

Mineralogical alteration of a type A CAI from Allende CV3 chondrite: Formation of secondary dmisteinbergite and its phase transition to anorthite

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Abstract—Dmisteinbergite, a hexagonal form of $\text{CaAl}_2\text{Si}_2\text{O}_8$, was found in a compact type A Ca-Al-rich inclusion (CAI) in the Allende CV3 chondrite. Scanning and transmission electron microscopic observations show that dmisteinbergite was always in contact with grossular and grossular was in contact with melilite. In addition, there is a crystallographic relationship between dmisteinbergite and anorthite. Based on the textural and crystallographic evidence, the following mineralogical alteration processes are proposed to have occurred in the CAI. (1) Melilite was replaced by grossular. High densities of vesicles in the grossular indicate that hydrogrossular might have been the primary alteration phase and dehydrated by later metamorphism. (2) Dmisteinbergite formed from (hydro)grossular through a reaction with Si-rich fluid. (3) Nano-sized minerals are formed within dmisteinbergite. (4) Dmisteinbergite was transformed to anorthite. (5) Both anorthite and dmisteinbergite were altered to nepheline. (6) Hydrogrossular was dehydrated to grossular. (Hydro)grossular, dmisteinbergite, anorthite, and nepheline in the CAI seem to have formed in the course of metasomatism that occurred in the Allende parent body. Except for the hydrogrossular dehydration, these reactions could have occurred at moderate temperature (200–250°C) in high pH fluids (pH 13–14) according to past experimental studies. Episodic changes in fluid composition seem to have occurred before reactions (2), (4), and (5), because these reactions were not completed before the next reaction started. Higher temperature is required for reactions (5) and (6) to occur. Our observation of the CAI suggests that it experienced multiple episodes of metasomatism as temperatures were rising in the Allende parent asteroid.

INTRODUCTION

$\text{CaAl}_2\text{Si}_2\text{O}_8$ has three polymorphs with triclinic (anorthite), orthorhombic (svyatoslavite), and hexagonal (dmisteinbergite) structures. Anorthite is the stable phase and commonly occurs in both terrestrial and

extraterrestrial rocks. Dmisteinbergite and svyatoslavite are the metastable phases that were first synthesized by crystallization from a $\text{CaAl}_2\text{Si}_2\text{O}_8$ supercooled melt (Davis & Tuttle, 1952). Dmisteinbergite was also synthesized in the following additional ways: (1) hydrothermal processing of a mixture of Ca, Al, and Si-

oxide powder at 350°C (Hong et al., 1999) and (2) hydrothermal processing of a mixture of monocalcium aluminate (CaAl_2O_4) and quartz at approximately 200°C (Borglum et al., 1993).

Several studies reported the occurrence of dmisteinbergite in natural terrestrial rocks. Dmisteinbergite was formed by rapid cooling of a melt in association with quartz in the pseudotachylyte-bearing fault veins in the Gole Larghe Fault zone of the Italian Southern Alps (Nestola et al., 2010). We hereafter define dmisteinbergite formed from a high-temperature melt as “primary dmisteinbergite.” On the other hand, “secondary dmisteinbergite,” replacing pre-existing minerals, was also reported in the altered gabbro in Kurumazawa, Japan in association with wairakite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$) (Downs, 2006). In addition, secondary dmisteinbergite and svyatoslavite, formed in natural burning processes of spoil-heaps, were reported in the Chelyabinsk coal basin (Sokol et al., 1998, and references therein).

Recently, dmisteinbergite was discovered in calcium–aluminum-rich inclusions (CAIs) in several carbonaceous chondrites (Brearley et al., 2014; Fintor et al., 2014; Ma et al., 2013). Ma et al. (2013) reported dmisteinbergite in an Allende fractionation and unidentified nuclear CAI STP-1. This dmisteinbergite has a euhedral and coarse-grained texture and ^{16}O -rich oxygen isotopic compositions; therefore, the authors concluded that this is a primary dmisteinbergite crystallized from a high-temperature melt. On the other hand, Fintor et al. (2014) reported fine-grained, lath-shaped dmisteinbergite in a compact type A CAI of the Northwest Africa (NWA) 2086 CV3 chondrite. This dmisteinbergite occurs in a fine-grained porous part in the CAI, together with other fine-grained minerals such as grossular, anorthite, nepheline, and sodalite that have formed by secondary parent body alteration. Therefore, they concluded that this lath-like dmisteinbergite was a secondary phase formed by aqueous alteration. The precursor phase of the secondary dmisteinbergite was considered to be melilite, because it coexists with dmisteinbergite (Fintor et al., 2014). However, the intricate texture of various secondary minerals makes it difficult to trace the formation sequence of dmisteinbergite and coexisting minerals. Fintor et al. (2014) reported that both secondary dmisteinbergite and secondary anorthite coexist in the NWA 2086 CAI. The two polymorphs are not in direct contact with each other and the genetic relationship between the two polymorphs remains unclear. To clarify the genetic relationship and the formation process of the two polymorphs observed in CAIs, we performed mineralogical and petrological observation of one large CAI in the Allende chondrite that contains both secondary dmisteinbergite and anorthite.

METHODS

Samples

One polished thin section of $\sim 1 \text{ cm} \times 1 \text{ cm}$ in size was prepared from a chip of the Allende CV3 chondrite. We examined a spheroidal CAI #1 ($\sim 1 \text{ mm}$ in diameter) in the polished section (Figure 1a). The center of the CAI has large pores which were produced during polishing, since minerals in this region were plucked out, probably due to high porosity.

Scanning Electron Microscopy and Electron Probe Microanalysis

The mineralogy and petrology of the Allende CAI in the polished thin section (Figure 1a) was examined using a scanning electron microscope (SEM; Hitachi S-3400N) and a field-emission SEM (FE-SEM; JEOL JSM-7001F). For most SEM observations, we used back-scattered electron (BSE) imaging. Quantitative chemical compositions of minerals were determined by a FE electron probe microanalyzer (FE-EPMA; JEOL JXA-8530F) equipped with wavelength dispersive X-ray spectrometers. The analyses were performed using a focused electron beam at an acceleration voltage of 15 keV and 10 nA beam current. The detection limits (wt%) are 0.02 for Na_2O , MgO , Al_2O_3 , K_2O , CaO , and TiO_2 , and 0.03 for SiO_2 , Cr_2O_3 , MnO , FeO , and Cl . Standard minerals used were as follows: albite (Na), olivine (Mg), almandine (Al), diopside (Si, Ca), sanidine (K), rutile (Ti), chromite (Cr), rhodonite (Mn), hematite (Fe), and NaCl (Cl).

Focused Ion Beam Technique and Transmission Electron Microscopy

For submicron-scale textural and chemical analyses, five sections were extracted from regions of interest from the CAI using a focused ion beam technique (FIB; Thermo Fisher Scientific Quanta 200 3DS). All the FIB sections are $\sim 15 \mu\text{m} \times 10 \mu\text{m}$ in size and were investigated by a transmission electron microscope (TEM; JEOL JEM-2100F) equipped with an energy dispersive X-ray spectrometer (EDX) operated at 200 keV. Data reduction was performed using the Cliff–Lorimer thin film approximation using experimentally determined k-factors. Mineral phase identifications were based on the analysis of selected area electron diffraction (SAED) patterns.

Raman Analyses

To identify dmisteinbergite and anorthite, Raman spectra were acquired using a micro-Raman spectrometer (JASCO NRS-5100) equipped with a frequency-doubled

