

Kushiroite, CaAlAlSiO₆: A new mineral of the pyroxene group from the ALH 85085 CH chondrite, and its genetic significance in refractory inclusions

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ABSTRACT

The new mineral kushiroite, belonging to the pyroxene group, was first discovered in a refractory inclusion in the CH group carbonaceous chondrite ALH 85085. The chemical formula is Ca_{1.008}(Mg_{0.094}Fe_{0.034}Al_{0.878})(Al_{0.921}Si_{1.079})O₆, containing 88% CaAlAlSiO₆ and 12% diopside components. We identified the exact nature of kushiroite by micro-Raman spectroscopy and electron backscatter diffraction (EBSD) analyses. The results are consistent with those obtained from the synthetic CaAlAlSiO₆ pyroxene, thus indicating a monoclinic structure (space group C2/c). Although CaAlAlSiO₆ has been one of the most important hypothetical components of the pyroxene group, it is here for the first time established to be a naturally occurring mineral. We named this pyroxene with >50% CaAlAlSiO₆ component kushiroite, which was recently approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2008-059). The name is for Ikuo Kushiro, Professor Emeritus at the University of Tokyo, Japan, and eminent experimental petrologist, for his outstanding experimental investigations on silicate systems involving the Ca-Tschermak component. There is no obvious evidence for impact in this inclusion. We suggest that metastable crystallization of this pyroxene took place from refractory melts in the solar nebula. Coexisting grossite-bearing refractory inclusions in the type specimen ALH 85085 show ²⁶Mg excesses with inferred initial ²⁶Al-²⁷Al ratios between 2.1 × 10⁻⁶ to 3.9 × 10⁻⁵, providing evidence that condensation, melting, and crystallization took place in the solar nebula when ²⁶Al was still extant.

Keywords: Kushiroite, pyroxene, Ca-Tschermak component, refractory inclusion, CH chondrite

INTRODUCTION

Pyroxene is one of the most common rock-forming minerals in igneous and metamorphic rocks, terrestrial and extraterrestrial. The pyroxene group has diverse members, such as enstatite, diopside, and jadeite. These names have been officially accepted by the pyroxene nomenclature committee (Morimoto et al. 1988). On the other hand, diopsidic pyroxene in many terrestrial rocks and meteorites commonly contains Al₂O₃, and the mineral is traditionally called fassaite, although this name is only unofficially tolerated. Such pyroxene includes the hypothetical Ca-Tschermak (hereafter CaTs), CaAlAlSiO₆, component. However, the end-member phase has not been reported from any natural sample, and Morimoto et al. (1988) proposed that aluminous pyroxene should be called “aluminian diopside.”

Although pyroxene with >50% CaTs component has been rarely reported from terrestrial rocks (Pascal et al. 2005), “aluminian diopside” is commonly encountered in refractory inclusions (Ca-Al-rich inclusions) in carbonaceous chondrites (e.g., Mason 1974). In particular, it often contains >30 wt% Al₂O₃, showing extreme enrichment in CaTs component, in some CH chondrites (Kimura et al. 1993; Weber and Bischoff 1994; Krot

et al. 1999, 2006; Petaev et al. 2001), and rarely in CV, CO, and CM chondrites (Grossman and Steele 1976; Simon et al. 1998, 2001). However, the nature of these pyroxenes has not been characterized in detail because of their tiny grain size.

Here we document the exact mineralogical and crystallographic nature of the CaTs-pyroxene we previously discovered in the CH chondrite ALH 85085 (Kimura et al. 1993). Kimura et al. (2008) reported concise results in an abstract. This mineral was recently approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association as a new mineral with the name kushiroite, on January 5, 2009 (IMA2008-059). The name is in honor of Ikuo Kushiro, for his seminal contributions to experimental petrology and mineralogy, including characterization of CaTs-bearing systems, planetary science, and meteoritics.

SAMPLE AND EXPERIMENTAL METHODS

We investigated a polished thin section of ALH 85085 (section no. 27). The type specimen of ALH 85085 is stored at the Lyndon B. Johnson Space Center, National Aeronautics and Space Administration in Houston, Texas.

