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Zolenskyite, $FeCr_2S_4$, a new sulfide mineral from the Indarch meteorite

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Abstract

Zolenskyite (IMA 2020-070), $FeCr_2S_4$, is a new sulfide mineral that occurs within troilite, with clinoenstatite and tridymite, in the matrix of the Indarch meteorite, an EH4 enstatite chondrite. The mean chemical composition of zolenskyite determined by electron probe microanalysis, is (wt%) S 43.85, Cr 35.53, Fe 18.94, Mn 0.68, Ca 0.13, total 99.13, yielding an empirical formula of $Fe_{0.99}Mn_{0.04}Ca_{0.01}Cr_{1.99}S_{3.98}$. The ideal formula is $FeCr_2S_4$. Electron backscatter diffraction shows that zolenskyite has the *C*2/*m* $CrNb_2Se_4$-Cr_3S_4-type structure of synthetic $FeCr_2S_4$, which has a = 12.84(1) Å, b = 3.44(1) Å, c = 5.94(1) Å, β = 117(1)°, V = 234(6) Å^3, and Z = 2. The calculated density using the measured composition is 4.09 g/cm^3. Zolenskyite is a monoclinic polymorph of daubréelite. It may be a high-pressure phase, formed from daubréelite at high pressures (several gigapascals) and moderate temperatures in highly shocked regions of the EH parent asteroid before becoming incorporated into Indarch via impact mixing. Zolenskyite survived moderate annealing of the Indarch whole-rock. The new mineral is named in honor of Michael E. Zolensky, an esteemed cosmochemist and mineralogist at NASA's Johnson Space Center, for his contributions to research on extraterrestrial materials, including enstatite chondrites.

Keywords: Zolenskyite, $FeCr_2S_4$, new mineral, sulfide, Indarch meteorite, enstatite chondrite

Introduction

The Indarch meteorite, which fell at Shusha, Azerbaijan on April 7, 1891, is an EH4 enstatite chondrite (Meteoritical Bulletin Database). The meteorite consists of (in wt%): 72.6% silicates (clinoenstatite and disordered orthoenstatite, averaging $En_{98.3}Fs_{1.1}Wo_{0.6}$; albite, averaging $Ab_{97.6}An_{1.6}Or_{0.8}$; tridymite); 17.5% Si-bearing low-Ni metallic Fe (kamacite); 7.3% Ti-, Cr-, Mn-, and Zn-bearing troilite; 1.0% niningerite; 0.39% oldhamite; trace amounts of rudashevskyite (Fe,Zn)S; 0.05% $FeCr_2S_4$ (listed as daubréelite, but is actually mainly zolenskyite, the new phase described here from the Indarch matrix, that in some cases is intimately intergrown with cronusite and schöllhornite—terrestrial weathering products of caswellsilverite and oldhamite); 1.1% schreibersite; 0.04% graphite; and trace amounts of cohenite, lawrencite, and nierite Si_3N_4 (e.g., Mason 1966; Keil 1968). During a nanomineralogical investigation of polished thick sections of Indarch, we identified the new sulfide mineral, $FeCr_2S_4$, with the monoclinic *C*2/*m* $CrNb_2Se_4$-Cr_3S_4-type structure, which we named "zolenskyite" (Fig. 1). All the $FeCr_2S_4$ in the Indarch matrix that we found is zolenskyite; one sulfide-rich patch containing daubréelite is present within a porphyritic pyroxene chondrule (Fig. 2). To characterize the chemical composition and structure of zolenskyite (as well as its associated phases), we used field-emission scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and electron probe microanalysis (EPMA). Synthetic $FeCr_2S_4$ and $(Fe_{0.6}Cr_{0.4})Cr_2S_4$ with the *C*2/*m* $CrNb_2Se_4$-Cr_3S_4-type structure have been reported (Tressler et al. 1968; Lutz et al. 1983); presented here is the first natural occurrence of this phase as a new mineral in a chondritic meteorite.

