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**Article**

# Discovery and structural characterization of zolenskyite, $FeCr_2S_4$, in the Muonionalusta meteorite: Advancing micron-scale mineralogy in planetary science

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**Abstract**

Here we present the first single-crystal X-ray diffraction analysis of zolenskyite, a chromium-bearing sulfide mineral ($FeCr_2S_4$) and newly identified polymorph of daubréelite, discovered in the Muonionalusta meteorite, a well-characterized IVA iron meteorite. Zolenskyite occurs as rare micron-scale grains associated closely with daubréelite and stishovite, within a troilite matrix. Chemical analysis confirms a pure, homogeneous $FeCr_2S_4$ composition. The crystal structure was refined in the monoclinic $C2/m$ space group, revealing a framework of face-sharing octahedra, consistent with a cation-deficient NiAs-type structure, distinct from the spinel-type structure of daubréelite. Zolenskyite forms under high-pressure (>7 GPa) and high-temperature (>1000 K) conditions, probably through solid-state transformation from daubréelite during shock events. The serendipitous recognition of zolenskyite emphasizes the value of careful micron-scale mineralogical investigations in revealing transient or metastable phases that record otherwise inaccessible physicochemical conditions. These findings contribute to understanding the thermal and shock history of meteorite parent bodies and the stability of Fe–Cr sulfides in extraterrestrial environments.

**Keywords:** zolenskyite; daubréelite; $FeCr_2S_4$; Muonionalusta; iron meteorite; shock metamorphism; crystal structure; thiospinel; nickeline derivative structure; X-ray diffraction; micron-scale mineralogical studies

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## Introduction

The study of extraterrestrial minerals provides critical insights into the physicochemical conditions that prevailed during the early history of the Solar System. Among these, sulfide minerals play a significant role in shedding light on thermal metamorphism, redox conditions, and differentiation processes within planetary bodies (e.g. Blander, 1971; Fleet, 2006). Among such minerals, zolenskyite, a chromium-bearing sulfide that represents a polymorph of $FeCr_2S_4$ after daubréelite, has recently been discovered in the Indarch meteorite (EH chondrite), but its crystal structure had not been determined conclusively (Ma and Rubin, 2022). This work presents the first single-crystal X-ray diffraction analysis of zolenskyite, identified for the first time in the Muonionalusta meteorite. Muonionalusta is classified as an octahedrite belonging to group IVA, which represents ~8% of all known iron meteorites. Its primary mineral composition – with the metal fraction containing ~9 wt.% nickel and 0.4 wt.% cobalt (Hidaka *et al.*, 2019) – has been documented thoroughly in earlier studies (Buchwald, 1975; Holtstam *et al.*, 2003; Ahlgren *et al.*, 2016). The Muonionalusta meteoroid is believed to have been ejected from its parent body roughly 400 million years ago during a high-energy impact event (Blichert-Toft *et al.*, 2010). It entered Earth's atmosphere, probably during the Middle Pleistocene, fragmented during atmospheric entry, and dispersed across a wide region (Lagerbäck and Wickman, 1997).

Zolenskyite is part of a broader group of sulfides that includes rare and metastable phases often formed under non-equilibrium conditions, such as shock or rapid cooling, commonly encountered in meteoritic environments (e.g. Leroux *et al.*, 2008; Miyahara *et al.*, 2021). Its occurrence in the Muonionalusta meteorite is particularly notable due to the meteorite's history of high-temperature processes, followed by slow cooling and multiple shock events (Yang *et al.*, 2010). The presence and characteristics of zolenskyite in this context can thus provide important clues regarding the metamorphic and impact history of its parent body.

