

**Grossmanite, Davisite, and Kushiroite: Three Newly-approved Diopside-Group Clinopyroxenes in CAIs**

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**Introduction:** Grossmanite ( $\text{CaTi}^{3+}\text{AlSiO}_6$ ), davisite ( $\text{CaScAlSiO}_6$ ) and kushiroite ( $\text{CaAlAlSiO}_6$ ) are newly-approved diopside group clinopyroxenes (cpx) in which trivalent cations dominate the M1 site with charge-balancing Al occupying the tetrahedral Si site. We named grossmanite and davisite and described their type occurrences in the CV3 Allende chondrite [1,2]. Kimura et al. [3] named kushiroite and reported type materials from the CH chondrite ALH 85085. Here, we outline simple procedures by which the electron probe analysis of a calcic cpx can be assigned the correct mineral name and then illustrate the usage with examples of each of the new minerals from CAIs.

**Mineral Names:** The newly approved dominant-valency rule for new minerals [4] as applied to diopside group cpx essentially states that mineral names follow the dominant valence in the M1 site and then the dominant cation of that valence. For cpx in refractory inclusions, naming the mineral based on an electron probe analysis proceeds by first calculating  $\text{Ti}^{3+}/\text{Ti}^{4+}$ , which allows the mineral formula to be constructed, and then considering the valence of cations occupying the M1 site. If there are more trivalent cations than either divalent or quadrivalent cations, then the mineral is grossmanite ( $\text{Ti}^{3+}$ ), davisite ( $\text{Sc}^{3+}$ ), or kushiroite ( $\text{Al}^{3+}$ ) depending on which trivalent cation is the most common one occupying M1 (Fig. 1). If divalent cations on M1 exceed both trivalent and quadrivalent cations, then the pyroxene is diopside ( $\text{Mg}^{2+}$ ) or hedenbergite ( $\text{Fe}^{2+}$ ) depending on whether  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  is the most common of the divalent cations. Most coarse-grained “fassaite” in type B CAIs are Ti-Al-rich diopsides according to this nomenclature. Although  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  often occur in significant concentrations in CAI cpx, they invariably sum on M1 to less than one or both of trivalent and divalent cations. Neither  $\text{Ti}^{4+}$  nor  $\text{Zr}^{4+}$  end-members have been named as minerals although they are legitimate for describing composition.

The term “fassaite” is commonly used to describe Ti-bearing and Al-rich cpx in chondrites. “Fassaite” was officially discredited in 1988 by the IMA-CNMNC [5] but this was widely ignored in the meteoritics community because the official term subsilicic titanian aluminian pyroxene proved unpalatable. In the current convention, most run-of-the-mill cpx in type B-C CAIs are Ti-Al-rich diopsides. Fassaite remains a convenient slang term that shouldn't be used.

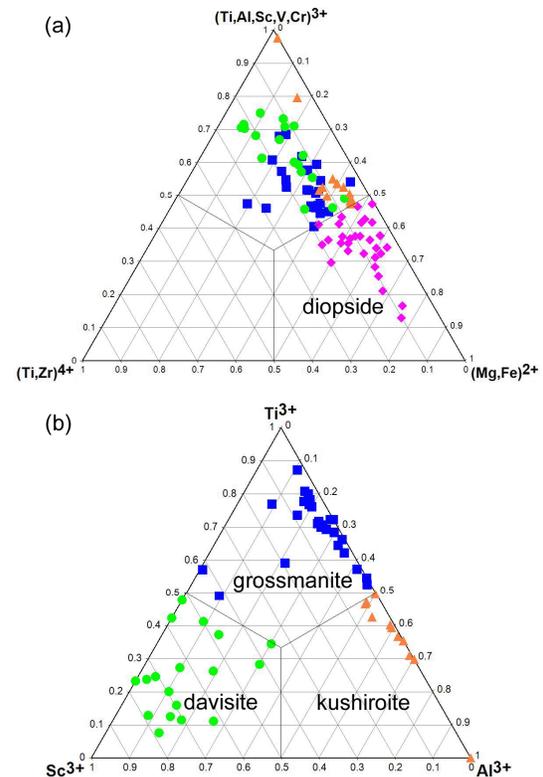


Fig. 1. (a) Molar ternary diagram of three cation groups in the M1 site from clinopyroxenes in CAIs; (b) normalized ternary diagram of  $\text{Ti}^{3+}$ - $\text{Sc}^{3+}$ - $\text{Al}^{3+}$  from the cpx where the trivalent cations are dominant in the M1 site. Square: grossmanite; circle: davisite; triangle: kushiroite; diamond: Ti-rich diopside. This is a replot from [1] with new and literature data.