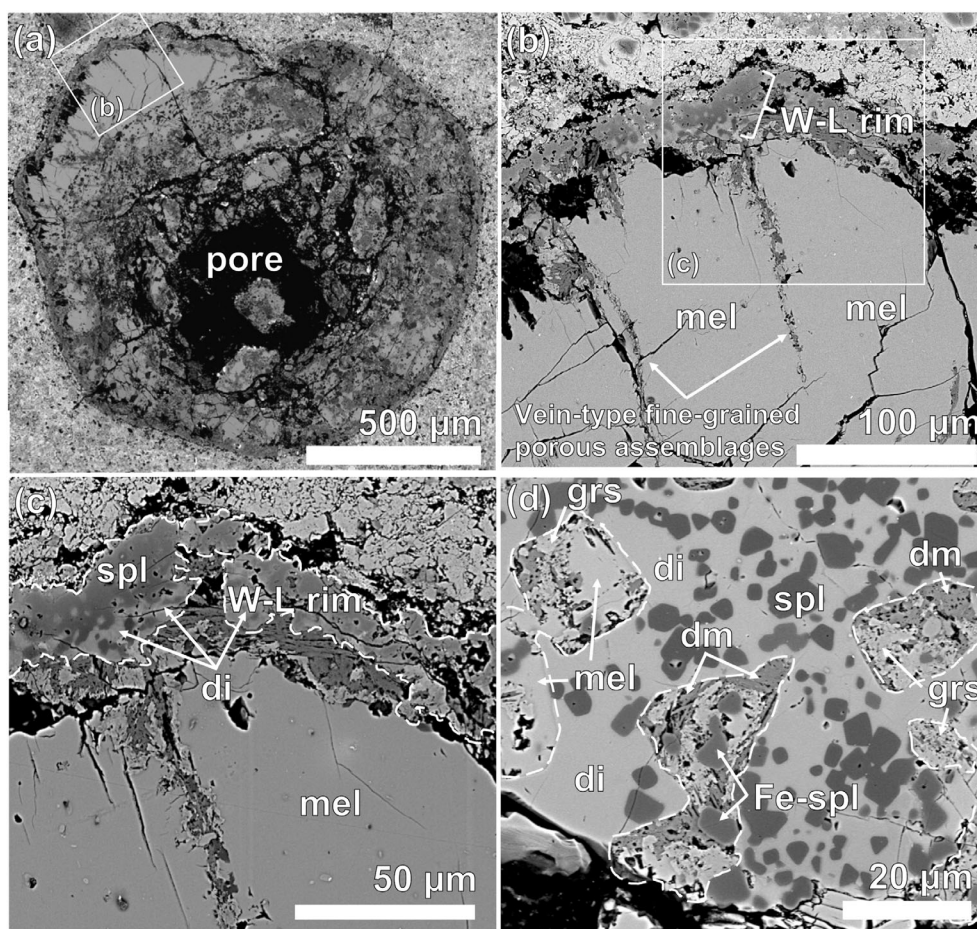


FIGURE 1. Backscattered electron images of the Allende calcium–aluminum-rich inclusion (CAI). a) Whole image of the CAI. The center of the CAI has large pores. b) Image of boxed area b in (a) showing that the CAI is surrounded by a Wark–Lovering (W–L) rim (indicated by dashed lines). Narrow veins of fine-grained porous assemblage occurred in large melilite (mel) grains. c) Image of boxed area c in (b). The W–L rim is composed of diopside (di) and spinel (spl). d) Image of inner part of the CAI showing that small melilites are replaced by fine-grained porous assemblages (indicated by dashed lines) are embedded in diopside. The assemblages are composed of dmisteinbergite (dm) and grossular (grs). Fe-spinel grains (Fe-spl) are in contact with the assemblages.

Nd:YAG laser of 532 nm excitation wavelength. The laser beam was focused on the sample using a $\times 20$ objective lens, giving a spot size of approximately $5\ \mu\text{m}$. The instrument has a spectral resolution better than $1\ \text{cm}^{-1}$. The calibration of the spectrometer was verified using a silicon wafer with a known major Raman peak at $524\ \text{cm}^{-1}$. The acquisition time for one measurement was 60 s and each spectrum was obtained twice. Acquired data were compared with RRUFF online data (Lafuente et al., 2015) for phase identification.

RESULTS

Mineralogy and Petrology of the CAI

The CAI we examined is heavily altered and surrounded by a Wark–Lovering (W–L) rim made of

spinel and Al, Ti-diopside layers (Figure 1b,c). The CAI consists mainly of Al, Ti-diopside (the abundance of Al_2O_3 is 14–27 wt% and that of TiO_2 is 4–12 wt%) (~20 vol%), gehlenitic melilite (Geh_{75-86}) (~40 vol%), spinel (~2 vol%), perovskite (minor phase), and fine-grained porous assemblages (~40 vol%) that are mainly composed of intimately intergrown anorthite, dmisteinbergite, grossular, nepheline, and sodalite (Figures 1d and 2a,b).

Gehlenitic melilites at the upper left in Figure 1a are about $100\ \mu\text{m}$ and the other melilites are $5\text{--}50\ \mu\text{m}$ in size. Narrow veins of the fine-grained porous assemblage are observed within and along the peripheries of the large melilite grains (Figure 1b). On the other hand, relatively small melilite grains commonly occur in this CAI and a large part of the small melilites are replaced to various extents by the fine-grained porous assemblages

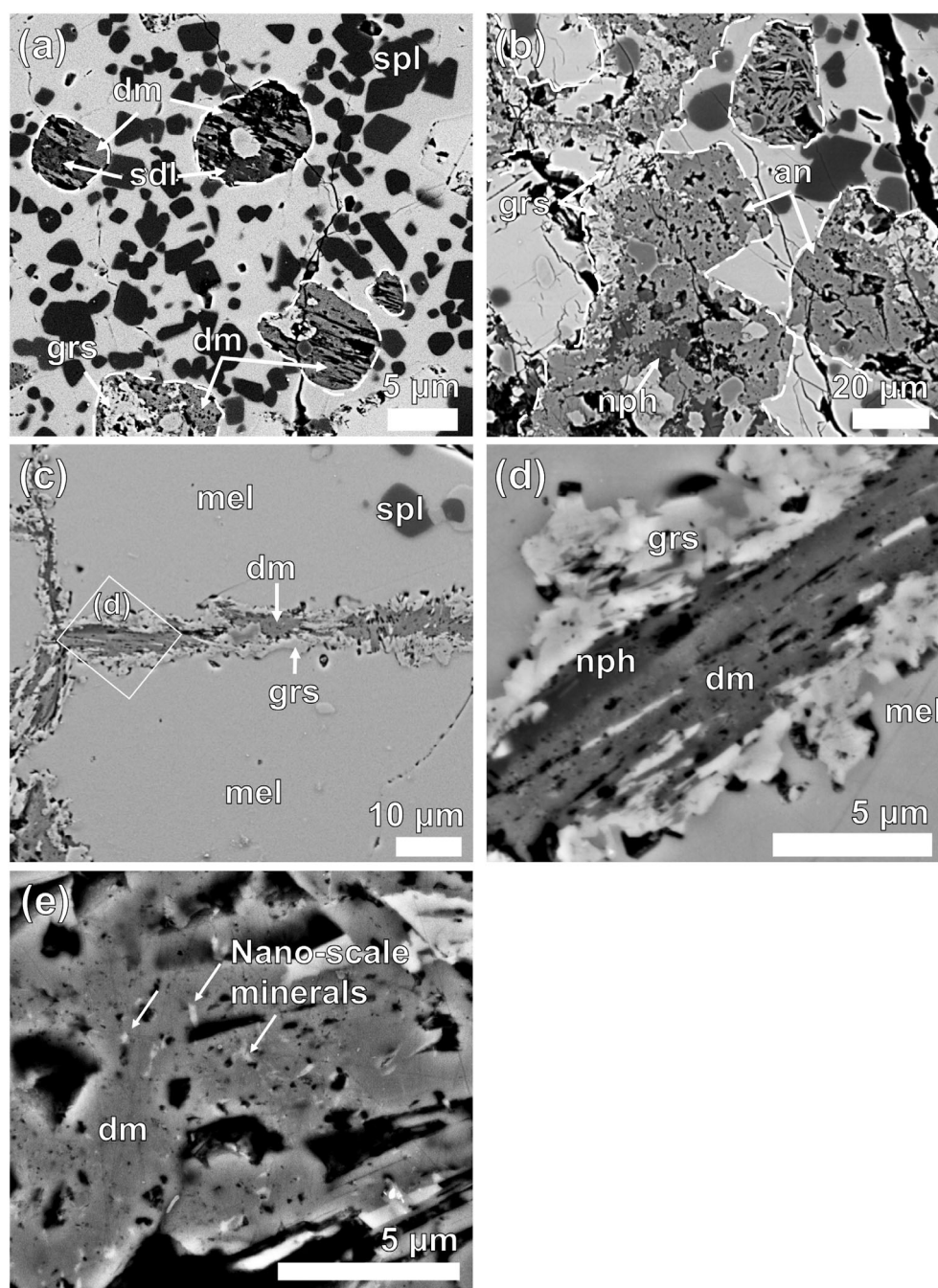


FIGURE 2. Back scattered electron images of fine-grained porous assemblages. a) Melilites completely replaced by fine-grained porous assemblages (indicated by dashed lines) are embedded in diopside. The assemblages are composed of dmisteinbergite (dm), grossular (grs), and sodalite (sdl). b) Image of fine-grained porous assemblages consisting of anorthite (an), grossular, and nepheline (nph) (indicated by dashed lines). c) Image of vein type of fine-grained porous assemblage cross cutting large melilite grains. d) Image of boxed area d in (c) showing that the inner and outer parts of the vein are composed mainly of dmisteinbergite and nepheline, and grossular, respectively. e) Image of nano-scale minerals occurring inside the dmisteinbergite.

