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LETTER

Davisite, $CaScAlSiO_6$, a new pyroxene from the Allende meteorite

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ABSTRACT

Davisite, ideally $CaScAlSiO_6$, is a new member of the Ca clinopyroxene group, where Sc^{3+} is dominant in the M1 site. It occurs as micro-sized crystals along with perovskite and spinel in an ultra-refractory inclusion from the Allende meteorite. The mean chemical composition determined by electron microprobe analysis is (wt%) SiO_2 26.24, CaO 23.55, Al_2O_3 21.05, Sc_2O_3 14.70, TiO_2 (total) 8.66, MgO 2.82, ZrO_2 2.00, Y_2O_3 0.56, V_2O_3 0.55, FeO 0.30, Dy_2O_3 0.27, Gd_2O_3 0.13, Er_2O_3 0.08, sum 100.91. Its empirical formula calculated on the basis of 6 O atoms is $Ca_{0.99}(Sc_{0.50}Ti^{3+}_{0.16}Mg_{0.16}Ti^{4+}_{0.10}Zr_{0.04}V^{3+}_{0.02}Fe^{2+}_{0.01}Y_{0.01})_{\Sigma 1.00}(Si_{1.03}Al_{0.97})_{\Sigma 2.00}O_6$. Davisite is monoclinic, $C2/c$; a = 9.884 Å, b = 8.988 Å, c = 5.446 Å, β =105.86°, V = 465.39 Å^3, and Z = 4. Its electron back-scattered diffraction pattern is an excellent match to that of synthetic $CaScAlSiO_6$ with the $C2/c$ structure. The strongest calculated X-ray powder diffraction lines are [d spacing in Å (I) (hkl)]: 3.039 (100) ($\bar{2}21$), 2.989 (31) (310), 2.943 (18) ($\bar{3}11$), 2.619 (40) (002), 2.600 (26) ($\bar{1}31$), 2.564 (47) (221), 2.159 (18) ($\bar{3}31$), 2.137 (15) ($\bar{4}21$), 1.676 (20) ($\bar{2}23$), and 1.444 (18) (531). The name is for Andrew M. Davis, a cosmochemist at the University of Chicago, Illinois.

Keywords: Davisite, $CaScAlSiO_6$, new mineral, Sc-rich pyroxene, refractory phase, ultra-refractory inclusion, Allende meteorite

INTRODUCTION

During a nano-mineralogy investigation of the Allende meteorite, a Sc-rich pyroxene was observed in an ultra-refractory inclusion. Electron-microprobe, high-resolution SEM, electron-backscatter diffraction (EBSD), and Raman analyses have been used to characterize its composition and structure. Synthetic $CaScAlSiO_6$ is known (Ohashi and Ii 1978). Highly Sc-enriched pyroxenes (13–16 wt% Sc_2O_3) have been found in four Ca-,Al-rich inclusions from the Ornans, Murchison, Efremovka, and Ningqiang meteorites based on chemical analyses (Davis 1984; Davis and Hinton 1985; Simon et al. 1996; El Goresy et al. 2002; Lin et al. 2003). We report here the occurrence, composition and crystal structure of a clinopyroxene from the Allende meteorite, $CaScAlSiO_6$, where scandium is the dominant trivalent component in the M1 site.

MINERAL NAME AND TYPE MATERIAL

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (IMA 2008-30). The name is for Andrew M. Davis, Professor of Cosmochemistry at the University of Chicago, born in 1950, in honor of his outstanding contributions to meteorite research. He observed a highly Sc-rich pyroxene (~15 wt% Sc_2O_3) from a meteorite in 1984 (Davis 1984). Holotype material (Caltech Section Allende12 MC2M) has been deposited in the Smithsonian Institution's National Museum of Natural History and is cataloged under USNM 7555.

OCCURRENCE, ASSOCIATED MINERALS, AND ORIGIN

A fine-grained aggregate of davisite occurs with REE-rich perovskite and spinel in a single Ca-,Al-rich refractory inclusion (CAI) from the Allende meteorite (Figs. 1–2). The fractured inclusion is exposed in one polished thick section, prepared from a 1 cm Allende specimen at Caltech. The mineral occupies most of the area in this CAI, which is about 130 μm wide in the section plane, surrounded by a matrix of mostly olivine and troilite. Nearby are fragments of a likely type-II chondrule. The Allende meteorite, which fell at Pueblito de Allende, Chihuahua, Mexico, on February 8, 1969, is a CV3 carbonaceous chondrite.

