Davisite, CaScAlSiO₆, a new pyroxene from the Allende meteorite

CHI MA* and GEORGE R. ROSSMAN

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.

ABSTRACT

Davisite, ideally CaScAlSiO₆, is a new member of the Ca clinopyroxene group, where Sc³⁺ 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%) SiO₂ 26.24, CaO 23.55, Al₂O₃ 21.05, Sc₂O₃ 14.70, TiO₂ (total) 8.66, MgO 2.82, ZrO₂ 2.00, V₂O₅ 0.56, Cr₂O₃ 0.55, FeO 0.30, Dy₂O₃ 0.27, Gd₂O₃ 0.13, Er₂O₃ 0.08, sum 100.91. Its empirical formula calculated on the basis of 6 O atoms is Ca₀.99(Sc₀.50Ti₀.29Mg₀.16Fe₀.10)Σ₁.00(Al₀.93Mg₀.06Sc₀.01Ti₀.02)Σ₁.08(Fe²⁺₀.02Fe³⁺₀.01)Σ₀.03(M₁₀.97Na₀.03)Σ₁.00O₆. Davisite is monoclinic, C2/c; a = 9.884 Å, b = 8.988 Å, c = 5.446 Å, β = 105.86°, V = 465.39 Å³, and Z = 4. Its electron back-scattered diffraction pattern is an excellent match to that of synthetic CaScAlSiO₆ with the C2/c structure. The strongest calculated X-ray powder diffraction lines are [d spacing in Å (I) (hkl)]: 3.039 (100) (221), 2.989 (31) (310), 2.943 (18) (311), 2.619 (40) (002), 2.600 (26) (231), 2.564 (47) (221), 2.159 (18) (331), 2.137 (15) (221), 1.676 (20) (223), and 1.444 (18) (531). The name is for Andrew M. Davis, a cosmochemist at the University of Chicago, Illinois.

Keywords: Davisite, CaScAlSiO₆, 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 CaScAlSiO₆ is known (Ohashi and Ii 1978). Highly Sc-enriched pyroxenes (13–16 wt% Sc₂O₃) have been found in four Ca-,Al-rich inclusions from the Ormans, 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, CaScAlSiO₆, 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% Sc₂O₃) from a meteorite in 1984 (Davis 1984). Holotype material (Caltech Section Allende 12 MC2M) has been deposited in the Smithsonian Institution’s National Museum of Natural History and is catalogued under USNM 7555.

* E-mail: chi@gps.caltech.edu

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/cm³. 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.
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 (CaKα, AlKα, SiKα), ScPO4 (ScKα), TiO2 (TiKα), zircon (ZrLα), YPO4 (YLα), fayalite (FeKα), V2O5 (VKα), forsterite (MgKα), DyPO4 (DyLα), GdPO4 (GdKα), and ErPO4 (ErLα). 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

\[
\text{Ca}_0.989(\text{Sc}_{0.502}\text{Mg}_{0.165}\text{Ti}_{3+}^{4+})\text{Al}_{0.972}\text{Si}_{1.028} \Sigma_6 \text{O}_6
\]

where Ti3+ is calculated based on stoichiometry. The ideal, end-member formula is CaScAlSiO6, which requires: CaO 23.75, Sc2O3 29.21, Al2O3 21.59, SiO2 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 CaScAlSiO6 (Ohashi and Ii 1978), esseneite (Cosca and Peacor 1987), and orthorhombic pyroxenes (Molin 1989).

The EBSD patterns can be indexed only by the monoclinic C2/c structure to give a best fit based on unit-cell data from CaScAlSiO6 (Ohashi and Ii 1978) (Fig. 3), showing a monoclinic structure, space group: C2/c, a = 9.884 Å, b = 8.988 Å, c = 5.446 Å, β = 105.86°, V = 465.39 Å3, 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 CaScAlSiO6 phase in Ohashi and Ii (1978).