(Figure 1d). The small melilites and other minerals are commonly enclosed in Al, Ti-diopside (Figure 1d). Spinel are 2–10 μm in size, have round or equant shape

(Figures 1d and 2a), and are distributed heterogeneously in the CAI. Fe-rich Spinel ($\text{Mg}\#0\text{--}15$) occur in the Al, Ti-diopside tends to be less Fe rich than Mg-rich ones

TABLE 1. Representative compositions of primary and secondary minerals in the Allende CAI.

	mel	Al, Ti-di	Mg-spl	Fe-spl	an	dm	grs
wt%							
SiO ₂	26.4	35.2	0.43	0.38	42.2	41.5	39.1
TiO ₂	0.05	9.65	0.33	0.30	b.d.	0.09	0.15
Al ₂ O ₃	30.0	22.4	67.7	64.4	36.3	37.5	23.3
FeO	0.12	0.08	6.45	17.7	0.39	0.34	1.49
MnO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.03
MgO	2.72	6.99	22.6	15.3	1.00	1.05	1.40
CaO	40.2	24.2	0.47	0.20	18.9	18.6	34.5
Na ₂ O	0.07	b.d.	b.d.	0.02	0.41	0.32	0.06
K ₂ O	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cr ₂ O ₃	b.d.	0.10	0.25	0.18	b.d.	b.d.	b.d.
Cl	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.03
Total	99.6	99.0	98.7	98.5	99.1	99.4	100.1
Number of O	7	6	4	4	8	8	12
Si	1.207	1.332	0.011	0.011	1.976	1.938	2.934
Ti	0.002	0.305	0.007	0.007	—	0.004	0.009
Al	1.614	0.998	1.984	1.984	1.998	2.059	2.058
Fe	0.005	0.003	0.134	0.387	0.015	0.013	0.093
Mn	—	—	—	—	—	—	0.002
Mg	0.185	0.394	0.838	0.596	0.07	0.073	0.156
Ca	1.969	0.981	0.013	0.006	0.948	0.93	2.774
Na	0.006	—	—	0.001	0.037	0.029	0.009
K	—	—	—	—	—	—	—
Cr	—	0.003	0.005	0.004	—	—	—
Cl	—	—	—	—	—	—	0.004
Cation total	4.998	4.015	2.991	2.994	5.044	5.046	8.040

Note: Detection limits (wt%) are 0.02 for Na₂O, MgO, Al₂O₃, K₂O, CaO, TiO₂; 0.03 for SiO₂, Cr₂O₃, MnO, FeO, Cl.

Abbreviations: an, anorthite; Al, Ti-di, Al, Ti-diopside; b.d., below detection limit; CAI, calcium-aluminum-rich inclusion; dm, dmisteinbergite; Fe-spl, Fe-rich spinel; grs, grossular; mel, melilite; Mg-spl, Mg-rich spinel.

(Mg#28–55) near the fine-grained porous assemblages and within the W–L rim (Table 1; Figure 1b,d). Perovskite occurs as small grains (~5 µm in size) and its chemical composition is almost pure CaTiO₃.

Fine-grained porous assemblages have abundant spaces between the constituent fine-grained minerals (Figure 2a,b). There are two types of fine-grained porous assemblages: the patches replacing the small melilites (Figures 1d and 2a,b) and the veins along and crosscutting the large melilites (Figures 1b and 2c,d). Raman analysis shows that dmisteinbergite occurs in both types of fine-grained porous assemblages. Dmisteinbergite has elongated morphology (1–2 µm in width and 10 µm in length on average) (Figures 1b,d and 2a,c,d). Dmisteinbergite grains are parallel to each other and form a cluster. In the vein-type fine-grained porous assemblages, the elongate

direction of the dmisteinbergite is parallel to the direction of the veins (Figure 2c,d). The dmisteinbergite cluster in the vein is about 5 µm in width. Raman analysis also shows that, in contrast to dmisteinbergite, anorthite grains show anhedral morphology (Figure 2b) and occurred only in the patch-type fine-grained porous assemblages. Dmisteinbergite and anorthite rarely occur in a single fine-grained porous assemblage. The anorthite-bearing patch-type assemblages are usually larger than the dmisteinbergite-bearing patch-type assemblages. Therefore, the anorthite-bearing assemblages are in contact with each other in contrast to the dmisteinbergite-bearing assemblages (Figure 2a,b). The total volume of the anorthite-bearing assemblages in the CAI is about six times larger than that of the dmisteinbergite-bearing assemblages. Nanometer-sized unknown minerals are observed in the dmisteinbergite and anorthite grains (Figure 2c). The number density of the nm-sized unknown minerals is about 2 grains µm^{−2} on average. Grossular grains always occur between dmisteinbergite and melilite and are ~5 µm in size in the vein-type fine-grained porous assemblages (Figure 2c,d). Minor amounts of fine-grained nepheline occur with dmisteinbergite or anorthite (Figure 2a). Sodalites also occur with dmisteinbergite or anorthite although the abundance of them is quite low (Figure 2b).

The chemical compositions of dmisteinbergite and anorthite are shown in Table 1. Both compositions show small variations which are slightly Mg, Al-rich, and Si-poor compared to the stoichiometric compositions (Table 1; Figure 3). Pores and nanometer-sized unknown minerals in them probably cause the compositional deviation from stoichiometric composition of dmisteinbergite and anorthite. The abundances of Na and K in dmisteinbergite and anorthite are less than 3 wt%. There is poor variation of Na and K in them. The averaged chemical compositions of grossular-rich crystals are Ca_{2.8}Mg_{0.2}Al₂Si₃O₁₂ (Grossular_{91.7}Almandine_{3.1}Pyrope_{5.2}; Table 1). We did not obtain the chemical composition of nepheline and sodalite because most of these grains are too small.

TEM Observations of the Fine-Grained Porous Assemblages

We studied five FIB sections by TEM. Three of them are removed from where dmisteinbergite and grossular coexist with melilite. Two of them were removed from where anorthite-bearing assemblages are in contact with the dmisteinbergite-bearing assemblages. We describe microtextural features of the composing minerals of the fine-grained porous assemblages (dmisteinbergite, anorthite, grossular, and nepheline) below.

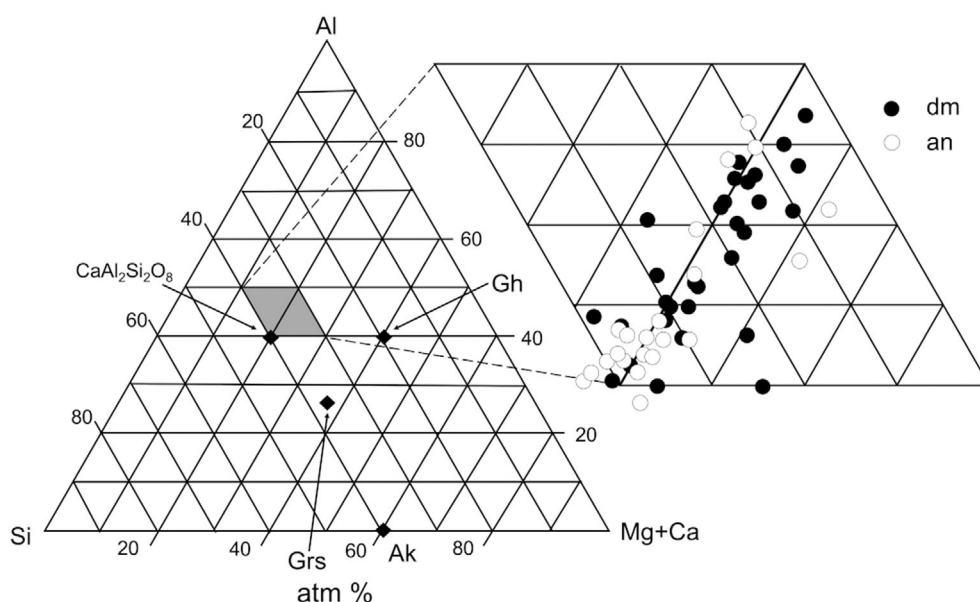


FIGURE 3. Focused-beam analyses of dmisteinbergite (dm) and anorthite (an) in a Al–Si–(Mg + Ca) (atom%) ternary diagram, obtained by electron probe microanalyzer-wavelength dispersive X-ray spectrometer. Most analyses of dmisteinbergite and anorthite plot along the line combining stoichiometric $\text{CaAl}_2\text{Si}_2\text{O}_8$ composition and a point at Al: Si: Mg + Ca = 2: 2: 1. The stoichiometric chemical compositions of grossular (Grs), gehlenite (Gh), and akermanite (Ak) are indicated by filled diamonds.

Mineralogical Features of Dmisteinbergite and Accessory Phases

The elongation direction of all dmisteinbergites is parallel to the (001) plane (Figure 4a). Many dmisteinbergites have abundant pores with characteristic elongated shapes parallel to (001) planes (~500 nm at most) (Figure 4b). Acicular inclusions (~20 nm in width) are observed within dmisteinbergite (Figure 5a). The elongate direction of the acicular minerals is not related to the orientation of the dmisteinbergite. The chemical compositions of dmisteinbergite measured by TEM-EDX are almost stoichiometric unlike those measured by EPMA. This is because we can measure the chemical composition of dmisteinbergite avoiding the nano-scale acicular inclusions by TEM-EDX. We attempted to measure the chemical compositions of the acicular minerals, as plotted in Figure 5. In the Al–Si–(Mg + Ca) ternary diagram (Figure 5), most of these analyses plot along a line joining the stoichiometric dmisteinbergite and a point on the Al–(Mg + Ca) join with Al/(Mg + Ca) = 4. This trend is the same as that of EPMA analyses of dmisteinbergite (Figure 3). This means that the acicular minerals in Figure 5a are the nano-scale minerals observed within dmisteinbergite by SEM (Figure 2e). Considering the contribution of the surrounding dmisteinbergite, the actual composition of the acicular minerals should be $(\text{Ca}, \text{Mg})\text{Al}_4\text{O}_7$. Combining the compositions and the high-resolution TEM image analyses of the acicular minerals

(Figure 5c), the acicular minerals seem to be grossite. The other nanometer-scale minerals are also observed on cleavages parallel to the (001) plane of dmisteinbergite (Figure 4c). These minerals are not grossite because their chemical composition and elongate direction differ. The mineral on the cleavage planes does not affect the composition of dmisteinbergite measured by EPMA because their number density is much lower than that of the grossite. The mineral in cleavages is Mg rich compared to dmisteinbergite, although it was impossible to accurately measure the chemical composition, even by TEM-EDX.