The fine texture of kushiroite was investigated using a field emission-scanning electron microscope (FE-SEM), JEOL JSM-71010, at Tohoku University in Sendai, Japan. Accelerating voltage and electron-beam current were 15 kV and ~1 nA, respectively. Quantitative mineral analyses were conducted at the Ibaraki University in Mito, Japan, using JEOL 733 electron-probe microanalyzer (EPMA).

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Operating conditions were 15 kV excitation voltage and 5 nA sample current, with a 2 μm focused beam. Matrix corrections were carried out using the Bence-Albee correction method (Bence and Albee 1968).

We identified the crystalline nature of kushiroite by using a laser micro-Raman spectrometer, JASCO NRS-2000 (Ar⁺ laser, 514.5 and 488.0 nm lines) at the Tohoku University. The laser power was 12–20 mW, and the laser beam was $\sim 1 \mu\text{m}$ in diameter. The crystalline nature of kushiroite was also investigated by a Thermo Noran Phase ID electron backscatter diffraction (EBSD) system installed on the Hitachi S-4500 FE-SEM at the University of Tokyo. The accelerating voltage of the incident beam was 20 kV, and the beam current was 2–3 nA. Calculations of Kikuchi patterns and analyses of the observed EBSD patterns were performed using a program by Kogure (2003). Mikouchi et al. (2009) reported the detailed analytical conditions for EBSD used here.

PETROGRAPHY AND MINERALOGY

ALH 85085 contains abundant Ca-Al-rich refractory inclusions (e.g., Grossman et al. 1988; Weisberg et al. 1988). Kimura et al. (1993) reported various types of inclusions in ALH 85085 and their genetic relationships. One of them, a spherical inclusion (no. 186), is $\sim 15 \mu\text{m}$ in diameter and consists only of grossite and pyroxene (Fig. 1). Two anhedral grains of grossite are located in the center of the inclusion, and up to four grains of kushiroite form along with another pyroxene, a mantle that has a maximum width of $\sim 6 \mu\text{m}$. The largest kushiroite grain (on the upper left of Fig. 1) is 9 μm long. Kushiroite is accompanied by two sickle-shaped, Ti-rich pyroxenes, which entirely engulf one grossite fragment (Fig. 1). The Ti-rich pyroxene is 2 μm in maximum width, and the boundary between kushiroite and Ti-rich pyroxene is not distinct.

Table 1 shows the chemistry of minerals in the no. 186 inclusion. Microprobe analyses of 5 points on kushiroite indicate a narrow composition range: 28.8–29.9 wt% SiO₂, 40.3–42.4 Al₂O₃, 1.1–1.2 FeO, 1.4–2.0 MgO, and 25.1–26.2 CaO. Kushiroite contains very low TiO₂ contents (<0.2%). We did not detect Cr, V, Ni, Mn, Zr, Sc, or Na in it. The average composition of kushiroite yields the formula Ca_{1.008}(Mg_{0.094}Fe_{0.034}Al_{0.878})(Al_{0.921}Si_{1.079})O₆, which indicates 88% CaTs with 12% diopside component. Wood and Henderson (1978) reported non-stoichiometric synthetic

CaTs phases. In comparison, kushiroite reported here has stoichiometric pyroxene composition.

The coexisting Ti-rich pyroxene (Fig. 1) contains 25.0–25.3 wt% SiO₂, 8.9–10.3 TiO₂, 34.8–37.8 Al₂O₃, 1.0–1.5 FeO, 1.7–2.0 MgO, and 23.7–25.5 CaO, which seems to indicate the presence of Ti³⁺, based on charge balance for stoichiometry as pyroxene. The formula is: Ca_{1.000}(Mg_{0.105}Fe_{0.041}Ti_{0.190}⁴⁺Ti_{0.084}³⁺Al_{0.579})(Al_{1.044}Si_{0.956})O₆. This pyroxene contains 52% CaTs, 20% diopside, 19% CaTi⁴⁺Al₂O₆, and 9% CaTi³⁺AlSiO₆ components, and it is hence a titanian kushiroite. This Ti-variety of kushiroite was not previously reported in any kushiroite-bearing CAI. Grossite has an almost stoichiometric composition as CaAl₄O₇.