Mineral name and type material

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2020-070) (Ma 2021). The mineral name is in honor of Michael E. Zolensky (born in 1955), esteemed planetary scientist, cosmochemist, and mineralogist at NASA's Johnson Space Center for his outstanding contributions to research on extraterrestrial materials, including enstatite chondrites. Caltech sections ICM1, ICM2, ICM3, and ICM6, taken from facing slices of the Indarch meteorite, contain the type material of zolenskyite. Section ICM3, hereafter referred to as USNM 7926, has been deposited in the Smithsonian Institution's National Museum of Natural History, Washington, D.C., U.S.A., under catalog USNM 7926. USNM 7926 also contains rare grains of joegoldsteinite ($MnCr_2S_4$; Isa et al. 2016).

Occurrence and appearance

Zolenskyite occurs within troilite, associated with clinoenstatite and tridymite in the Indarch matrix in sections ICM1, ICM2, ICM6, and USNM 7926 (Fig. 1). Zolenskyite occurs as euhedral-subhedral single crystals, ~10–20 μm in size, with oxidation alteration patches within each grain. Only the brighter clean regions (up to 2 μm in size) in the backscattered electron images are the type material of zolenskyite, whereas the darker regions are oxidized areas (Fig. 1).

Zolenskyite is opaque. Color, luster, streak, hardness, tenacity, cleavage, fracture, density, and optical properties could not be

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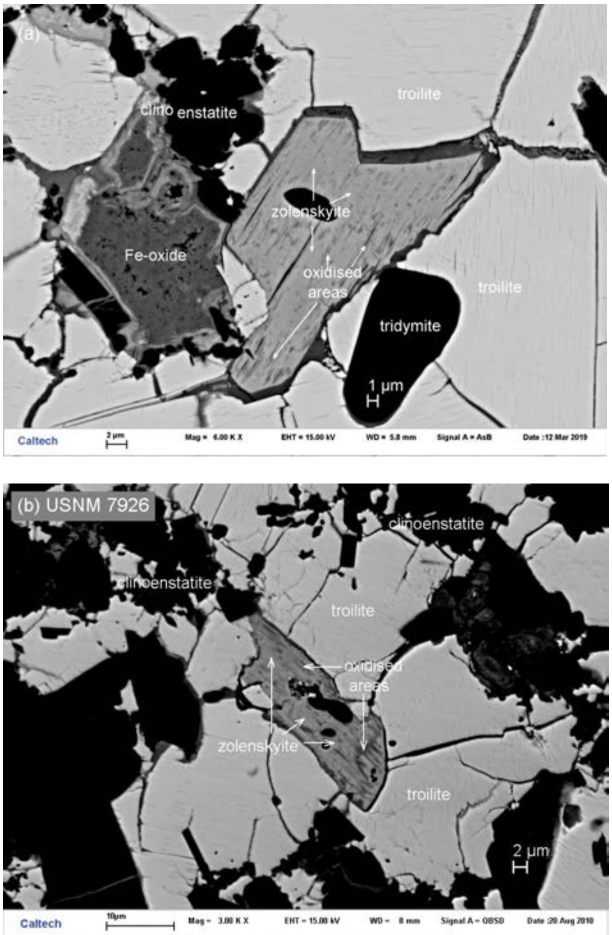

Figure 1. SEM BSE images showing zolenskyite with troilite, clinoenstatite, tridymite, and Fe-oxide in the Indarch matrix. (**a**) Section ICM1. (**b**) Section USNM 7926 (ICM3). In both cases, the zolenskyite grains are flanked by a rind of oxidation/alteration products.

determined because of the small grain size but are likely close to those of its Cr-analog brezinaite (Cr_3S_4). All occurrences of $FeCr_2S_4$ in the Indarch matrix are zolenskyite. The only occurrence of daubréelite we encountered in Indarch is associated with troilite and is adjacent to schöllhornite in chondrule *Ind-1* in ICM7 (Fig. 2); the chondrule (530 µm diameter) consists of clinoenstatite, interstitial albite, and sulfide patches (mainly troilite with minor niningerite).

Chemical composition

Backscattered electron (BSE) images were obtained at Caltech using a ZEISS 1550VP field emission SEM and a JEOL 8200 electron microprobe with solid-state BSE detectors. Four quantitative WDS elemental microanalyses of type zolenskyite were carried out using the JEOL 8200 electron microprobe operated at 10 kV (for smaller interaction volume) and 8 nA in focused beam mode. The focused electron beam is ~120 nm in diameter. The interaction volume for X-ray generation in zolenskyite is ~800 nm in diameter, estimated using the Casino Monte Carlo simulation of electron trajectory. Analyses were processed with the CITZAF correction procedure (Armstrong 1995) using the Probe for EPMA program from Probe Software, Inc. Possible interferences on peak position and background position were checked and corrected for all measured elements based on WDS scans. Analytical results are given in Table 1. WDS scans did not reveal other elements such as Na and Zn.