Vein-Type Fine-Grained Porous Assemblages

As shown by SEM observations (Figure 2c,d), in the veins, most grossular grains occur between melilite and dmisteinbergite (Figure 6a). In the center of the veins, dmisteinbergite grains (~100 nm in width) form a cluster (Figure 6a). This cluster is elongated parallel to the elongation direction of the vein (Figure 6b). Nepheline has similar elongated morphology and similar size with dmisteinbergite. Finer dmisteinbergite occurs in grossular grains (Figure 6c). No crystallographic relationship between this dmisteinbergite and grossular was confirmed (Figure 6c). Some elongated nanopores (less than 50 nm) are present in grossular (Figure 6e). The elongate direction of the pores is parallel to the *a*-axis of grossular crystals. None of the crystallographic relationships were observed

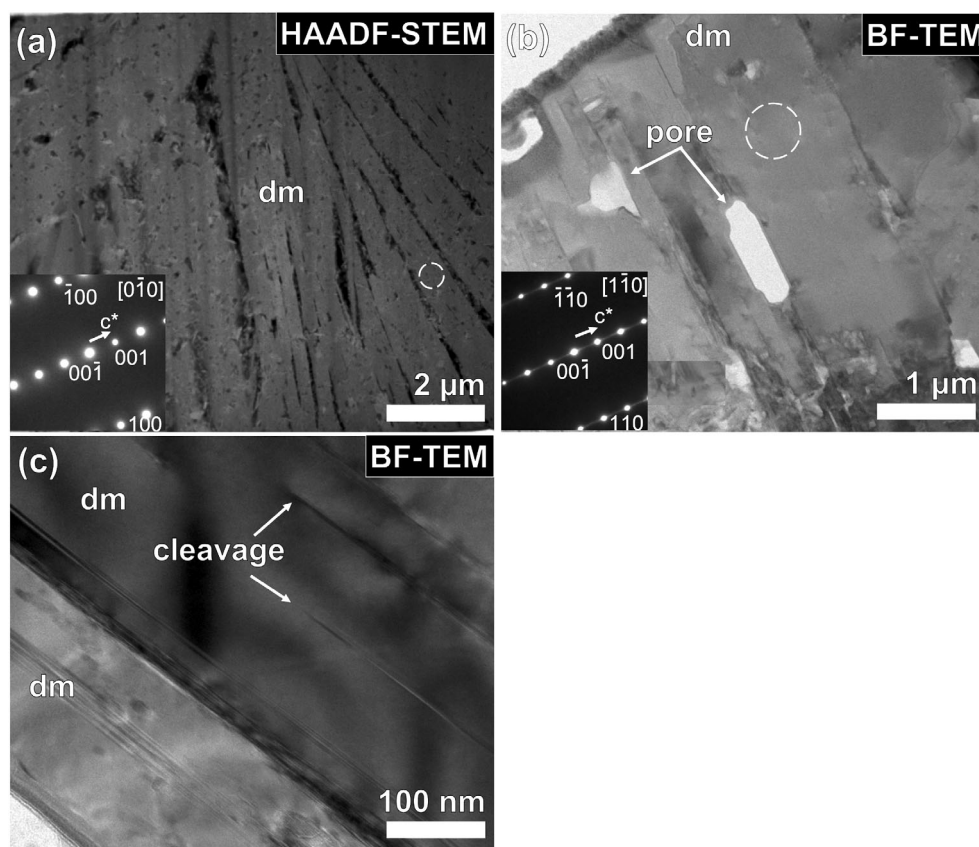


FIGURE 4. Transmission electron microscope (TEM) observations of dmisteinbergite in fine-grained porous assemblage. a) High-angle annular dark-field scanning TEM (HAADF-STEM) image of dmisteinbergite (dm) elongated parallel to the (001) plane. The inset is an selected area electron diffraction pattern from the area indicated by a dashed circle. b) Bright field (BF) TEM image of dmisteinbergite elongated parallel to the (001) plane. Pores in the dmisteinbergite are also elongated parallel to the (001) plane. c) High-resolution BF-TEM image of dmisteinbergite showing cleavage parallel to the (001) plane.

between grossular and melilite (Figure 6d). The boundaries between grossular and melilite are usually sharp and decorated with pores (Figure 6b–d).

Textual Observation of the Regions Where Dmisteinbergite Grains and Anorthite Grains Are in Contact

As we mentioned above, dmisteinbergite and anorthite rarely coexist in a single fine-grained porous assemblage. However, in some parts of the CAI, dmisteinbergite is in direct contact with anorthite (Figure 7a,b). We studied two FIB sections extracted from the relevant area (boxed areas in Figure 7a,b) by TEM. In the FIB section extracted from the boxed area of Figure 7a, grossular and dmisteinbergite are the main components. In this sample, elongation direction of several dmisteinbergites is parallel to the (001) plane and similarly form a cluster (Figure 8a,b). Each grain is 100 nm to 1 μm in width. Some of the dmisteinbergite grains enclose finer-grained anorthite grains, whose size is 100 nm to 1 μm, almost the same width as dmisteinbergite

(Figure 8a–c). The *b*-axis of most anorthite grains is nearly parallel to the *c*-axis of the dmisteinbergite grains (Figure 8c). The FIB section extracted from the boxed area of Figure 7b is composed mainly of anorthite grains measuring 1–3 μm in size. They are coarser than the anorthites observed in the FIB section in Figure 7a (Figure 9a). In this FIB section, anorthite crystals share a similar crystallographic orientation and are aligned along the (010) direction, which makes up three parallel lines of long crystals (Figure 9a). There are no dmisteinbergite grains that are in contact with these anorthite grains at the TEM scale, although a few dmisteinbergite grains separately occur in this section. The chemical composition of anorthite in the two FIB sections (Figures 8 and 9) is close to stoichiometric composition $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Na_2O and $\text{K}_2\text{O} < 1 \text{ wt}\%$) unlike the composition of anorthite analyzed by EPMA. In these anorthites, acicular grossite can be observed as in dmisteinbergite (Figure 9d). The abundance of acicular minerals in anorthite is lower than that in dmisteinbergite.

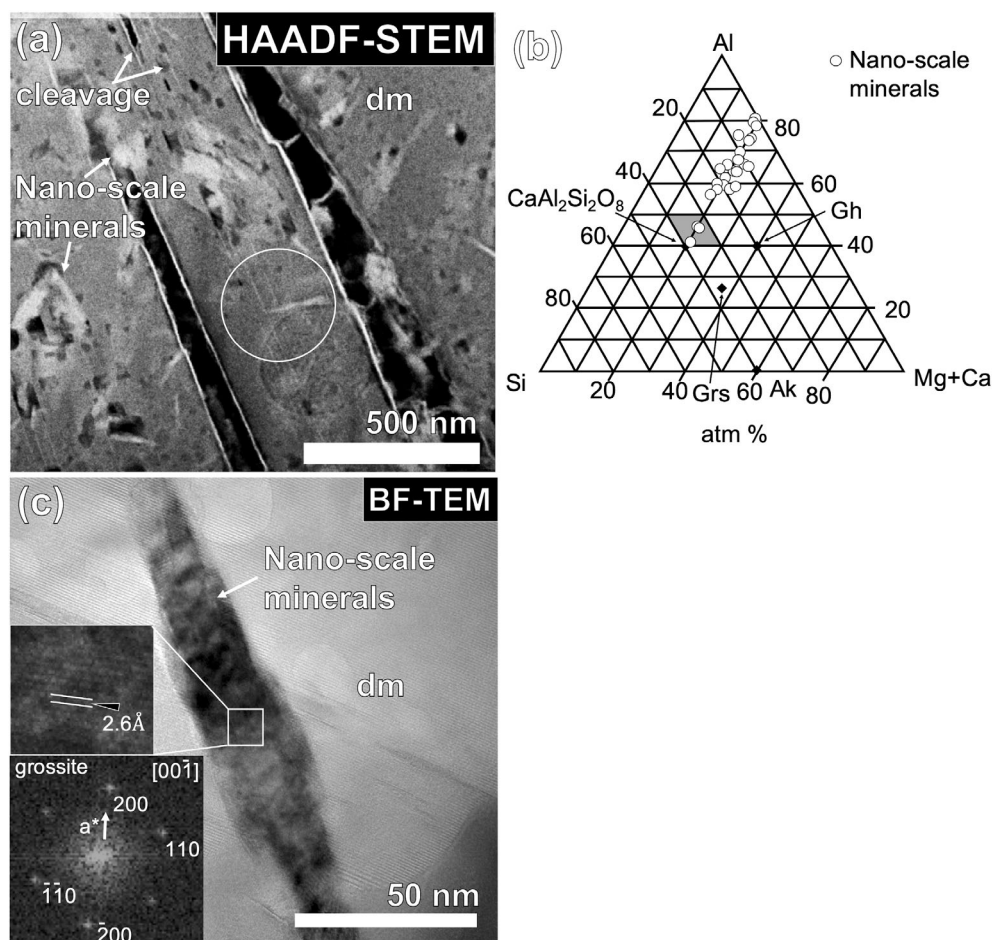


FIGURE 5. Transmission electron microscope (TEM) observations of nano-scale mineral grains in dmisteinbergite. a) High-angle annular dark-field scanning TEM (HAADF-STEM) image of dmisteinbergite (dm) containing nano-scale minerals. The nano-scale minerals occur abundantly and cross the cleavage planes in dmisteinbergite (indicated by circles). b) Focused-beam analyses of the nano-scale minerals in an Al–Si–(Mg + Ca) (atomic%) ternary diagram. Most of the analyses plot along the trend line of compositional variation of dmisteinbergite obtained by electron probe microanalyzer (EPMA)-wavelength dispersive X-ray spectrometer (WDS). c) High-resolution bright-field (BF) TEM image of a nano-scale mineral in dmisteinbergite. The insets are the enlargement and a first Fourier transform (FFT) pattern of the area indicated by a rectangle. The FFT pattern corresponds to the [0 0–1] diffraction pattern of grossite.