APPEARANCE, PHYSICAL, AND OPTICAL PROPERTIES

The type material occurs as an aggregate. Electron backscatter diffraction mapping reveals that the aggregate consists of crystals that are about 2–12 μm in width with different orientations. In thin section, it is transparent with a light-gray color, which may be caused by adjacent and underlying phases. Streak, luster, hardness, tenacity, cleavage, fracture, and density were not determined because of the small grain size. The density, calculated from the empirical formula, is 3.38 g/cm^3. It is non-fluorescent under the beams of the electron microprobe and SEM. Optical properties were not determined because of the small grain size; n (calc) = 1.736. In the section, the crystal grains are irregular to subhedral. No forms or twinning were observed. The a:b:c ratio calculated from the unit-cell parameters is 1.0997:1:0.6059.

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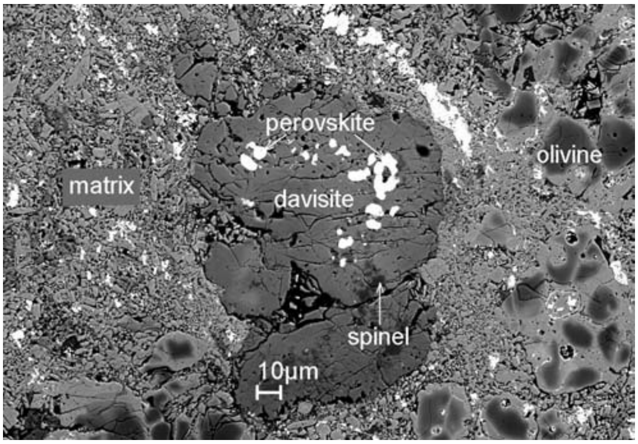

FIGURE 1. Backscatter electron image of the davisite-containing refractory inclusion in a polished section (USNM 7555) of the Allende meteorite.

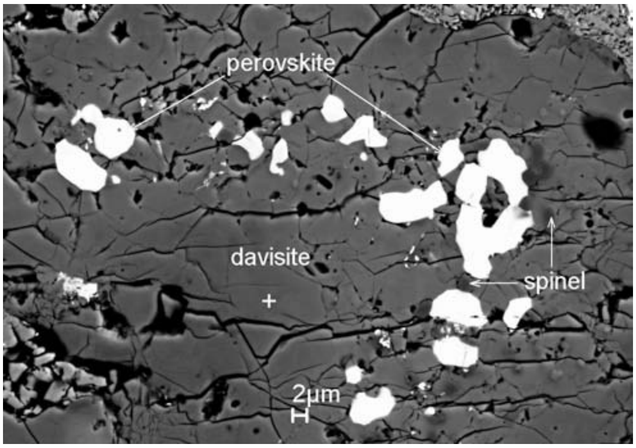

FIGURE 2. Enlarged BSE image showing davisite with perovskite and spinel (Fig. 1). The cross marks where the EBSD pattern (shown in Fig. 3) was collected.

CHEMICAL COMPOSITION

Quantitative elemental microanalyses were conducted with the JEOL 8200 electron microprobe operated at 15 kV and 25 nA in a focused beam mode. Standards for the analysis were anorthite (Ca*K*α, Al*K*α, Si*K*α), $ScPO_4$ (Sc*K*α), TiO_2 (Ti*K*α), zircon (Zr*L*α), YPO_4 (Y*L*α), fayalite (Fe*K*α), V_2O_3 (V*K*α), forsterite (Mg*K*α), $DyPO_4$ (Dy*L*α), $GdPO_4$ (Gd*L*α), and $ErPO_4$ (Er*L*α). Analyses were processed with the CITZAF correction procedure (Armstrong 1995). Six individual analyses reported in Table 1 were carried out using WDS mode. No other elements with atomic number >4 were detected by WDS scans.

The empirical formula, based on 6 O atoms, is

$$Ca_{0.989}(Sc_{0.502}Mg_{0.165}Ti^{3+}_{0.152}Ti^{4+}_{0.105}Zr_{0.038}V_{0.017}Y_{0.012}Fe^{2+}_{0.010}Dy_{0.003}Gd_{0.002}Er_{0.001})_{\Sigma 1.007}(Si_{1.028}Al_{0.972})_{\Sigma 2.000}O_6$$

where Ti^{3+} is calculated based on stoichiometry. The ideal, end-member formula is $CaScAlSiO_6$, which requires: CaO 23.75, Sc_2O_3 29.21, Al_2O_3 21.59, SiO_2 25.45, Total 100.00 wt%.

CRYSTALLOGRAPHY

Crystallography by EBSD at a sub-micrometer scale was carried out using the methods described in Ma and Rossman (2008, 2009) with an HKL EBSD system on the ZEISS 1550VP scanning electron microscope, operated at 20 kV and 8 nA in a focused beam with a 70° tilted stage. The structure was determined and cell constants were obtained by matching the experimental EBSD pattern (Fig. 3) with the structures of synthetic synthetic $CaScAlSiO_6$ (Ohashi and Ii 1978), esseneite (Cosca and Peacor 1987), and orthorhombic pyroxenes (Molin 1989).