The empirical formula of type zolenskyite (based on 7 atoms pfu) is $Fe_{0.99}Mn_{0.04}Ca_{0.01}Cr_{1.99}S_{3.98}$. The ideal formula is $Fe^{2+}Cr^{3+}_2S_4$, which is equivalent to a composition of (in wt%): Fe 19.38, Cr 36.10, S 44.52.

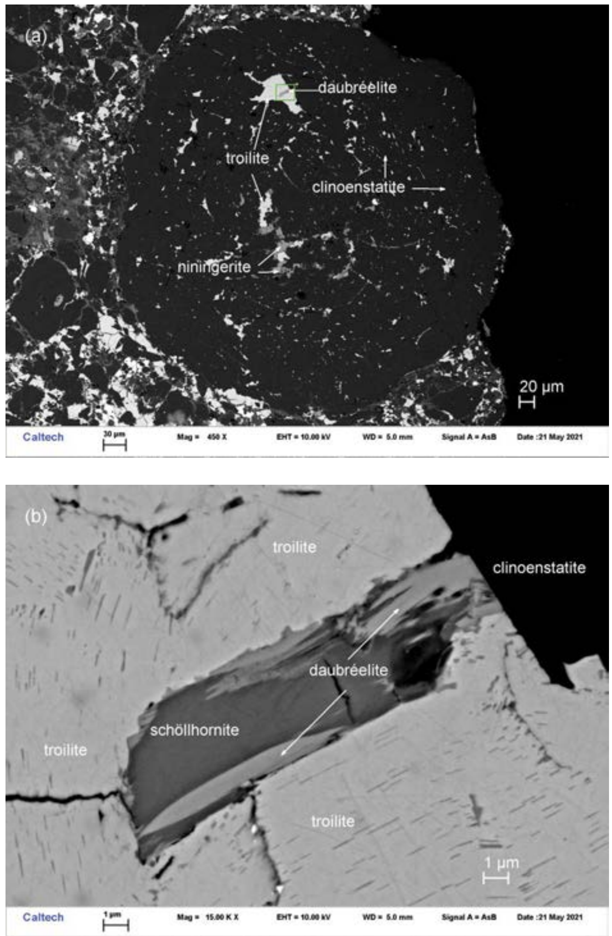

Figure 2. SEM BSE images of a porphyritic pyroxene chondrule *Ind-1* with sulfide-rich patches, one of which contains daubréelite, in section ICM7. (**a**) Entire chondrule (530 µm diameter) consists of clinoenstatite, interstitial albite, and sulfide patches. (**b**) High-magnification view (small box in **a**) of an inclusion of daubréelite flanking schöllhornite within a patch of troilite.

Table 1. Average elemental composition of four-point EPMA analyses for type zolenskyite

Constituent	wt%	Range	SD	Probe standard
S	43.85	43.55–44.32	0.34	Pyrite
Cr	35.53	34.18–36.76	1.24	Cr metal
Fe	18.94	17.72–20.36	1.22	Pyrite
Mn	0.68	0.54–0.91	0.17	Mn metal
Ca	0.13	0.12–0.16	0.02	Anorthite
Total	99.13			

Associated Cr-bearing troilite has an empirical formula (based on 4 atoms pfu) of $(Fe_{0.97}Cr_{0.02})S_{1.00}$. Nearby clinoenstatite has an empirical formula (based on 6 atoms pfu) of $(Mg_{1.95}Fe_{0.05})Si_2O_6$.

Crystallography

Electron backscatter diffraction (EBSD) analyses, using methods described in Ma and Rossman (2008, 2009), were performed using an HKL EBSD system on the ZEISS 1550VP Field-Emission SEM operated at 20 kV and 6 nA in focused-beam mode with a 70° tilted stage and in a variable pressure mode (25 Pa). The focused electron beam is several nanometers in diameter. The spatial resolution for diffracted backscattered electrons is ~30 nm in size. The EBSD system was calibrated using a single-crystal silicon standard. The structure was determined and cell constants were obtained by matching the experimental EBSD patterns with the known structures of Fe-Cr-S and Cr-S phases, including $FeCr_2S_4$, $(Fe_{0.6}Cr_{0.4})Cr_2S_4$, and Cr_3S_4.