DISCUSSION

The Classification of the CAI

It is not difficult to determine the classification of the CAI because (1) many materials in the CAI core were lost during the thin section preparation (see the pore in Figures 1a and 2) and (2) primary melilite was largely replaced by secondary alteration phases. As we discuss later, the melilite in this CAI was replaced by other phases during alteration and the abundance of melilite before alteration was higher than the present abundance. There are anorthites occurring in fine-grained porous assemblages in the CAI. Although primary anorthite which is nebular origin can also occur,

all anorthites in the CAI seem to be asteroidal in origin. Therefore, the abundance of melilite is estimated as ~80 vol% before the alteration. We assumed that the modal abundance of hole part of the CAI is similar to that of the rest of the CAI. In that case, the CAI we examined is classified as compact type A CAI based on the mineralogical and chemical compositional characteristics (Grossmann, 1975; Mason & Taylor, 1982).

Mineralogical Alteration in the CAI

Based on our petrologic and mineralogical observations, we clarified the alteration sequence occurring in the CAI: first grossular replaced melilite

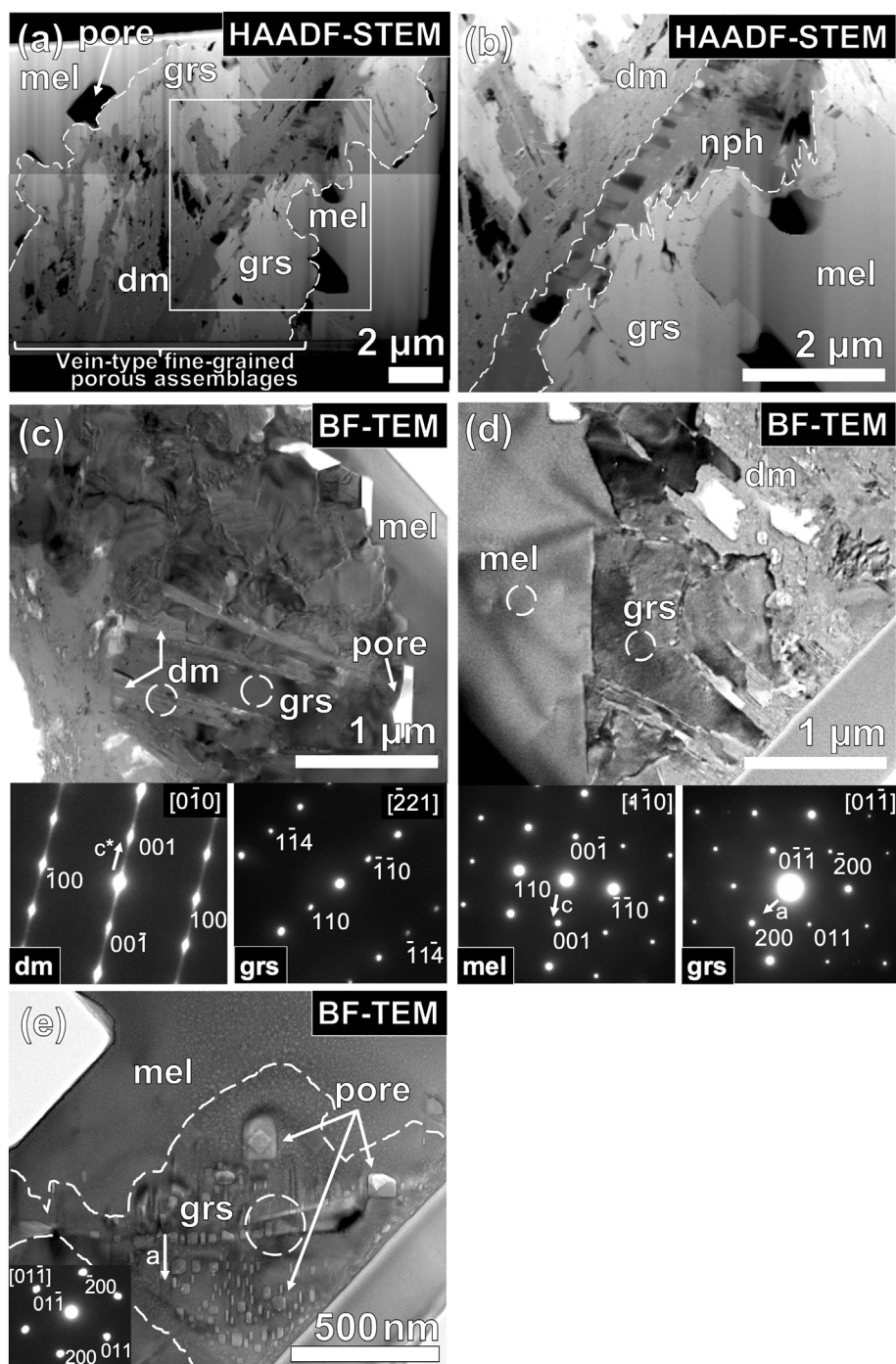


FIGURE 6. Transmission electron microscope (TEM) observations of a vein type fine-grained porous assemblage. a) High-angle annular dark-field scanning TEM (HAADF-STEM) image of a vein-type fine-grained porous aggregate cross cutting a melilite (mel) grain. Dashed lines indicate boundaries between melilite and the assemblage. The vein type porous assemblage consists mainly of grossular (grs), dmisteinbergite (dm), and nepheline (nph). b) Image of boxed area b in (a) showing that the nepheline (indicated by dashed lines) is elongated parallel to the elongation direction of adjacent dmisteinbergite. c) Bright-field (BF) TEM image of boxed area c in (b) showing that a large grossular grain was replaced by lath-shaped dmisteinbergite. Some pores exist at the boundary of melilite and grossular. The insets are selected area electron diffraction (SAED) patterns from the areas indicated by dashed circles. d) BF-TEM image of the linear boundary between melilite and grossular. The insets are SAED patterns from the areas indicated by dashed circles. e) BF-TEM image of grossular containing abundant rectangular shaped nano-pores. The nanopores are elongated parallel to the a -axis of the grossular. The inset is an SAED pattern from the area indicated by a dashed circle.

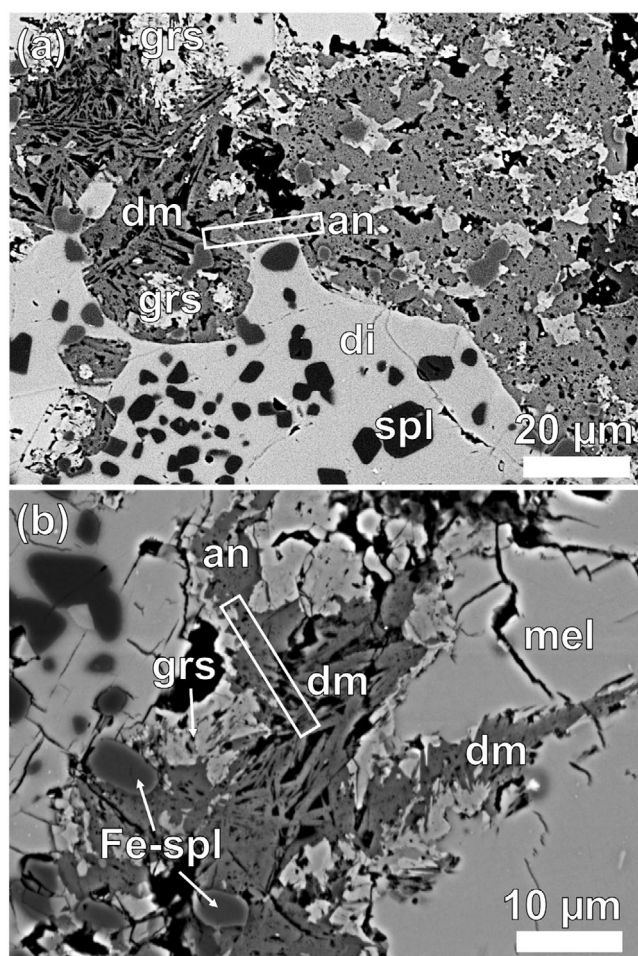
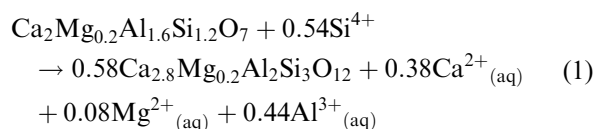


FIGURE 7. Back-scattered electron images of fine-grained porous assemblages. a, b) Images of the areas where dmisteinbergite (dm) and anorthite (an) coexist in fine-grained porous assemblages. Two focused ion beam sections were extracted from the rectangle areas. Transmission electron microscope images of the two sections are shown in Figures 8 and 9.