X-ray powder-diffraction data (CuKα1) 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 (hkl): 3.039 (100) (221), 2.989 (31) (310), 2.943 (18) (311), 2.619 (40) (002), 2.600 (26) (T31), 2.564 (47) (221), 2.159 (18) (331), 2.137 (15) (221), 1.676 (20) (223), 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 H2O or CO2 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 CaScAlSiO6 (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 C2/c (Morimoto et al. 1988), the Sc-dominant analog of esseneite (CaFe3+AlSiO6). Scandium is

**Table 1. The mean analytical results of davisite**

<table>
<thead>
<tr>
<th>Constituent*</th>
<th>wt%</th>
<th>Range</th>
<th>Stand. Dev.</th>
<th>EPMA Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>26.24</td>
<td>25.11–25.88</td>
<td>1.15</td>
<td>anorthite</td>
</tr>
<tr>
<td>CaO</td>
<td>23.55</td>
<td>23.37–23.65</td>
<td>0.10</td>
<td>anorthite</td>
</tr>
<tr>
<td>Al2O3</td>
<td>21.05</td>
<td>19.39–22.05</td>
<td>0.92</td>
<td>anorthite</td>
</tr>
<tr>
<td>Sc2O3</td>
<td>14.70</td>
<td>13.05–15.49</td>
<td>0.88</td>
<td>ScPO4</td>
</tr>
<tr>
<td>TiO2  †</td>
<td>8.66</td>
<td>8.40–8.89</td>
<td>0.19</td>
<td>TiO2</td>
</tr>
<tr>
<td>MgO</td>
<td>7.62</td>
<td>7.15–8.10</td>
<td>0.85</td>
<td>forsterite</td>
</tr>
<tr>
<td>ZrO2</td>
<td>2.00</td>
<td>1.66–2.15</td>
<td>0.18</td>
<td>zircon</td>
</tr>
<tr>
<td>Y2O3</td>
<td>0.56</td>
<td>0.53–0.60</td>
<td>0.03</td>
<td>YPO4</td>
</tr>
<tr>
<td>FeO</td>
<td>0.55</td>
<td>0.49–0.64</td>
<td>0.05</td>
<td>V2O5</td>
</tr>
<tr>
<td>Dy2O3</td>
<td>0.30</td>
<td>0.27–0.33</td>
<td>0.02</td>
<td>fayalite</td>
</tr>
<tr>
<td>Gd2O3</td>
<td>0.27</td>
<td>0.16–0.33</td>
<td>0.07</td>
<td>DyPO4</td>
</tr>
<tr>
<td>Er2O3</td>
<td>0.13</td>
<td>0.08–0.21</td>
<td>0.05</td>
<td>GdPO4</td>
</tr>
<tr>
<td>Total</td>
<td>100.91</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* All listed constituents are above their detection limits at 99% confidence
† Total TiO2 wt% recalculated to 4.64 wt% Ti2O3 + 3.57 wt% TiO2 to obtain stoichiometry and valency balance, gives a new analytical total = 100.46 wt%.
including oxides, pyroxenes, and perovskites in Ca-Al-rich refractory inclusions. The newly discovered mineral allendeite (Sc₄Zr₃O₁₂, IMA 2007-027) and its associated Sc-stabilized tazheranite [cubic zirconia, (Zr,Sc,Ca)O₁.₇₅] 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 (ScPO₄), thortveitite [(Sc,Y)₂Si₂O₇], kolbeckite (ScPO₄·2H₂O), and the newly approved mineral allendeite.

Refactory 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 (Ca₀.₈₁Y₀.₀₇Dy₀.₀₂Gd₀.₀₂Sc₀.₀₁)(Ti⁴⁺₀.₉₄Al₀.₀₃V₀.₀₁Fe₀.₀₁)O₃ 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 ferromagnesians chondrule fragments.

Other pyroxenes from CAIs in the Ornans, Murchison, Efremovka, and Ningqiang chondrites where Sc³⁺ 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 C₂/c by EBSD or other diffraction methods. Ca-pyroxenes containing up to several weight percent of Sc₂O₃ 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.