The EBSD patterns can be indexed only by the monoclinic *C*2/*c* structure to give a best fit based on unit-cell data from $CaScAlSiO_6$ (Ohashi and Ii 1978) (Fig. 3), showing a monoclinic structure, space group: *C*2/*c*, $a = 9.884$ Å, $b = 8.988$ Å, $c = 5.446$ Å, $\beta = 105.86°$, $V = 465.39$ Å^3, and $Z = 4$ with the mean angular deviations as low as 0.18. No errors are stated because the cell parameters are taken directly from the data of the matching $CaScAlSiO_6$ phase in Ohashi and Ii (1978).

X-ray powder-diffraction data (Cu*K*α1) are calculated from the cell parameters from Ohashi and Ii (1978) with the empirical formula from this study using Powder Cell version 2.4 (2000). The strongest X-ray powder diffraction lines are [*d* spacings in Å (*I*) (*hkl*)]: 3.039 (100) ($\bar{2}21$), 2.989 (31) (310), 2.943 (18) ($\bar{3}11$), 2.619 (40) (002), 2.600 (26) ($\bar{1}31$), 2.564 (47) (221), 2.159 (18) ($\bar{3}31$), 2.137 (15) ($\bar{4}21$), 1.676 (20) ($\bar{2}23$), and 1.444 (18) (531).

SPECTROSCOPIC PROPERTIES

Raman microanalysis was carried out using the methods described in Ma and Rossman (2008, 2009). The Raman spectrum gave no indication of either H_2O or CO_2 in davisite. Raman microanalyses show that the spectrum of davisite (using a 514.5 nm laser) has intense fluorescent features and is not comparable to that of synthetic $CaScAlSiO_6$ (Sekita et al. 1988), which only covers a limited range, as shown in Figure 4. The intense fluorescence features are due to the significant amount of REE elements. Consequently, the identification of davisite is based on EBSD and electron-probe results only.

DISCUSSION

Davisite is a new member of the Ca clinopyroxenes (diopside group) with space group *C*2/*c* (Morimoto et al. 1988), the Sc-dominant analog of esseneite ($CaFe^{3+}AlSiO_6$). Scandium is

TABLE 1. The mean analytical results of davisite

Constituent*	wt%	Range	Stand. Dev.	EPMA Standard
SiO_2	26.24	25.11–28.58	1.25	anorthite
CaO	23.55	23.37–23.65	0.10	anorthite
Al_2O_3	21.05	19.39–22.05	0.92	anorthite
Sc_2O_3	14.70	13.05–15.49	0.88	$ScPO_4$
TiO_2†	8.66	8.40–8.89	0.19	TiO_2
MgO	2.82	2.20–4.03	0.65	forsterite
ZrO_2	2.00	1.66–2.15	0.18	zircon
Y_2O_3	0.56	0.51–0.60	0.03	YPO_4
V_2O_3	0.55	0.49–0.64	0.05	V_2O_5
FeO	0.30	0.27–0.33	0.02	fayalite
Dy_2O_3	0.27	0.16–0.33	0.07	$DyPO_4$
Gd_2O_3	0.13	0.08–0.21	0.05	$GdPO_4$
Er_2O_3	0.08	0.03–0.14	0.04	$ErPO_4$
Total	100.91			

* All listed constituents are above their detection limits at 99% confidence

† Total TiO_2 wt% recalculated to 4.64 wt% Ti_2O_3 + 3.57 wt% TiO_2 to obtain stoichiometry and valency balance, gives a new analytical total = 100.46 wt%.