(Reaction 1) and then dmisteinbergite replaced the grossular (Reaction 2).



In the vein of fine-grained porous assemblages, grossular is always in contact with melilite (Figures 1b, 2b, d and 6a,d). This indicates that the first aqueous alteration reaction is grossular formation from melilite.

Nomura and Miyamoto (1998) reported that the hydrothermal treatment of gehlenite in a high pH fluid at 200–400°C forms a variety of alteration minerals. In their

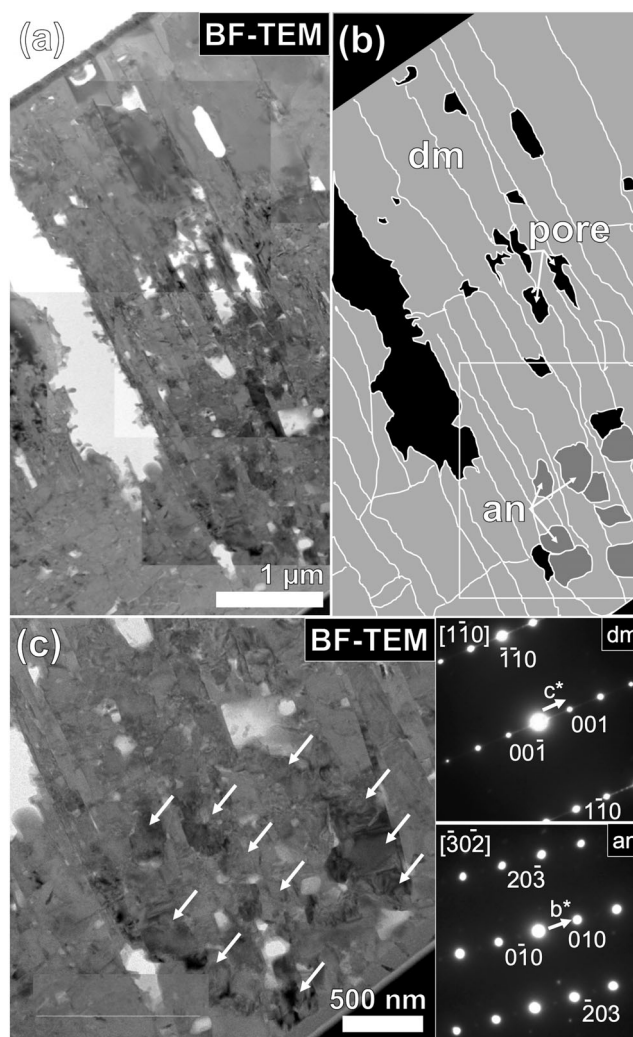


FIGURE 8. Transmission electron microscope (TEM) observations of dmisteinbergite and anorthite. a) Bright field (BF) TEM image of an area containing both dmisteinbergite and anorthite in the focused ion beam section extracted from the rectangle area in Figure 7a. b) Illustration of (a) showing dmisteinbergite (dm; gray color), anorthite (an; dark gray) in direct contact with each other. Perovskite (prv) is also seen. c) BF-TEM image of boxed area c in (b). Anorthite grains are indicated by arrows. The insets are selected area electron diffraction patterns from the areas indicated by dashed circles.

experiments, hydrogrossular forms by the dissolution and precipitation reaction of melilite in an NaOH solution (pH 13–14) at 200–250°C. The chemical composition of hydrogrossular is $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$. They did not report the direct formation of (anhydrous) grossular from melilite. In our observation, no hydrogrossular was found in the Allende CAI studied: only grossular was observed. Therefore, the grossular in the CAI might have formed

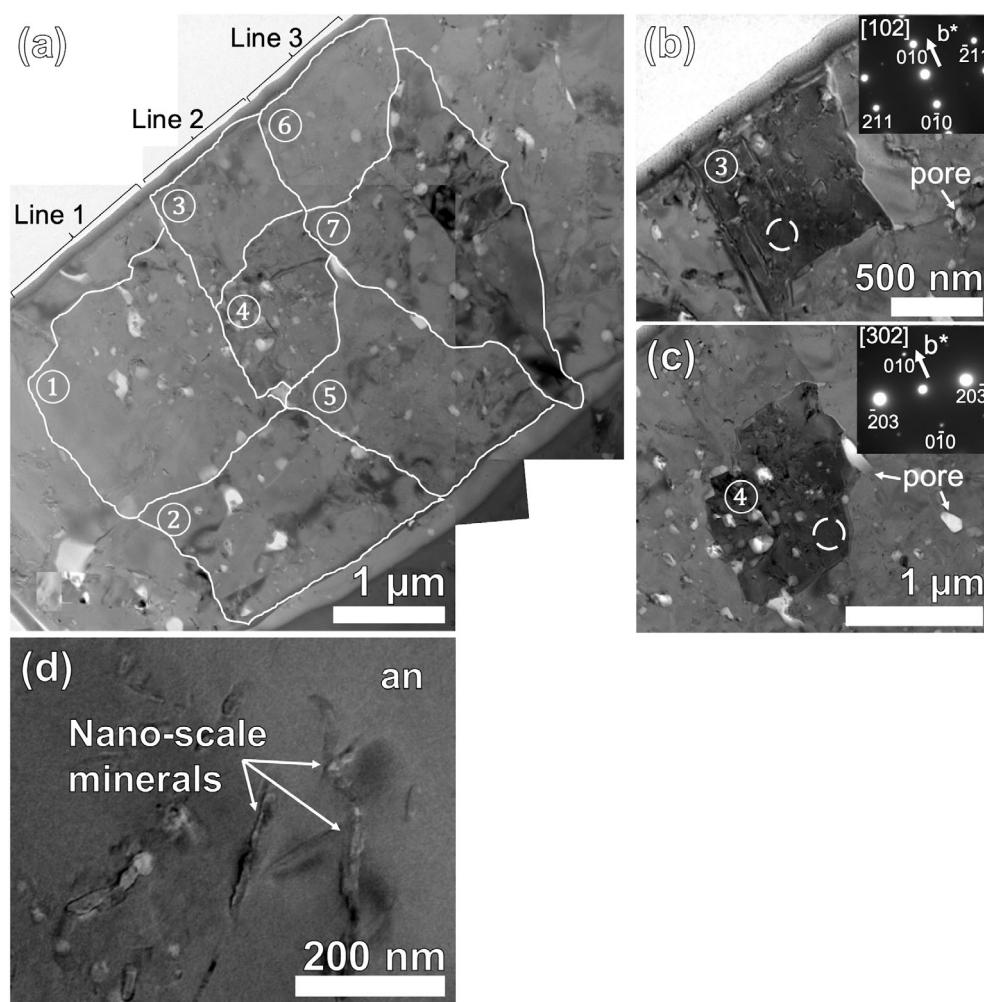
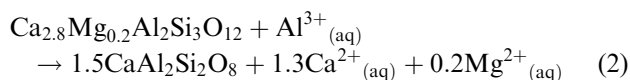


FIGURE 9. Transmission electron microscope (TEM) observations of anorthite. a) Bright field (BF) TEM image of the area containing seven anorthite grains (indicated by 1 to 7) in the focused ion beam section extracted from the rectangle area in Figure 7b. Anorthite crystals make up three parallel lines of long crystals. b), c) BF images of anorthite grains 3 and 4 in (a). The insets are selected area electron diffraction patterns from the areas indicated by dashed circles showing that the b^* axes of the two grains are in the same direction. d) Image of boxed area d in (a) showing that anorthite contains nano-scale acicular minerals.

(1) primarily as hydrogrossular which was then dehydrated to grossular or (2) directly from melilite under conditions that were not achieved in the experiments by Nomura and Miyamoto (1998). We prefer process (1) based on evidence derived from TEM observation as mentioned below although process (2) cannot be ruled out.

We discovered numerous nano-pores (less than 50 nm) parallel to the a -axis of grossular grains in an FIB section (Figure 6e). The occurrence and textures of these nano-pores are similar to those formed by dehydration of hydrous minerals. For instance, dehydration of goethite forms various nano-pores which are also parallel to its crystal orientations (Pomies et al., 1999). The size of

nanopores is less than 50 nm, which is close to the size of nano-pores in grossulars. We suggest that the nanopores in grossular in the CAI might have formed during the dehydration of hydrogrossular and thus the grossular was originally formed as hydrogrossular which was later transformed to grossular by heating. Nomura and Miyamoto (1998) reported that the dehydration of hydrogrossular to grossular occurs at 400–600°C in the experimental heating. During the transition from hydrogrossular to grossular, the crystallographic orientation does not change (Valentina et al., 2015). Therefore, no crystallographic relationship between melilite and hydrogrossular is expected, nor was it found by us (Figure 6d).