The structural determination of zolenskyite is essential not only for mineralogical classification but also for understanding the conditions of its formation and stability. Previous studies have relied primarily on electron-backscatter diffraction, limiting the accuracy of atomic positional data (Ma and Rubin, 2022). By applying single-crystal X-ray diffraction techniques, we here provide a

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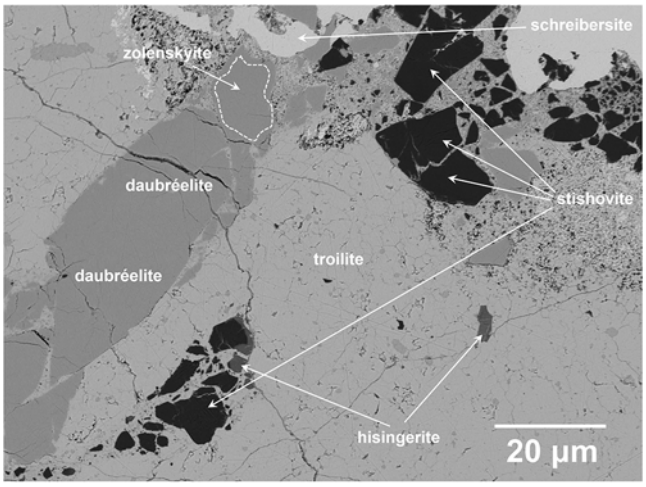


**Figure 1.** SEM back-scattered electron image of a portion of the studied Muonionalusta sample. All the phases have been labelled.

precise and unambiguous characterization of this mineral, contributing significantly to the mineralogical dataset of meteoritic sulfides.

Moreover, the recognition and structural resolution of µm-sized phases such as zolenskyite underscore the growing importance of micron-scale mineralogy in planetary science. Submicron-sized mineral inclusions often record high-resolution signatures of physicochemical processes that are otherwise undetectable in bulk analyses (e.g. Xu *et al.*, 2017). Such studies do not only expand our mineralogical knowledge but also aid in a better reconstruction of the formation environments of meteorites and their parent bodies.

This paper reports the occurrence, description, and crystal structure of zolenskyite from the Muonionalusta meteorite. The findings provide new constraints on the formation conditions of Fe–Cr sulfides in iron meteorites and highlight the value of high-resolution mineralogical analysis in decoding planetary processes.

## Occurrence of zolenskyite in Muonionalusta

Zolenskyite occurrence in Muonionalusta is very rare. It occurs in µm-sized grains associated closely with daubréelite (the other $FeCr_2S_4$ polymorph) in a troilite matrix (Fig. 1). Zolenskyite was found in the Muonionalusta sample originally studied by Holtstam *et al.* (2003), from the collections of the Swedish Museum of Natural History, catalogue no. GEO-NRM 20020049. These authors identified stishovite (pseudomorph after tridymite), chromite, hisingerite and schreibersite by means of a combination of micron-Raman spectroscopy, chemical spot microanalysis and powder X-ray diffraction.

## Chemical composition

The chemical composition of zolenskyite was analysed qualitatively with energy-dispersive microanalysis (EDS, Fig. 2) with a ZEISS EVO 15-MA scanning electron microscope (SEM) equipped with microanalysis EDS system Oxford UltimMax 40 (Oxford Instruments, UK). SEM-EDS X-ray maps and analyses were performed with an acceleration voltage of 15 kV and nominal beam

