TROILITE FORMED BY SULFURIZATION: A CRYSTAL STRUCTURE OF SYNTHETIC ANALOGUE. R. Skála[1], M. Drábek[1] and I. Císařová[2], [1]Czech Geological Survey, Klárov 3/131, CZ-118 21 Praha 1, Czech Republic, skala@cgu.cz, [2]Dept. of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, CZ-12843 Praha 2, Czech Republic.

Introduction: While troilite represents a ubiquitous mineral in many meteorite groups, the terrestrial occurrences are rather scarce, limited to several localities worldwide. Troilite is frequently reported also from lunar rocks being the most common sulfide mineral there. Papike et al. [1] note a secondary troilite formed in solid rocks by a process of sulfurization of native iron due to rapid temporary increase of partial pressure of sulfur during the high-temperature shock metamorphism. Here we report on the crystal structure of a synthetic analogue of such troilite which has been prepared by sulfurization process.

Crystal structure of troilite was determined first time by Alsen [2] on the material from Alta Mine, Del Norte County, CA, USA. In that refinement, Alsen considered troilite as hexagonal with space group $P6_3/mmc$ (space group number 194) and unit cell parameters a = 3.43 Å, c = 5.79 Å and V = 58.99 Å^3. Later studies, however, revealed that the refinement of Alsen, based on powder data, is incorrect. Evans [3] solved and refined the crystal structure of troilite on material from the Moon and found that the space group is $P\bar{6}2c$ (space group number 190) with unit-cell parameters a = 5.962 Å, c = 11.75 Å and V = 361.7 Å^3. The latter space group is non-centrosymmetric which results in two possible different spatial arrangements of constituting atoms within the unit cell related by the inversion symmetry operation.

Sample, Procedures, and Results: The starting chemicals used to prepare the troilite analogue were Fe wire 1mm in diameter, 99.998 % purity (Koch-Light Laboratories, Ltd.) and sulfur powder 99.999 % purity (Specpure, Johnson Matthey Chemicals, Ltd.). Iron wire was reduced before use for 3 hours at 800 °C in a stream of hydrogen to eliminate oxides from the surface. The starting material was weighed into a silica tube, which was evacuated and sealed under vacuum. The sample was heated at 900 °C for 12 hours. After run, the silica tube was chilled in ice-water.

Single crystal data were collected on a four-circle diffractometer Nonius KappaCCD equipped with a position sensitive CCD detector using molybdenum radiation. Crystal structure was solved from collected data using software SIR97 [4]. Absorption was corrected using an empirical approach [5]. Crystal structure was refined using SHELXL-97 program [6]. The refinement was against F^2 values. Alternative refinement was carried out minimizing against F values applying the program package JANA2000 [7]. Since the crystal structure of troilite is non-centrosymmetric, both possible atomic arrangements have been tested. Refinements revealed that the synthesized troilite represents so-called racemic twin [8] – it contains both possible atomic configurations related by the inversion symmetry operation. The volume of inverted twin domains in this racemic twin refined by either of applied

Table 1. *Crystal data and structure refinement for synthetic troilite.*

Empirical formula	FeS
Formula weight	87.91
Wavelength	0.71073 Å
Crystal system, space group	hexagonal, $P\bar{6}2c$
Unit cell dimensions	a = 5.9660(4) Å c = 11.7650(8) Å
Volume	362.65(4) Å^3
Z, Calculated density	12, 4.830 g/cm^3
Absorption coefficient	13.309 mm^{-1}
F(000)	504
θ range for data collection	3.94 to 27.41°
Limiting indices	$-7 \le h \le 7$ $-6 \le k \le 6$ $-15 \le \ell \le 15$
Reflections collected / unique	1040 / 296 [R(int)= 0.0130]
Completeness to θ = 27.41°	98.40%
Refinement method	Full-matrix LSQ on F^2
Data / restraints / parameters	296 / 0 / 23
Goodness-of-fit on F^2	1.146
Final R indices [$I > 2\sigma$(I)]	$R1$ = 0.0308, $wR2$ = 0.0762
R indices (all data)	$R1$ = 0.0347, $wR2$ = 0.081
Absolute structure parameter	0.0(8)
Inverted twin domain volume	0.55(8)
Extinction coefficient	0.0059(15)
Largest diff. peak and hole	1.088 and -0.768 e.Å^{-3}

approached attained 55 % (Table 1). Atomic coordinates and equivalent isotropic displacement parameters yielded with SHELX are given in Table 2. Table 3 lists the anisotropic displacement parameters. Crystal structure is layered (Fig. 1) with alternating layers consisting of iron and sulfur atoms.