Figure 2 shows the Raman spectrum of kushiroite, with main

TABLE 1. Average compositions of kushiroite and coexisting minerals in refractory inclusion no. 186 of the CH chondrite ALH85085

No. of analysis	Kushiroite 5	Titanian kushiroite 2	Grossite 5
SiO ₂	29.28 (0.46)	25.16	0.92 (0.44)
TiO ₂	0.10 (0.08)	9.59	0.17 (0.12)
Al ₂ O ₃	41.41 (0.88)	36.27	75.82 (1.38)
Cr ₂ O ₃	b.d.	b.d.	b.d.
FeO	1.11 (0.06)	1.29	0.79 (0.05)
MnO	b.d.	b.d.	b.d.
MgO	1.71 (0.25)	1.85	0.40 (0.08)
CaO	25.53 (0.44)	24.58	19.90 (0.92)
Na ₂ O	b.d.	b.d.	b.d.
K ₂ O	b.d.	b.d.	b.d.
Total	99.14	98.74	97.68
O	6	6	7
Si	1.079	0.949	0.041
Ti	0.003	0.272	0.006
Al	1.799	1.613	3.940
Cr	b.d.	b.d.	b.d.
Fe	0.034	0.041	0.029
Mn	b.d.	b.d.	b.d.
Mg	0.094	0.104	0.026
Ca	1.008	0.994	0.940
Na	b.d.	b.d.	b.d.
K	b.d.	b.d.	b.d.
Total	4.017	3.973	4.983

Notes: b.d. = below detection limits (3 σ , in wt%), 0.09 for Cr₂O₃, 0.15 for MnO, 0.04 for Na₂O, and 0.07 for K₂O. Standard deviation (1 σ) in parentheses.

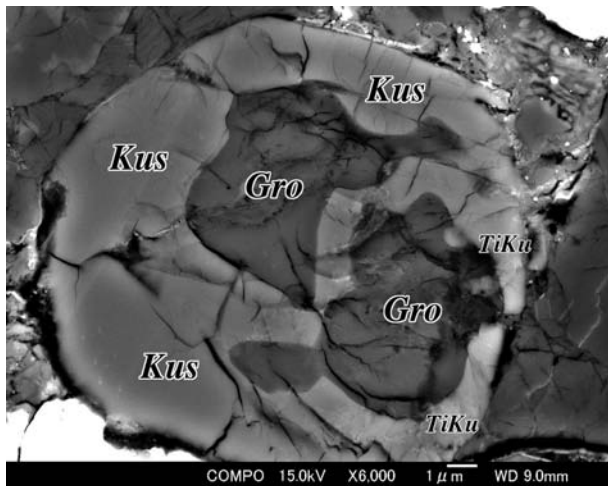


FIGURE 1. Back-scattered electron image of refractory inclusion no. 186 in ALH 85085. Kushiroite (Kus) surrounds grossite (Gro). A small area of titanian kushiroite (TiKu) is also observed in close association with kushiroite, although the boundary between the two is not distinct.

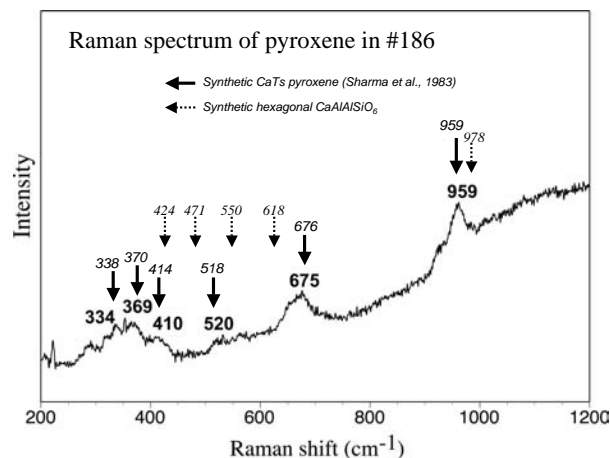


FIGURE 2. Raman spectrum of kushiroite. Raman bands of synthetic CaTs (solid arrows) (Sharma et al. 1983) and synthetic hexagonal CaAlAlSiO₆ phase (dotted arrows) are also shown. The former peaks are consistent with those of kushiroite.

bands at 959, 675, 369, and 334 cm⁻¹, consistent with those of synthetic CaTs pyroxene (Sharma et al. 1983). Kirkpatrick and Steele (1973) also synthesized a hexagonal unknown CaAlAlSiO₆ phase. We also synthesized this phase under the same conditions as Kirkpatrick and Steele (1973), yet the Raman spectrum is inconsistent with those of kushiroite and synthetic CaTs (Fig. 2). The spectrum indicates a single phase, kushiroite, without any overlapping Raman bands from the coexisting phases in the inclusion and the phases surrounding the inclusion.