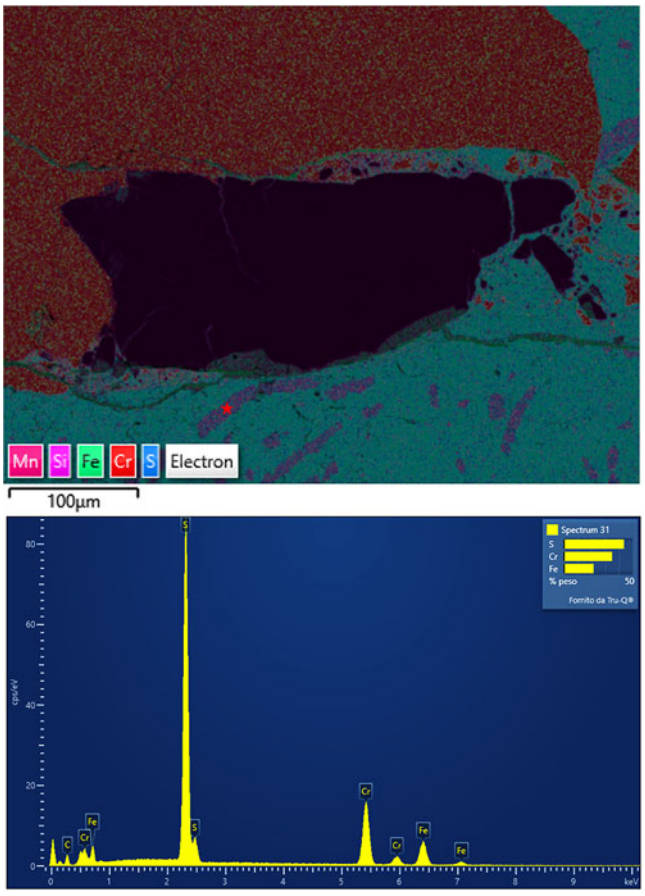


**Figure 2.** X-ray compositional map of the studied sample (top) together with an EDS spectrum of region composed of daubréelite/zolenskyite (bottom).

current of 0.7 nA, acquiring spectra for 20 s live time. The analyses (4 spot analyses) did not show the presence of elements ($Z > 9$) other than Fe, Cr and S (Fig. 2b) and indicate a chemically homogeneous mineral within analytical uncertainties of our measurements. X-ray compositional maps were also collected from a large area (Fig. 2a). The derived empirical formula for zolenskyite is close to pure $FeCr_2S_4$.

## X-ray single-crystal diffraction

A small zolenskyite fragment (0.02 × 0.02 × 0.01 mm in size) from Muonionalusta (Fig. 1) was extracted from the polished section under a reflected light microscope and mounted on a 5 µm diameter carbon fibre, which was, in turn, attached to a glass rod. The fragment consists of crystalline zolenskyite [unit-cell parameters: $a = 12.8345(11)$, $b = 3.4359(3)$, $c = 5.9345(5)$ Å, $\beta = 116.832(6)°$, $V = 233.52(4)$ Å$^3$ and $Z = 2$; space group $C2/m$] associated to minor, fine-grained polycrystalline troilite. Single-crystal X-ray diffraction intensity data of zolenskyite were collected with a Bruker D8 Venture Photon 100 CMOS equipped with graphite-monochromatized Mo$K\alpha$ radiation (Table 1). The detector-to-crystal distance was 5 cm. Data were collected using ω and φ scan modes, in 0.5° slices, with an exposure time of 20 s per frame. The data were corrected for Lorentz and polarization factors and absorption using the software package *APEX3* (Bruker, 2023). A total of 633 unique reflections was collected.

**Table 1.** Data and experimental details for the selected zolenskyite crystal

| | | | |
|---|---|---|---|
| **Crystal data** | | **Refinement** | |
| Formula | $FeCr_2S_4$ | Refinement | Full-matrix least squares on $F^2$ |
| Crystal size (mm) | 0.02 × 0.02 × 0.01 | Final $R_1$ [$F_o > 4\sigma(F_o)$] | 0.0176 |
| Form | block | Final $R_1$ (all data) | 0.0206 |
| Colour | black | Final $wR$ | 0.0861 |
| Crystal system | monoclinic | Number refined parameters | 23 |
| Space group | $C2/m$ (#12) | GoF | 1.271 |
| $a$ (Å) | 12.8345(11) | $\Delta\rho_{max}$ ($e$ Å$^{-3}$) | 0.40 (at 1.52 Å from S1) |
| $b$ (Å) | 3.4359(3) | $\Delta\rho_{min}$ ($e$ Å$^{-3}$) | −0.51 (at 0.79 Å from Cr) |
| $c$ (Å) | 5.9345(5) | | |
| β (°) | 116.832(6) | | |
| $V$ (Å$^3$) | 233.52(4) | $R_{int}$ = | $(n/n-1)^{½}$ $\|F_o^2-F_o(mean)^2\|/\Sigma F_o^2$ |
| Z | 2 | $R_1$ = | $\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ |
| **Data collection** | | Goof = | $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{½}$ |
| Instrument | Bruker D8 Venture | | where $n$ = no. of reflections, |
| Radiation type | Mo$K\alpha$ ($\lambda$ = 0.71073) | | $p$ = no. of refined parameters |
| Temperature (K) | 293(3) | $wR_2$ = | $\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$ |
| Detector to sample distance (cm) | 5 | | |
| Number of frames | 854 | | |
| Measuring time (s) | 20 | | |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.865 | | |
| Absorption correction | multi-scan | | |
| Collected reflections | 2156 | | |
| Unique reflections | 633 | | |
| Reflections with $F_o > 4\sigma(F_o)$ | 431 | | |
| $R_{int}$ | 0.0256 | | |

