

Caswellsilverite, NaCrS_2 : a new mineral in the Norton County enstatite achondrite

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Abstract

Caswellsilverite, NaCrS_2 , occurs in the Norton County enstatite achondrite as anhedral grains up to 1 mm in size. It is associated with daubréelite, titanioan troilite, ferromagnesian alabandite, oldhamite, kamacite, perryite, and a dark-gray phase, also a new Na–Cr sulfide that contains 13% H_2O and is the terrestrial weathering product of caswellsilverite. Caswellsilverite is yellowish-gray to light-gray in reflected light and exhibits strong bireflectance and anisotropism. Electron microprobe analysis shows that it is stoichiometric NaCrS_2 and contains only minor Ti and Mn. Caswellsilverite has a NaHF_2 -type hexagonal rhombohedral structure ($R\bar{3}m$), and its lattice parameters calculated from X-ray powder patterns are $a = 3.55\text{Å}$ and $c = 19.5\text{Å}$, based on a hexagonal unit cell. Seven of the strongest lines in the X-ray powder pattern are: 6.49(7)(003), 2.60(10)(014), 2.07(8)(017), 1.910(8)(108), 1.779(8)(110), 1.465(6)(204) and 1.134(6)(01.16). Caswellsilverite formed at very low oxygen fugacities after most of the Norton County enstatite achondrite melt had already crystallized. This new mineral was named in honor of Dr. Caswell Silver, distinguished alumnus and benefactor of the Department of Geology and Institute of Meteoritics at the University of New Mexico.

Introduction

During a detailed mineralogic–petrologic study of the Norton County enstatite achondrite, we noticed in the reflected light microscope a gray-colored mineral with conspicuous optical properties, notably strong bireflectance and marked anisotropism. The phase coexists with sulfide minerals and occasionally metallic nickel-iron, and superficially resembles graphite. In fact, the occurrence of graphite in Norton County was first reported by Beck and LaPaz (1951) and was confirmed by us both by microscopy and electron microprobe analysis. The phase is brighter than graphite in reflected light and tarnishes gradually into a brown color by exposure to the atmosphere. Electron microprobe analysis and X-ray powder diffraction shows that this phase is a new mineral, NaCrS_2 . Actually, sodium-chromium sulfide was first noted as a new mineral by Keil (1968) in the enstatite chondrite Indarch, but was not studied in detail. We have named this new mineral caswellsilverite, in honor of Dr. Caswell Silver, distinguished alumnus and benefactor of the Department of Geology and Institute of Meteoritics

at the University of New Mexico. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Occurrence and physical properties

Caswellsilverite occurs in opaque inclusions within enstatite crystals as well as in the brecciated matrix of Norton County. It is a rare mineral in this meteorite, and a total of 11 grains, ranging in size from 0.01 to 1 mm, were found in polished thin sections with a total surface area of about 70 cm^2 . Associated with caswellsilverite are daubréelite, titanioan troilite, ferromagnesian alabandite, oldhamite, kamacite and perryite (Fig. 1), the intergrowth with daubréelite being the most common occurrence. Occasionally, thin bands of caswellsilverite occur within or in contact with daubréelite. In one case, caswellsilverite contains thin veins of daubréelite. Caswellsilverite is anhedral and exhibits a distinct lamellar structure similar to pressure-induced deformation lamellae (Fig. 1). In air and reflected light, caswellsilverite has a metallic luster and shows strong bireflectance. It is distinctly pleochroic: O = pale yellow and E' = gray in air, and O = pale yellow with greenish tint and E' = dark gray

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in oil. In comparison to associated minerals, caswellsilverite is slightly lighter than ferromagnesian alabandite and darker than daubr elite and titanoo troilite. Between crossed polarizers, caswellsilverite shows very strong optical anisotropy. Between nearly crossed polarizers, the color changes from yellowish orange to dark greenish gray when rotating the microscope stage. Internal reflection was not observed in air or in oil. Caswellsilverite is very soft and difficult to polish.

Associated with caswellsilverite is a dark gray phase (G in Fig. 1) that is also a new mineral. Its composition (see below) indicates that it is also a Na-Cr sulfide, but contains ~13% H₂O. It is the terrestrial weathering product of caswellsilverite; this phase will be described elsewhere later. However, since the phase is clearly related to caswellsilverite, a brief description of its important properties is warranted here. The dark gray phase generally occurs as thin bands and blades within caswellsilverite. However, it is also present as individual grains adjacent to caswellsilverite (Fig. 1). Both caswellsilverite and the dark gray phase exhibit a similar lamellar structure, indicating a similar crystal structure. In reflected light, the dark gray phase is darker than caswellsilverite, ferromagnesian alabandite, titanoo troilite and daubr elite. Medium-strong bireflection was observed, and the phase is distinctly pleochroic, showing brownish-gray colors and dark-gray colors. Between crossed polarizers, the phase shows strong anisotropy.