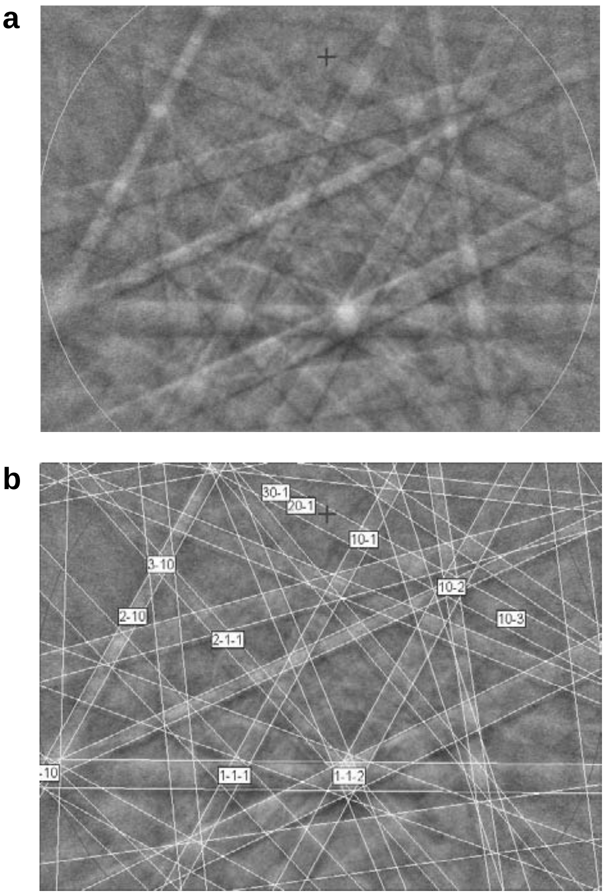

FIGURE 3. (**a**) EBSD pattern of the labeled davisite crystal (marked with a cross) in Figure 2; (**b**) the pattern perfectly indexed with the *C*2/*c* $CaScAlSiO_6$ structure.

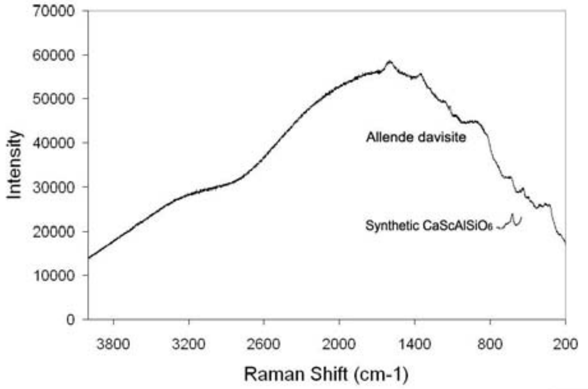

FIGURE 4. Raman spectra of davisite (this study) and synthetic $CaScAlSiO_6$ (Sekita et al. 1988), collected under different conditions, showing relative intensities. The spectrum for the synthetic sample covers a very limited range, and is displaced vertically from the zero line to facilitate comparison with the davisite spectrum.

a sparsely distributed element in the Earth's crust, but is significantly more abundant in the sun and primitive meteorites (Weaver and Tamey 1984; Anders and Grevesse 1989). The Allende meteorite containing 11~12 ppm (Jarosewich et al. 1987) has provided a variety of phases with high scandium contents including oxides, pyroxenes, and perovskites in Ca-,Al-rich refractory inclusions. The newly discovered mineral allendeite ($Sc_4Zr_3O_{12}$, IMA 2007-027) and its associated Sc-stabilized tazheranite [cubic zirconia, $(Zr,Sc,Ca)O_{1.75}$] from Allende are the most Sc-rich oxides found to date (Ma et al. 2009). Davisite is one of the more Sc-rich phases ever reported currently surpassed only by pretulite ($ScPO_4$), thortveitite [$(Sc,Y)_2Si_2O_7$], kolbeckite ($ScPO_4 \cdot 2H_2O$), and the newly approved mineral allendeite.

Refractory inclusions are the first known solids formed in the solar system. Davisite is a new refractory mineral from Allende, associated with REE-rich perovskite with a formula $(Ca_{0.81}Y_{0.07}Dy_{0.03}Gd_{0.02}Sc_{0.02}Na_{0.01})(Ti^{4+}_{0.94}Al_{0.03}V_{0.01}Fe_{0.01})O_3$ and Mg-Al spinel in an ultra-refractory inclusion. This fine-grained inclusion shows an irregular shape without a rim. Its mineralogy is characterized by high refractory and rare earth elements enrichment in perovskite and davisite. The inclusion is likely formed through high-temperature condensation in the solar nebula, followed by partial melting and crystallization. A more detailed geochemical investigation of refractory elements and REE in this ultra-refractory inclusion is in progress (Ma et al. in prep). It is unlikely that this CAI is associated with the nearby Type-II ferromagnesian chondrule fragments.

Other pyroxenes from CAIs in the Ornans, Murchison, Efremovka, and Ningqiang chondrites where Sc^{3+} dominates the M1 site with 44 to 56% occupancy (Davis 1984; Davis and Hinton 1985; Simon et al. 1996; El Goresy et al. 2002; Lin et al. 2003) would be davisite as well if their structure can be verified to be *C*2/*c* by EBSD or other diffraction methods. Ca-pyroxenes containing up to several weight percent of Sc_2O_3 are not rare in CAIs (e.g., Simon et al. 1996; El Goresy et al. 2002; this study). It is apparent that a solid solution exists between Al-,Ti-rich diopside and davisite.

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