The next aqueous alteration product in the CAI is dmisteinbergite. Dmisteinbergite always occurs within/between the grossular crystals in FIB sections (e.g., Figure 6c), which clearly indicates that the dmisteinbergite was formed at the expense of grossular. We did not find a clear crystallographic orientation relationship between grossular and dmisteinbergite (Figure 6c). In dmisteinbergite grains, there are pillar-like pores parallel to the direction of long segments of dmisteinbergite (Figure 4b). Their size is typically 100 nm and occasionally up to 500 nm. It seems that these anisotropic pores (Figures 4b and 8a) are left over from hydrogrossular (Figure 6e). However, the number density of the pores in grossular grains (Figure 6e) is much higher than that in dmisteinbergite and also the pore size in grossular is much smaller. Therefore, pores in dmisteinbergite grains are probably not residual from preexisting grossular. Thus, the pores in dmisteinbergite appear to have been newly formed during dmisteinbergite formation, probably due to the volume decrease (~50 vol%) from hydrogrossular to dmisteinbergite. Borglum et al. (1993) reported hydrothermal experiments in which dmisteinbergite was formed from hydrogrossular. At first, they produced hydrogrossular by the hydrothermal reaction between mono-calcium aluminate (CaAl_2O_4) and SiO_2 in water at 80°C. Next, they raised the temperature to 200–350°C to form the dmisteinbergite from hydrogrossular. Therefore, in the CAI, dmisteinbergite could have formed from hydrogrossular at the same temperature range (200–350°C).

Many of the fine-grained porous assemblages retain residual melilites (Figures 1b,d, 2c,d and 6a–d). This means that reaction (2) must have begun before the completion of reaction (1). This suggests a change in fluid conditions between reactions (1) and (2). As we described above, both hydrogrossular and dmisteinbergite were experimentally produced in the fluid with similar temperatures (about 200–250°C) and pH (pH 13–14) (Borglum et al., 1993; Nomura & Miyamoto, 1998). Therefore, if the Allende CAI was altered continuously at similar conditions, all melilites should have been consumed to make first hydrogrossular and subsequently dmisteinbergite. To retain melilite in the CAI, some other conditions except temperature and pH had changed in the fluid, which would have stopped reaction (1) and started reaction (2). Reaction (2) required abundant SiO_2 in fluids to stabilize the hydrogrossular (Borglum et al., 1993). On the other hand, the level of SiO_2 in the fluids was probably not so high during reaction (1), or else other minerals such as hydrosodalite and/or

nepheline hydrate would have formed instead (Nomura & Miyamoto, 1998). Therefore, we can conclude that the increase in SiO_2 abundance in fluids caused the change from reaction (1) to reaction (2).

The Accessory Reactions (Nano-Scale Mineral Formation in Dmisteinbergite)

Dmisteinbergite contains two kinds of nano-scale minerals; thin minerals in cleavages (Figure 4c) and acicular minerals (Figure 5a,c). The thin minerals are enriched in Mg, but we could not identify the exact mineral species due to its finer crystal size (several nm in width). Nano-scale minerals with very similar occurrence and size (15–50 nm in width) were found within cleavages of dmisteinbergite and identified by Brearley et al. (2014) as a biopyribole. In addition, clintonite and marganite were also identified in the Allende compact type A CAIs (e.g., Keller & Buseck, 1991). Therefore, the thin minerals we found might also be these minerals. The thin minerals occur along (001) the dmisteinbergite (Figure 4c) and therefore they probably formed together. We propose that Mg^{2+} ions were released from hydrogrossular during reaction (2), because dmisteinbergite does not contain Mg, and supplied to the thin minerals that formed.

Detailed TEM observation of the acicular minerals indicates that they are grossite, judging from the chemical composition and the high-resolution TEM imaging (Figure 5). It is known that grossite occurs in CH3, CO3, and Acfer 094 carbonaceous chondrites and is thought to have formed in the solar nebula (Simon et al., 2019). However, these grossite grains are about 10 μm and far larger than the acicular grossite that we observed in the dmisteinbergite (20 nm in width). They crosscut the thin minerals in many places (Figure 5a), which suggests late formation of the grossites. Therefore, we concluded that the grossite is a secondary mineral formed by alteration of the CAI, which shows a clear contrast to grossite of condensation origin.

The Relationship between Dmisteinbergite and Anorthite

Phase Transition from Dmisteinbergite to Anorthite

We investigated the relationship between dmisteinbergite and anorthite by TEM observation in two FIB sections. In the FIB section cut from the box in Figure 7a, dmisteinbergites consist of a set of long, parallel crystals, forming a foliation texture in the (001) direction (Figure 8a,b). Parts of the long crystals seem to have been replaced by small anorthites (Figure 8c). The size of anorthites corresponds to the width of individual dmisteinbergite crystals which are in contact with each anorthite crystal. In addition, anorthite grains show a preferred orientation and the *b*-axis of anorthite grains is parallel to the *c*-axis of dmisteinbergite.

In the FIB section from the boxed area in Figure 7b, seven anorthite crystals show a similar crystallographic orientation and are aligned to the (010) direction, which make three parallel lines of long crystals (Figure 9). The width of the long crystals is about 1.5 μm , similar to that of the dmisteinbergite clusters (Figures 4 and 8). Therefore, the textural similarity between long parallel anorthite crystals and dmisteinbergite crystals suggests that the anorthite formed by replacement of dmisteinbergite. The observation of a contact plane between dmisteinbergite and anorthite (Figure 8c) indicates that they have a common topotactic relationship where (010) of anorthite is parallel to (001) of dmisteinbergite. This relation also supports that anorthite formed from dmisteinbergite. The elongated direction of the long anorthite crystals is (010) (Figure 9). It corresponds to the (001) direction of elongated dmisteinbergite crystals which previously occurred here (Figure 8).

Another line of evidence comes from small associated minerals. Nanometer-sized grossite crystals are dispersed in both anorthites and dmisteinbergites with a similar density (Figures 5 and 9). In addition, small pores parallel to the elongated direction of anorthite (Figure 9b) are similar to those in dmisteinbergite (Figure 8a). All mineralogical and crystallographic evidence taken together, we concluded that the anorthites formed from dmisteinbergites, while preserving a crystallographic orientation relationship. Anorthite/dmisteinbergite areal ratios differ between places, which suggests variable extents of the phase transition.

Possible Triggers for the Phase Transition

What was the trigger for the phase transition from dmisteinbergite to anorthite? It is difficult to determine the trigger due to the lack of previous studies. There are some previous studies about the phase transition of dmisteinbergite above the melting point of dmisteinbergite (1400°C; Abe et al., 1991; Abe & Sunagawa, 1995). However, the CAI studied has not experienced such a high temperature after the formation of anorthite and dmisteinbergite on the parent body. The stability of dmisteinbergite below the melting point was investigated only by Borglum et al. (1993); dmisteinbergite does not change its crystal structure when it is heated at 1000°C in air without water and also does not change when it is heated at 100°C in pure water. As discussed later, the peak metamorphic temperature of the Allende parent body is no more than 750°C (e.g., Krot et al., 2007) and usually considered as 300–600°C (e.g., Bonal et al., 2007; Miura et al., 2020), which is far below 1000°C. Therefore, no phase transition of dmisteinbergite should have taken place. This suggests that the phase transition in the CAI must have occurred in wet conditions at temperatures higher than 100°C.

In the CAI, the extent of alteration degree of melilites varies. Most dmisteinbergites occurred in fine-grained porous assemblages replacing a small part of the coarse melilites (Figure 2c) or a large part of the tiny melilites (Figures 1d and 2a). On the other hand, most anorthites occurred in fine-grained porous assemblages replacing large part of the coarse melilites (Figure 2b). This indicates that the proceeding of alteration caused the phase transition from dmisteinbergite to anorthite. For example, the rates of phase transition of vaterite, a polymorph of CaCO_3 , are strongly affected by fluid conditions (e.g., temperature, pH, cation, and organic matter). Similarly, changes in pH, cation, or organic matter supply from the fluid to the dmisteinbergite might have caused the phase transition to anorthite, although we could not identify which parameter change was responsible for the transition.

Formation of Nepheline

Dmisteinbergite and anorthite are sometimes in contact with nepheline (Figure 2a,b). Nepheline is in contact with dmisteinbergite and has an elongate morphology, similar to the dmisteinbergite (Figures 2a and 6b). Therefore, this nepheline is proposed to have formed from dmisteinbergite. In addition, nepheline that is in contact with anorthite does not have such an elongated texture and rather has an anhedral texture similar to anorthite (Figure 2b). Therefore, we propose that the nepheline in contact with anorthite was formed from anorthite. The presence of two types of nepheline precursors indicates that nepheline formation occurred after the phase transition of dmisteinbergite to anorthite.