**Analytical Techniques:** We conducted nano-mineralogy investigations emphasizing trivalent cation dominated diopside-group cpx in meteoritic inclusions. Electron-microprobe and FE-SEM were used for backscatter electron (BSE) imaging and elemental analysis. Electron-backscatter diffraction (EBSD) and Raman were used for single-crystal structure determination.

**Grossmanite:** This mineral is common in Allende fluffy (FTA) and compact (CTA) type A CAIs and also observed in the mantles of type B1s with a general formula  $\text{Ca}(\text{Ti}^{3+}, \text{Mg}, \text{Ti}^{4+}, \text{Al}, \text{Sc})(\text{Al}, \text{Si})_2\text{O}_6$ . Previously described Ti-rich “fassaite” (16-18 wt% Ti as  $\text{TiO}_2$ ) [e.g., 6,7,8] are all grossmanite. The lower bound on Ti content for grossmanites is fuzzy because of the inter-

play among multiple cations in M1 but grossmanites are generally restricted to  $>10$  wt% Ti as  $\text{TiO}_2$ .

Grossmanite often occurs in CAIs along with spinel (sp) and perovskite (pv) in melilite (mel). The example shown in Fig. 2 is taken from the outermost portion of the melilite-rich mantle of a type B1 CAI (in-board of the Wark-Lovering rim). This grossmanite has a formula of  $\text{Ca}_{1.01}[(\text{Ti}^{3+}_{0.28}\text{Al}_{0.16}\text{Sc}_{0.01}\text{V}_{0.01})_{\Sigma 0.46}(\text{Ti}^{4+}_{0.28}\text{Zr}_{0.01})\text{Mg}_{0.25}]_{\Sigma 0.98}(\text{Al}_{1.01}\text{Si}_{0.99})_{\Sigma 2.00}\text{O}_6$ . These grains may have crystallized in residual melt pockets formed as growing mel crystals swept over sp grains or are partially dissolved relicts.

Grossmanite is named in honor of Lawrence Grossman at the University of Chicago.

**Davisite:** We observed three ultra-refractory inclusions containing davisite (10 – 16 wt%  $\text{Sc}_2\text{O}_3$ ) as a new refractory mineral in Allende. Davisite (type-material) occurs as a fine-grained aggregate with sp and REE-rich pv in an ultra-refractory inclusion fragment (Fig. 3), with formula

$\text{Ca}_{0.99}(\text{Sc}_{0.50}\text{Mg}_{0.17}\text{Ti}^{3+}_{0.15}\text{Ti}^{4+}_{0.11}\text{Zr}_{0.04}\text{V}_{0.02}\text{Y}_{0.01}\text{Fe}^{2+}_{0.01})_{\Sigma 1.01}(\text{Si}_{1.03}\text{Al}_{0.97})_{\Sigma 2.00}\text{O}_6$ . The inclusion mineralogy is characterized by high refractory and rare earth elements enriched pv and davisite. The inclusion likely formed through high temperature condensation/evaporation in the solar nebula, possibly followed by partial melting and crystallization. Davisite was also identified as the dominant phase in ultra-refractory domains within an amoeboid olivine aggregate and in a fine-grained inclusion where the ultra-refractory domains likely formed earlier in the solar nebula. Previously reported Sc-rich “fassaite” (13-16 wt%  $\text{Sc}_2\text{O}_3$ ) from four CAIs [e.g., 9,10] are davisite.

Davisite is named in honor of Andrew M. Davis at the University of Chicago.

**Kushiroite:** Kushiroite is the name applied to the Ca-Tschermak’s molecule,  $\text{CaAlAlSiO}_6$ . Type materials described by Kimura et al. [3] form rims on aluminous phases grossite and/or hibonite and have ~41 wt%  $\text{Al}_2\text{O}_3$ . The most Al-rich cpx’s in type B1s (20-22 wt%  $\text{Al}_2\text{O}_3$ ) are also consistent with kushiroite.