We determined the crystalline nature of kushiroite by using the EBSD technique, and compared the obtained EBSD patterns with those of several known pyroxene structures. The patterns obtained (Fig. 3a) convincingly match those of synthetic monoclinic CaAlAlSiO₆ pyroxene with *C2/c* type structure (Fig. 3b) (Okamura et al. 1974). The patterns are evidently inconsistent with those of the synthetic hexagonal CaAlAlSiO₆ phase (Figs. 3c and 3d). The obtained EBSD patterns from the no. 186 inclusion showed different orientations on a scale of several micrometers. Therefore, it is composed of several kushiroite grains of different orientations.

DISCUSSION

Combining all the above results, we can unambiguously exclude the possibility that the natural kushiroite is the hexagonal CaAlAlSiO₆ phase, any other Ca-Al-silicate, or a fine-grained aggregate of breakdown products (Simon et al. 2001). It is evident from the Raman and EBSD investigations we conducted, that kushiroite has the same monoclinic structure as synthetic CaAlAlSiO₆ pyroxene (space group *C2/c*). Previously determined cell parameters for synthetic CaTs are $a = 9.609(3)$, $b = 8.652(2)$, and $c = 5.274(2)$ Å (Okamura et al. 1974).

Our study demonstrates, for the first time, the occurrence

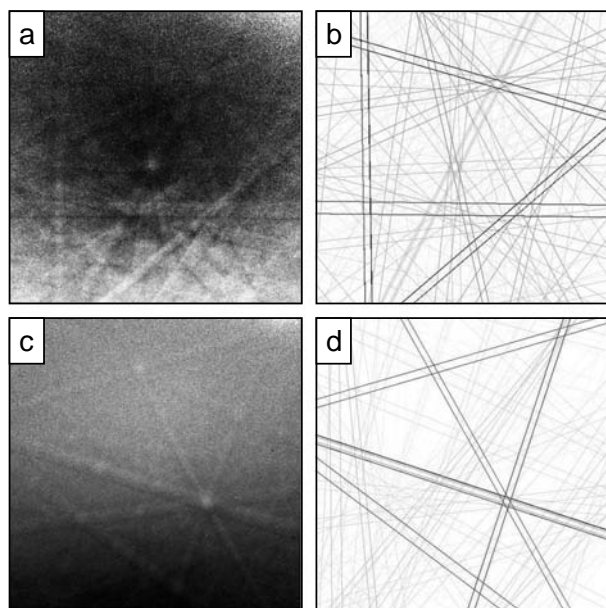


FIGURE 3. Observed (a) and calculated (b) EBSD patterns of kushiroite, and those (c and d) of hexagonal CaAlAlSiO₆, respectively. The patterns of kushiroite match well those of synthetic monoclinic CaAlAlSiO₆ pyroxene with *C2/c* structure.

of CaTs-pyroxene as a natural mineral in a refractory inclusion in a carbonaceous chondrite. Hence, CaTs is no longer a hypothetical component, but a real naturally occurring mineral, kushiroite. Diopside and CaTs make a complete solid solution (Hijikata 1973). The kushiroite grains studied here have a CaTs component much higher than 50 mol% in the diopside-CaTs solid solution. We proposed that this new natural pyroxene with >50% CaTs component should be called kushiroite, not aluminian diopside. This is the same nomenclature scheme as for esseneite with >50% CaFe³⁺AlSiO₆ component (Cosca and Peacor 1987). Pyroxenes reported from refractory inclusions of other carbonaceous chondrites that are highly enriched in Al₂O₃ with similar compositions as our new mineral must therefore be called kushiroite, although it is rigorously necessary to identify their nature as such by Raman and/or EBSD techniques.