Constraints from Allende Parent-Body Alteration on the CAI Alteration Conditions

The Summary of Aqueous Alteration Occurring in the CAI

We constrained a series of aqueous alteration reactions occurring in the Allende CAI (summarized in Figure 10). The main reactions started from reaction (1) (hydrogrossular formation from melilite) followed by reaction (2) (dmisteinbergite formation from hydrogrossular). Biopyribole-like minerals formed at the same time and nano-scale grossites formed after dmisteinbergite. Then, portions of unprotected dmisteinbergite crystals transformed to anorthite. Even after the phase transitions, fluids seem to have been retained in the CAI. Subsequent reactions of anorthite and dmisteinbergite with Na-bearing fluids and heating at higher temperature formed nepheline. Reactions (1) and (2) and nepheline formation have been produced by previous hydrothermal

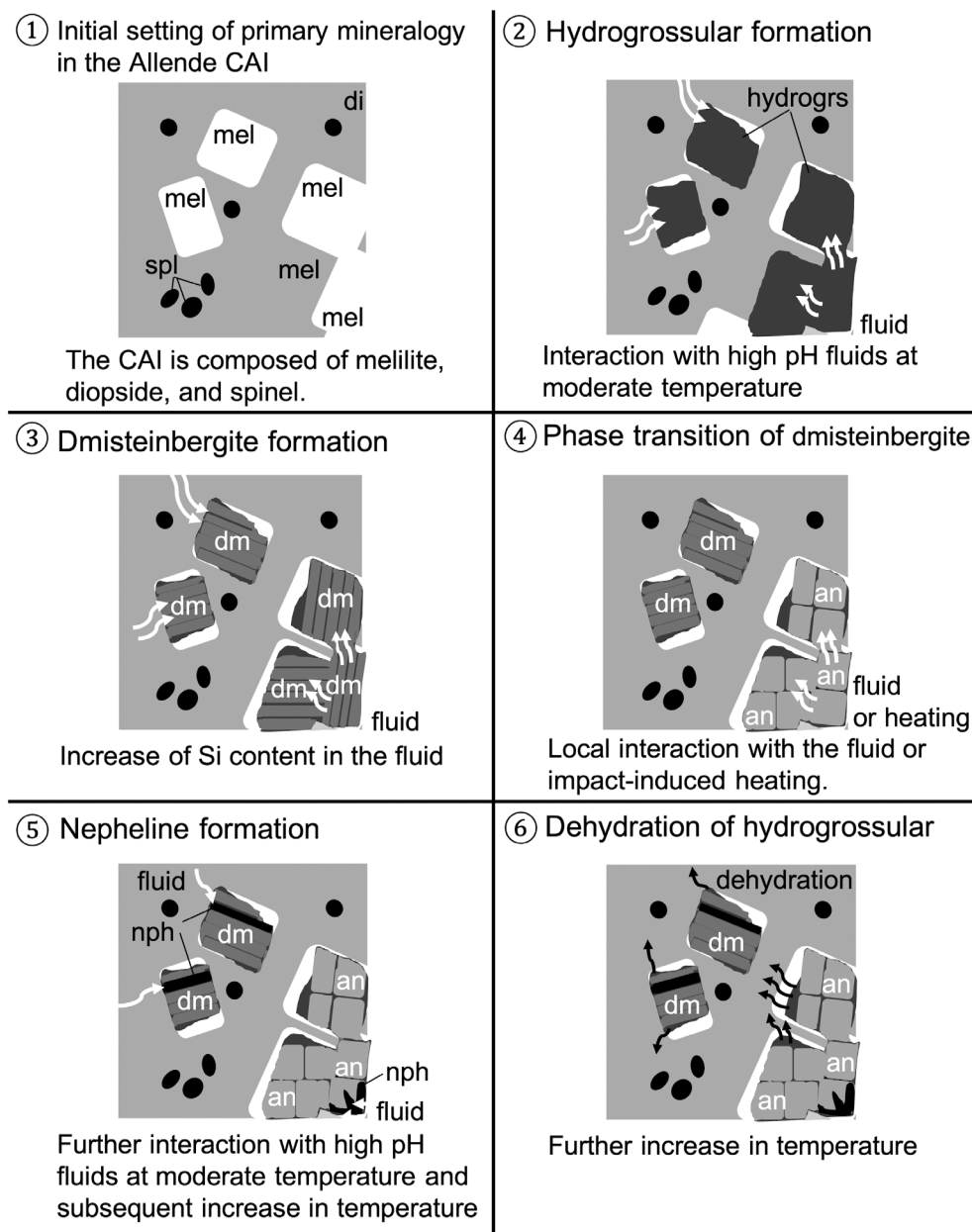


FIGURE 10. Schematic of alteration and metamorphism sequence of the Allende calcium–aluminum-rich inclusion (CAI). The primary minerals in the CAI are mainly melilite (mel), diopside (di), and spinel (spl) (Stage 1). Melilite changed to hydrogrossular (hydrogrs) with high pH fluids at moderate temperature (Stage 2). Dmisteinbergite (dm) formed from hydrogrossular through a reaction with Si-rich fluid (Stage 3). Dmisteinbergite transformed to anorthite (an) locally (Stage 4). Both anorthite and dmisteinbergite were altered to nepheline (nph) by reactions with Na-rich fluids (Stage 5). Increasing temperature caused the dehydration of hydrogrossular to grossular (Stage 6).

experiments (Ichimura et al., 2017). According to these experiments, these reactions occur in high pH fluids (pH 13–14) at about 200–250°C.

Aqueous Alteration and Metasomatism in the Allende Parent Body

The major alteration phases of Allende and other CV_{oxA} chondrites are anhydrous phases rather than

hydrous phases such as phyllosilicates. Nepheline is one of the major anhydrous phases in Allende (Krot, Petaev, Scott, et al., 1998; Krot, Petaev, Zolensky, et al., 1998), which are interpreted to have formed by Fe-alkali-halogen metasomatism within the parent body (e.g., Brearley & Krot, 2013; Krot et al., 1995). Metasomatism changes the chemical composition of minerals and promotes the dissolution of minerals and precipitation of new minerals by

maintaining a constant volume. A good example of metasomatism is the pseudomorphic replacement of a mineral crystal by other minerals with preservation of the former shape and volume (Harlov & Austrheim, 2013). Therefore, the formation of grossular, dmisteinbergite, and nepheline we observed in the CAI also seems to have been typical metasomatism.

Zolotov et al. (2006) calculated that the fayalite in CV chondrites can form at temperatures below 350°C in a narrow range of water/rock ratio (0.06–0.2) with or without aqueous solution. The fayalite number depends on the formation temperature and water/rock ratio. They showed that, considering that the chemical composition of fayalite varies considerably (Fa_{40-100}) in Allende, alteration conditions of fayalite formation in Allende chondrite varied (below 350°C, water/rock ratio 0.06–0.2). The pH of fluids during fayalite formation is strongly alkaline condition (Zolotov et al., 2006).

The evolution from reactions (1) and (2) required significantly increased Si^{4+} abundance in the fluids. In Allende, fayalite plausibly formed in a Si^{4+} -rich fluid although various formation processes of fayalite are suggested (by alteration of opaque phases or olivine, condensation from fluids, or dehydration of phyllosilicates; Krot et al., 1995, 2004). Therefore, our reaction (2) (dmisteinbergite formation from hydrogrossular) could (or should) have occurred at the same time as fayalite formation. The temperature during reaction (2) is estimated at 200–250°C (Borglum et al., 1993). This temperature is consistent with the estimation that the formation temperature of fayalite is close to 350°C (Zolotov et al., 2006). After these reactions, the temperature in the Allende parent body rose further because nepheline formed from zeolite and hydrogrossular dehydrated to grossular at higher temperature (Ichimura et al., 2017; Nomura & Miyamoto, 1998). Therefore, a series of formation reactions of minerals composing the fine-grained porous assemblages occurred when the temperature of the Allende parent body was rising.

Dmisteinbergite Occurrence in Other CV Chondrites

The occurrence of secondary dmisteinbergite was reported only from CV_{oxA} chondrites and not from CV_{red} (Enokido et al., 2014) or CV_{oxB} chondrites (Krot et al., 2019). The CV_{oxA} chondrites experienced higher metamorphic temperatures than CV_{red} chondrites, based on the organic matter (Bonai et al., 2006). The temperature at which the CV_{oxB} chondrites metamorphosed did not exceed 150°C, based on the mineralogy and chemical composition of matrix (Zolensky et al., 1993). Hydrothermal experiments also showed that hydrogrossular and dmisteinbergite formation did not occur at temperatures lower than 200°C. Therefore, the lower temperature which $\text{CV}_{\text{oxB}}/\text{CV}_{\text{red}}$ chondrites

experienced may have prevented the formation of dmisteinbergite.

CONCLUSIONS

We clarified the formation process of various alteration minerals in a compact type A CAI in the Allende CV chondrite. Melilite is the major precursor mineral that was subjected to aqueous alteration. In the first alteration reaction, hydrogrossular was formed from melilite. Although grossular in the present CAI is not hydrated, we found nanopores in the grossular that probably formed by dehydration of preexisting hydrogrossular. Dmisteinbergite was formed from hydrogrossular and, at the same or a later time, nano-scale mineral inclusions were produced in dmisteinbergite. TEM observations demonstrated that anorthite was formed from dmisteinbergite by a phase transition. In a later stage of aqueous alteration, nepheline was formed from both dmisteinbergite and anorthite. Except for the hydrogrossular dehydration and completion of nepheline formation, these reactions occurred at moderate temperature (200–250°C) in high pH fluids (pH 13–14). In the Allende chondrite parent body, these conditions seem to have been achieved as temperatures were rising.

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