Essentially pure end-member kushiroite was identified as irregular grains in grossular alteration after mel from an Allende FTA [11,12]. This kushiroite has the highest CaTs component yet reported in a natural cpx with 46 wt%  $\text{Al}_2\text{O}_3$ , 97 mol% Al in the M1 site, and a formula of  $\text{Ca}_{1.02}(\text{Al}_{0.97}\text{Fe}_{0.01}\text{Mg}_{0.01})_{\Sigma 0.99}(\text{Si}_{1.00}\text{Al}_{1.00})_{\Sigma 2.00}\text{O}_6$ . It seems likely that this is an alteration phase.

Kushiroite was named by [3] in honor of the well known igneous petrologist Ikuo Kushiro.

**Discussion:** Based on data from this study and the literature (e.g., Fig. 1), there are likely complete solid solutions between grossmanite and either davisite or kushiroite in CAIs. An apparent gap between kushi-

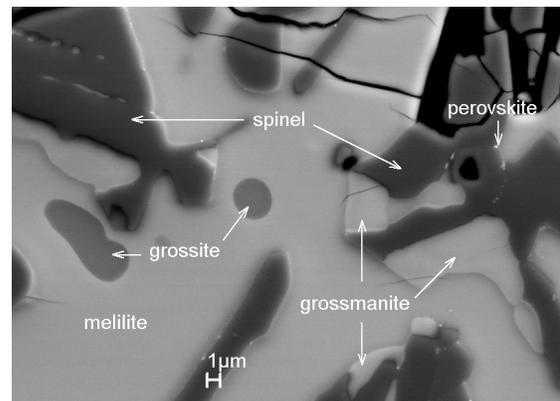


Fig. 2. BSE image of grossmanite in an Allende Type B1 CAI in USNM 7555.

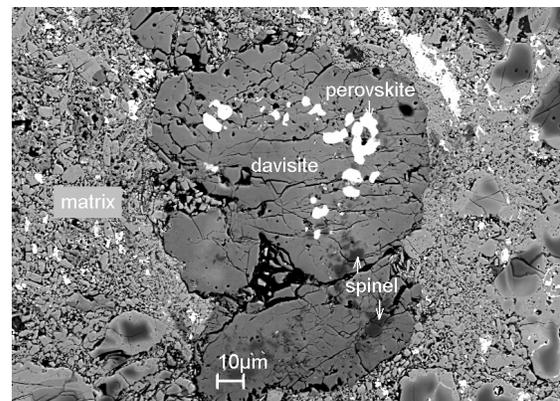


Fig. 3. BSE image of davisite (type-material) in an Allende ultra-refractory fragment in USNM 7555.

roite and davisite may reflect the bulk compositions of systems accessed by CAIs. In general, CAI bulk compositions are too V-, Cr-, REE-poor for trivalent dominated cpx end-members like  $\text{CaVAISiO}_6$  but it is possible under the current rules for naming minerals that a  $\text{Ti}^{4+}$  dominant phase occurs, although without solid solution all the way to the end-member  $\text{CaTi}^{4+}\text{Al}_2\text{O}_6$  due to energetic penalties associated with Al in adjacent tetrahedral sites.

**References:** [1] Ma C. and Rossman G.R. (2009) *Am Min* 94, 1491. [2] Ma C. and Rossman G.R. (2009) *Am Min* 94, 845. [3] Kimura M. et al. (2009) *Am Min* 94, 1479. [4] Hatert F. and Burke E.A.J. (2008) *Can Min* 46, 717. [5] Morimoto N. et al. (1988) *Am Min* 73, 1123. [6] Dowty E. and Clark J.R. (1973) *Am Min* 58, 230. [7] Fuchs L.H. (1971) *Am Min* 56, 2053. [8] Simon S.B. et al. (1999) *GCA* 63, 1233. [9] Davis A.M. (1984) *Meteoritics* 19, 214. [10] El Goresy et al. (2002) *GCA* 66, 1459. [11] Simon S.B. et al. (2001) *Meteoritics & Planet Sci* 36, 331. [12] Ma C. et al. (2009) *Am Min* 94, 1483.