**Table 2.** Atoms, fractional atomic coordinates, and equivalent isotropic displacement parameters (Å$^2$) for the selected zolenskyite crystal

| Atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|---|---|---|---|---|
| Fe | 0 | 0 | 0 | 0.04483(17) |
| Cr | 0.74115(4) | 0 | 0.69181(9) | 0.04187(16) |
| S1 | 0.63884(8) | 0 | 0.9779(2) | 0.0564(2) |
| S2 | 0.88906(9) | 0 | 0.55072(19) | 0.0546(2) |

**Table 3.** Selected bond distances (in Å) for cations in the zolenskyite crystal analysed

| | | | |
|---|---|---|---|
| Fe–S2 (×2) | 2.3894(10) | Cr–S2 (×2) | 2.3758(8) |
| Fe–S1 (×4) | 2.5208(8) | Cr–S2 | 2.3958(12) |
| <Fe–S> | 2.477 | Cr–S1 (×2) | 2.5378(8) |
| | | Cr–S1 | 2.5727(12) |
| | | <Cr–S> | 2.466 |

Given the similarity in unit-cell values and space groups, the structure was refined starting from the atomic coordinates reported for the $C2/m$ $CrNb_2Se_4$–$Cr_3S_4$-type structure of synthetic $FeCr_2S_4$ (Tressler *et al.*, 1968), using the program *SHELXL-2018* (Sheldrick, 2015). The site occupancy factor at the cation sites was allowed to vary [Fe (and Cr) vs. structural vacancy for the two octahedral sites] using scattering curves for neutral atoms taken from the *International Tables for Crystallography* (Wilson, 1992) but was found to be 26 and 24 $e^-$ for the Fe and Cr positions, respectively. It was then fixed in the subsequent refinement cycles. At the last stage, with anisotropic displacement parameters for all the atoms, the structure was refined to $R1 = 0.0206$ using 633 independent reflections.

Atomic coordinates are given in Table 2. Selected bond distances are shown in Table 3. A Crystallographic Information File (CIF) is deposited with supplementary material (see below)

## Results and discussion

### *Crystal-chemical remarks*

$FeCr_2S_4$ can crystallize in two distinct structural forms – one adopting the thiospinel structure and the other based on a nickeline-type (NiAs-derived) structure – each exhibiting quantitatively different crystallographic, electronic and magnetic properties that reflect their underlying atomic arrangements. In the thiospinel structure, the mineral daubréelite, $FeCr_2S_4$ crystallizes in the cubic system with space group $Fd\bar{3}m$, exhibiting a lattice parameter typically of ∼9.97 Å (Lundqvist, 1943). In this configuration, $Fe^{2+}$ occupies the tetrahedral (8*a*) sites while $Cr^{3+}$ resides at the octahedral (16*d*) sites, leading to a well-ordered distribution of cations. The sulfur anions form a close-packed face-centred cubic sublattice, creating a three-dimensional network of Fe–S–Cr super-exchange paths.

By contrast, in the NiAs-type derivative structure, $FeCr_2S_4$ can show two distinct arrangements: (1) the classic hexagonal structure in which the cations and vacancies are disordered; (2) the monoclinic structure in which $A^{2+}$ ions and vacancies occupy the same plane, and the $B^{3+}$ ions occupy filled alternate planes. Zolenskyite crystallizes in this second type with the structure made up of face-sharing octahedra (Fig. 3).

