et al. (2001) suggested O-isotopic alteration of fine-grained melilite crystals by dissolution and reprecipitation on the parent body to account for the ^{16}O -poor melilite in FGIs from the less primitive CO chondrites. Such a process could have occurred partly in melilite crystals in the Allende Type A CAI as demonstrated by Park et al. (2012). Secondary minerals replacing melilite (e.g., anorthite and grossular) are not observed in HKD01 from NWA 8613 and thus effects of the O-isotopic alteration of the HKD01 melilite could be very small, although O-isotope disturbances of less than $2\text{ }\mu\text{m}$ might occur.

In the large melilite aggregate of HKD01, melilite crystals are all ^{16}O -poor (Fig. 8) and a large ($\sim 20\text{ }\mu\text{m}$) melilite crystal with homogeneously ^{16}O -poor composition ($\Delta^{17}\text{O} \sim 0\text{‰}$) and repetitive oscillation of chemical zoning across the single crystal was found (Fig. 10). The contrast between the presence of a large ($\sim 20\text{ }\mu\text{m}$) ^{16}O -poor melilite crystal and $2\text{ }\mu\text{m}$ -scale O-isotope variations in the mantle melilite indicates that the ^{16}O -poor ($\Delta^{17}\text{O} \sim 0\text{‰}$) melilite in HKD01 originally formed by condensation, which strongly suggests the presence of ^{16}O -poor nebular gas for the formation. Both ^{16}O -rich and ^{16}O -poor gaseous reservoirs could have existed in the forming region of the FGI HKD01.

The O- and Al-Mg isotope systematics of the HKD01 minerals imply that formation with the co-existing ^{16}O -rich and ^{16}O -poor gaseous reservoirs occurred at $0.09 \pm 0.02\text{ Myr}$ after the birth of our Solar System, under the assumption of homogeneous distributions of ^{26}Al in the forming region (Jacobsen et al., 2008; Larsen et al., 2011). The co-existence of ^{16}O -rich and ^{16}O -poor gaseous reservoirs has also been suggested for the formation of fluffy Type A CAIs (Katayama et al., 2012; Kawasaki et al., 2012, 2017) and coarse-grained, igneous CAIs in CV chon-

drites (e.g., Yurimoto et al., 1998; Yoshitake et al., 2005; Aléon et al., 2007; Aléon, 2016; Kawasaki et al., 2018). The CAIs with variable O-isotopic compositions could have formed at the inner edge of the solar protoplanetary disk, where a boundary between the contrasting O-isotopic reservoirs, ^{16}O -rich solar (McKeegan et al., 2011) and ^{16}O -poor planetary signatures (Yurimoto and Kuramoto, 2004), may have existed and both gases mixed (Itoh and Yurimoto, 2003; Yurimoto et al., 2008).

5. CONCLUSIONS

A combined study involving detailed petrographic observations and *in situ* O-isotope analysis for the FGI HKD01 from NWA 8613 revealed the presence of an ^{16}O -poor nebular gaseous reservoir during its formation. Hibonite and spinel are uniformly ^{16}O -rich ($\Delta^{17}\text{O} = -23\text{‰}$) despite their occurrences. Melilite crystals in the hibonite-rich core, spinel-rich core, and mantle parts typically have grain sizes of less than $10\text{ }\mu\text{m}$ and normal chemical zoning. They exhibit O-isotope variations ranging between $\Delta^{17}\text{O} \sim -23\text{‰}$ and 0‰ . Measurements of O-isotopic compositions in linear traverse show that O-isotopic compositions of the melilite in the mantle change abruptly within $\sim 2\text{ }\mu\text{m}$, suggesting the O self-diffusion distance in melilite after condensation is less than $\sim 2\text{ }\mu\text{m}$. This indicates that melilite crystals in HKD01 preserve the O-isotopic compositions of the nebular gas from which they condensed. In the large melilite aggregate found in the mantle, melilite crystals exhibit larger grain sizes ($10\text{--}25\text{ }\mu\text{m}$) and ^{16}O -poor compositions with small variations ranging between $\Delta^{17}\text{O} \sim -4$ and 1‰ . Measurements of O-isotopic compositions in linear traverse shows the presence of a large melilite crystal ($\sim 20\text{ }\mu\text{m}$) with homogeneously ^{16}O -poor composition ($\Delta^{17}\text{O} \sim 0\text{‰}$) across the single crystal.

The contrast between the large, homogeneously ^{16}O -poor crystal and the inferred diffusion distance of O-isotopes of less than $\sim 2\ \mu\text{m}$ in HKD01 melilite indicates that the ^{16}O -poor melilite crystal originally had an ^{16}O -poor composition ($\Delta^{17}\text{O} \sim 0\text{‰}$) at condensation, suggesting the presence of an ^{16}O -poor nebular gaseous reservoir during the formation of HKD01. Moreover, the O-isotopic compositions of individual mineral crystals of HKD01 correspond to the O-isotopic compositions of nebular gas when the crystals condensed. Our data demonstrate that the formation of FGI HKD01 occurred in the protoplanetary disk with co-existing ^{16}O -rich and ^{16}O -poor gaseous reservoirs. The ^{26}Al – ^{26}Mg mineral isochron for HKD01 gives $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.795 \pm 0.078) \times 10^{-5}$. Under the assumption of homogeneous distribution of ^{26}Al in the forming region, both ^{16}O -rich and ^{16}O -poor gaseous reservoirs could have existed in the forming region at 0.09 ± 0.02 Myr after the birth of our Solar System.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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