The EBSD patterns of all $FeCr_2S_4$ grains in the Indarch matrix are indexed only by the *C*2/*m* $CrNb_2Se_4$-Cr_3S_4-type structure and give the best fit by the synthetic $FeCr_2S_4$ cell from Tressler et al. (1968) (Fig. 3), in which a = 12.84(1) Å, b = 3.44(1) Å, c = 5.94(1) Å, β = 117(1)°, V = 234(6) Å^3, and Z = 2. The mean angular deviation of the patterns is 0.38°. The calculated density based on the empirical formula is 4.09 g/cm^3. Calculated X-ray powder diffraction data for zolenskyite are given in Online Materials[1] Table S1. The $FeCr_2S_4$ grain within chondrule *Ind-1* is daubréelite, identified by EBSD to have a cubic spinel-type structure.

Discussion

Zolenskyite ($FeCr_2S_4$) is the Fe-analog of brezinaite (Cr_3S_4), or the Cr-analog of heideite (ideally $FeTi_2S_4$) (Keil and Brett 1974), joining the wilkmanite group. Zolenskyite is a monoclinic polymorph of daubréelite.

It is unclear if some previous reports of daubréelite in enstatite chondrites are, in fact, zolenskyite. Our analyses of zolenskyite in EH4 Indarch show it to be Zn free, thus differing from the phase identified as daubréelite in EH3 Kota-Kota [5.2 wt% Zn; Keil (1968)] and EL3 MAC 88136 [up to 5.7 wt% Zn; Lin et al. (1991)]. Grossman et al. (1985) reported $FeCr_2S_4$ in chondrules in EH3 Qingzhen and identified the phase as daubréelite but did not analyze it. Zincian daubréelite is present in EH5 (4.3 wt% Zn) and EL6 (up to 0.55 wt% Zn) chondrites (Keil 1968) and commonly occurs as exsolution lamellae in troilite parallel to {0001} (e.g., Keil 1968; Rubin 1984). Daubréelite is also present as exsolution lamellae in troilite within the clastic matrix component of EH3 Y-691 (Rubin et al. 2009).

Many aubrites (enstatite achondrites) contain small grains of daubréelite averaging 0.09 wt% Zn (Watters and Prinz 1979). The Norton County aubrite breccia contains individual daubréelite grains ranging up to 700 μm, associated with Ti-bearing troilite, ferroan and ferromagnesian alabandite, and kamacite (Okada et al. 1988); daubréelite also occurs in Norton County as exsolution lamellae in troilite.

It seems likely that the $FeCr_2S_4$ phase in enstatite chondrites and aubrites that occurs as exsolution lamellae in troilite is daubréelite, but additional studies are required to determine which $FeCr_2S_4$ polymorphs are present in different EH3 and EL3 chondrites. Any zolenskyite that may have originally been present in unmetamorphosed enstatite chondrites could have transformed into daubréelite in those samples that were heated to higher metamorphic temperatures (e.g., 800–1000 °C for EH5 and EH6 chondrites; Zhang et al. 1996).

Indarch EH4 consists principally of chondrules and moderately coarse interchondrule material. It does not contain fine-grained matrix material (which occurs in EH3 and EL3 chondrites;