The NiAs-derived phase often displays semi-metallic or metallic conductivity due to increased cation–anion–cation orbital overlap and reduced cation ordering, resulting in diminished electronic localization (Motizuki *et al.*, 1986). Magnetically, this phase may exhibit weaker long-range order or different transition behaviour, often lacking the well-defined ferrimagnetic transition seen in the

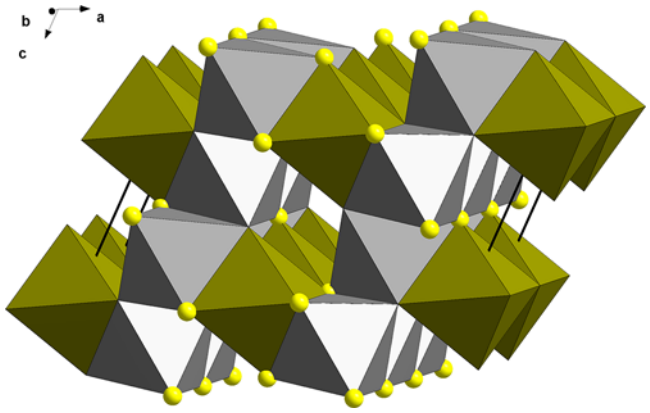


**Figure 3.** The crystal structure of zolenskyite. Yellow and grey octahedra refer to Fe and Cr atoms, respectively. Sulfur atoms are given as yellow circles. The unit cell and the orientation of the structure is given.

spinel form. The effective magnetic moments in the NiAs-type structure can be significantly reduced due to itinerant behaviour or spin compensation effects, and the magnetic susceptibility typically shows a more Pauli-like response.

From a thermodynamic standpoint, the thiospinel structure is the stable equilibrium phase under ambient pressure and moderate temperatures, while the NiAs-type derivative is generally metastable or stabilized only under non-ambient conditions, such as pressures above 5 GPa or through rapid quenching techniques. The energy difference between these phases is subtle – estimated in DFT calculations to be within tens of meV per formula unit – making the relative stability sensitive to factors like stoichiometry, strain, or defect chemistry (e.g. Amiel *et al.*, 2011).

Zolenskyite is the Fe-analogue of brezinaite (ideally $Cr_3S_4$) or the Cr-analogue of heideite ($FeTi_2S_4$).

### *Origin*

Shock conditions estimated for the Muonionalusta meteorite are in the *P* range 13–40 GPa and *T* range 1200–1300 K (Jain and Lipschutz, 1970; Buchwald, 1975). Experiments show that daubréelite can convert into zolenskyite at high pressures and relatively low temperatures (e.g. 5.5 GPa, 520°C; 3 GPa, 200°C; Tressler *et al.*, 1968). On the basis of the coexistence of zolenskyite with stishovite (Fig. 1), we suggest that zolenskyite crystallized by solid-state transformation from daubréelite at a temperature > 1000 K and pressure ≥ 7 GPa.

## Implications

The micron-scale mineralogy studies of meteorites carry profound implications for understanding planetary processes across the solar system. The studies of high-pressure minerals can help to shed light on high-temperature events, shock metamorphism, and aqueous alteration that occurred during the early formation and evolution of planetary bodies. Micron and submicron-sized minerals, indeed, often preserve conditions that are otherwise lost at larger scales, enabling the reconstruction of thermal histories, chemical exchanges, and dynamic processes within asteroids and protoplanets. Furthermore, micron-scale mineralogical analyses can reveal the presence of exotic or transient phases, offering clues about the environments in which these materials formed.

Although zolenskyite in shock veins may be due to kinetic factors such as a metastable crystallization due to rapid cooling during decompression from the peak shock pressures experienced by the meteorite, new theoretical and experimental studies of the stability of thiospinel-related structures are clearly needed.

**Supplementary material.** The supplementary material for this article can be found at https://doi.org/10.1180/mgm.2025.10119

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**Competing interests.** The authors declare none.

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