Kushiroite, along with other Ca-Al-rich phases, is encountered in refractory inclusions, suggesting its formation in the early solar nebula. However, the formational mechanism of kushiroite is not clear. There are several possibilities for how kushiroite formed: (1) condensation from the nebular gas (Petaev et al. 2001); (2) decomposition of gehlenite (Simon et al. 2001); (3) crystallization under high-pressure conditions; and (4) metastable crystallization from refractory melt (Kimura et al. 1993; Simon et al. 1998; Krot et al. 1999).

Simon et al. (2001) proposed that kushiroite in a fluffy Type A inclusion of the Allende meteorite may be a decomposition product of gehlenite. Petaev et al. (2001) suggested that the irregular shape and chemical zonation of a possible kushiroite-bearing inclusion in the CH chondrite NWA 470 is consistent with a nebular condensation origin for kushiroite. However, the occurrence of kushiroite in spherical inclusions and the igneous texture (Simon et al. 1998; Krot et al. 1999, 2006; this work) are inconsistent with the condensation or decomposition origin, and suggest that it is the product of crystallization from a refractory melt, as previously suggested (Kimura et al. 1993; Simon et al. 1998; Krot et al. 1999).

Kimura et al. (1993) reported that some grossite-bearing inclusions in ALH 85085 show ²⁶Mg excesses, resulting from decay of ²⁶Al with (²⁶Al/²⁷Al)₀ between 2.1 × 10⁻⁶ and 3.9 × 10⁻⁵. This was the first report of excess in radiogenic ²⁶Mg in grossite-bearing inclusions. We have refrained from conducting any ion microprobe analysis of kushiroite to check for the existence of excess radiogenic ²⁶Mg because we wanted to keep the pristine nature of the specimen intact. We did not want to induce any physical damage or overprinting of the oxygen isotopic composition of the kushiroite type specimen (no. 186 inclusion) from the ¹⁶O primary ion beam of the SIMS. However, we measured the ²⁶Mg-²⁶Al systematics of grossite in other refractory inclusions in the type specimen. SIMS measurements of grossite in other coexisting refractory inclusions indicated the presence of excess of ²⁶Mg with an inferred initial ²⁶Al-²⁷Al ratio of 2.1 × 10⁻⁶ to 3.9 × 10⁻⁵, thus confirming that formation and melting took place when ²⁶Al (t_{1/2} = 750 000 years) was still extant in the solar nebula. This indicates that grossite- and kushiroite-bearing inclusions may have formed in the earliest stage in the solar nebula and probably melted when ²⁶Al was still extant.

CaTs is stable under high-pressure conditions, such as >11 kbar (1.1 GPa) at 1020 °C, and breaks down to gehlenite,

anorthite, and corundum at atmospheric pressure (Hays 1966; Hijikata and Yagi 1967). Although some constituents of ALH 85085 experienced heterogeneous shock effects (Grossman et al. 1988; Scott 1988; Brearley 1997), this chondrite and in particular inclusion no. 186 escaped heavy shock on the whole. No high-pressure phases have been discovered in ALH 85085. Other carbonaceous chondrites containing kushiroite seldom experienced shock metamorphism, with shock degrees typically S1 to S2 (Koblitz 2003). Kushiroite is also encountered in a fragile fluffy Type A inclusion (Simon et al. 2001). These observations exclude the crystallization of kushiroite under high-pressure conditions in the parent bodies.

We suggest that the metastable crystallization from a melt under low-pressure conditions in the solar nebula is the most plausible explanation for the formation of kushiroite. This is consistent with the occurrence and texture of kushiroite observed in refractory inclusions.

The discovery of kushiroite is significant for identifying an important new naturally occurring member of the pyroxene group. Recently Ma and Rossman (2009) reported the finding of a Sc-rich pyroxene (Davis 1984; El Goresy et al. 2002; Lin et al. 2003), declared it a new mineral from the CV chondrite Allende, and named it davisite CaScAlSiO₆. Thus, meteorites are important material for study of pyroxene mineralogy and exploration for new species of this group. Another significant result of our discovery is that the finding can be used to elucidate details of physical conditions of the solar nebula in its earliest stages.

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