Table 2. *Atomic coordinates and equivalent isotropic displacement parameters for synthetic troilite. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.*

Atom	*x*	*y*	*z*	U_{eq}
Fe1	0.3787(2)	0.0547(2)	0.1230(1)	0.0181(3)
S1	0.0	0.0	0.0	0.0160(6)
S2	0.3333	0.6667	0.0200(2)	0.0139(4)
S3	0.6656(3)	-0.0029(3)	0.25	0.0136(5)

Conclusions: Crystal structure of synthetic analogue of troilite prepared by sulfurization of an iron wire is consistent with that reported by Evans [3] for lunar troilite. Structure refinement revealed that the material contains roughly equivalent volumes of two inversion-related spatial atomic arrangements thus representing the racemic twin as defined in [8]. Further experiments are planned to find out whether the absolute structure (i.e. the volume of twin domains in a racemic twin) depends on formation conditions.

Table 3. *Anisotropic displacement parameters ($Å^2$) for synthetic troilite. The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$.*

	Fe1	S2	S3	S4
U_{11}	0.0216(4)	0.0147(9)	0.0124(9)	0.0132(7)
U_{22}	0.0183(5)	0.0147(9)	0.0130(9)	0.0132(7)
U_{33}	0.0155(4)	0.0186(11)	0.0158(8)	0.0144(8)
U_{23}	-0.0013(3)	0.0	0.0	0.0
U_{13}	-0.0005(3)	0.0	0.0	0.0
U_{12}	0.0108(3)	0.0073(4)	0.0060(6)	0.0066(3)

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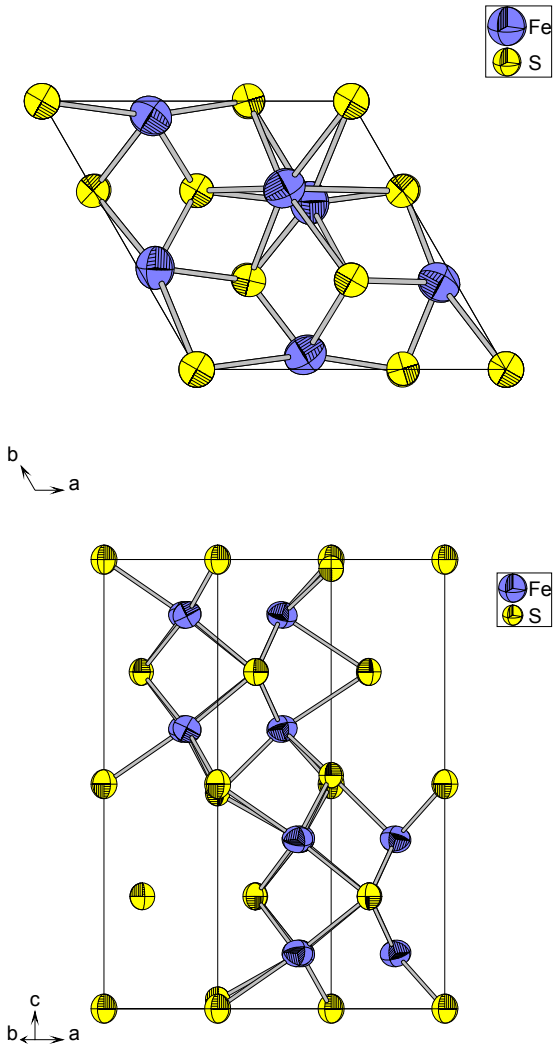

Fig.1. *Crystal structure of synthetic troilite analogue prepared by sulfurization as seen along [001] and projected onto (010), respectively. In the projection onto (010), alternating layers of iron and sulfur atoms are well documented.*