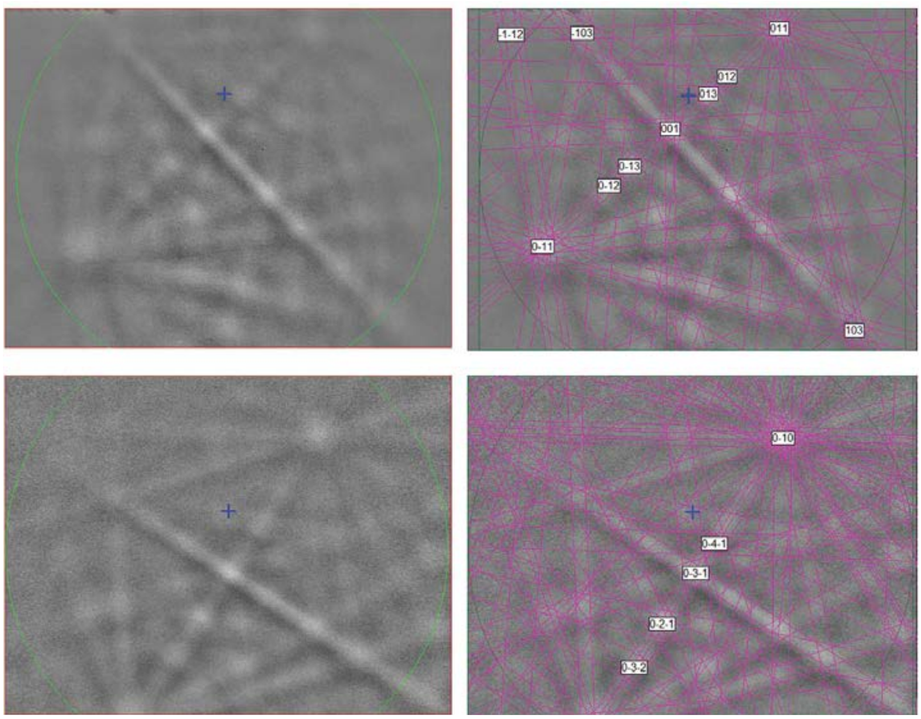

Figure 3. (**left**) EBSD patterns of the zolenskyite crystals in Figure 1 at different orientations, and (**right**) the patterns indexed with the *C*2/*m* $FeCr_2S_4$ structure. (Color online.)

e.g., Rubin et al. 2009; Rubin 2010). A significant fraction of the interchondrule material in Indarch is probably derived from crushed chondrules (e.g., Nelson and Rubin 2002). In Indarch, the identification of daubréelite only in a chondrule and zolenskyite exclusively in the matrix suggests that daubréelite formed at high temperatures during chondrule formation and that zolenskyite formed from daubréelite in disaggregated chondrules by later-stage parent-body processes.

Chondrules formed at high temperatures [in many cases ~1430–1730 °C (e.g., Lofgren and Lanier 1990; Radomsky and Hewins 1990)] and very low pressures, consistent with the stability field of daubréelite (Tressler et al. 1968). This can account for the presence of daubréelite in Indarch chondrule *Ind-1*.

Experiments show that daubréelite can transform into zolenskyite at high pressures and moderate temperatures (e.g., 5.5 GPa, 520 °C; 3 GPa, 200 °C) (Tessler et al. 1968). Such conditions likely pertained in highly shocked EH6 chondrites (Rubin and Wasson 2011). Zolenskyite may have formed from daubréelite in highly shocked regions of the EH parent asteroid, later to be incorporated into Indarch as aberrant grains during small-scale impact-mixing events (e.g., Rubin 1990).

Whereas the daubréelite grain in the chondrule is optically homogeneous and unaltered (Fig. 2), all zolenskyite grains in the matrix appear moderately altered (Fig. 1). This alteration could be due to the same type of alkali metasomatic processes that occurred in EH3-chondrite matrices and produced djerfisherite [$K_6(Fe,Cu,Ni)_{25}S_{26}Cl$] (El Goresy et al. 1988).

Indarch is apparently unbrecciated (Rubin 2015) and only weakly shocked [shock-stage S3 (Rubin et al. 1997)]; its orthopyroxene grains exhibit undulose extinction and contain clinoenstatite lamellae on (100). Because Indarch contains zolenskyite that likely formed at high-shock pressures, we suggest that annealing of the Indarch whole rock to ~640 °C (Huss and Lewis 1994) obliterated the evidence of brecciation.

Implications

Indarch is a mildly metamorphosed EH4 chondrite. It contains the first-known natural occurrence of monoclinic $FeCr_2S_4$ (zolenskyite), a polymorph of daubréelite (cubic $FeCr_2S_4$). Zolenskyite probably formed from daubréelite at high-shock pressures during collisions on the parent body. The phase may also occur in some other EH3 and EH4 chondrites; some previous reports of daubréelite in enstatite chondrites may actually be zolenskyite.

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Endnote:

[1]Deposit item AM-22-68094, Online Materials. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2022/Jun2022_data/Jun2022_data.html).