Chemical composition

Caswellsilverite was analyzed with an ARL-EMXSM electron microprobe X-ray analyzer at an excitation voltage of 15 kV and a sample current of about 0.02 μ A. Synthetic NaCrS₂ and minerals of known compositions were used as standards, and corrections for differential matrix effects were made by the ZAF method. Correction factors were determined on Mn-free substances rich in Cr to correct for the partial overlap in wavelength of the CrK β with the MnK α line. For NaCrS₂, this value is 0.11% Mn. Manganese values in the text and in Table 1 are corrected for this overlap. Caswellsilverite varies little in composition within individual grains and from grain to grain. For 12 analyses, the compositional variations are Na 14.9–16.4, Cr 36.7–38.0, Ti 0.13–0.21, Mn <0.02–0.23, and S 46.0–46.9 (in wt.%). Atomic proportions of Na:Cr:S for the average of 12 analyses of caswellsilverite are very near 1:1:2, thus indicating that caswellsilverite is

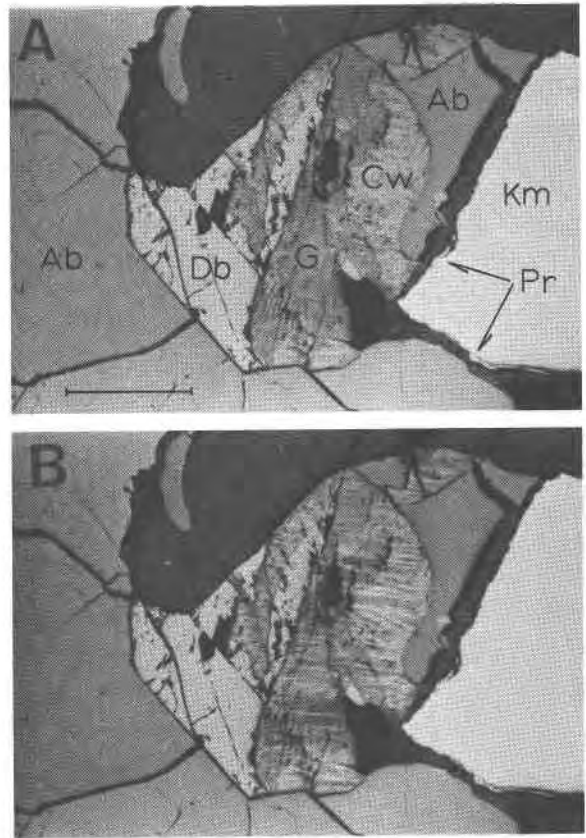


Fig. 1. Occurrence of caswellsilverite (Cw) and coexisting dark gray phase (G) in the Norton County enstatite achondrite. Caswellsilverite is anhedral and is associated with daubr elite (Db), ferromagnesian alabandite (Ab) and kamacite (Km) containing perryite (Pr), as well as enstatite (En). Both caswellsilverite and the dark gray phase exhibit lamellar twinning. Scale bar is 0.1 mm long. A: Plane polarized light. B: Polarized light, partially crossed polarizers.

NaCrS₂. Microprobe analyses indicate that Fe, Ni, Co, Cu, Zn, Mg, Ca and K contents are less than their detection limits (about 0.05%). The molecular formula suggests that the valence state of Cr is trivalent in caswellsilverite, as it is in coexisting daubr elite (FeCr₂S₄). The minor amounts of Ti and Mn could be replacing Cr in the lattice.

We have synthesized NaCrS₂ by Scheel's (1974) method to examine whether caswellsilverite is compositionally and structurally identical to synthetic NaCrS₂, and to use the synthetic compound as a secondary microprobe standard. A ceramic crucible containing coarse chromium powder (1 g), Na₂S·9H₂O (13 g) and sulfur powder (2.2 g) was covered with a lid, and placed in an electric furnace. The space around the crucible was filled with alumina powder to prevent access of oxygen during

Table 1. Average compositions of caswellsilverite (12 analyses), the dark gray phase (5 analyses) and synthetic NaCrS_2 (8 analyses), as obtained by electron microprobe techniques, compared to the composition of stoichiometric NaCrS_2 (in wt.%).

	1	2	3	4
Na	15.7	5.08	16.5	16.5
Cr	37.4	36.3	37.0	37.4
Ti	0.18	0.17	<0.02	-
Mn	0.08	0.17	<0.02	-
S	46.3	45.5	46.3	46.1
Total	99.66	87.22	99.8	100.0
1. Caswellsilverite				
2. Dark gray phase				
3. Synthetic NaCrS_2				
4. Stoichiometric NaCrS_2				

heating. After heating to 1000°C , the furnace was cooled down to 300°C at a rate of $25^\circ\text{C}/\text{hour}$ and was then allowed to cool without rate control to room temperature. With this procedure, crystals consisting of thin hexagonal plates with metallic luster were obtained that are 5 mm in maximum size. X-ray powder diffraction and electron microprobe analysis confirmed that the synthetic compound is identical to caswellsilverite.

The dark gray phase that coexists with caswellsilverite is also a sodium-chromium sulfide but is lower in Na (avg. 5.08 wt.%) compared to caswellsilverite (avg. 15.7 wt.%) and also shows a low total summation of 87.2 wt.% (Table 1). Its compositional range, based on 5 analyses, is Na 3.91–6.15, Cr 35.8–37.1, Ti 0.16–0.18, Mn 0.05–0.29, and S 45.1–46.2 (in wt.%), and Fe, Ni, Co, Cu, Zn, Mg and K contents are below the detection limits (~ 0.05 wt.%). Furthermore, we could not detect fluorine, carbon and nitrogen in the dark gray phase, using electron microprobe techniques, but found it to contain oxygen. Ion microprobe analysis identified hydrogen in amounts commensurate with a content of $\sim 13\%$ H_2O . Thus, the dark gray phase is a water-bearing Na–Cr-sulfide, a new mineral that formed by terrestrial weathering of caswellsilverite. It will be described in detail later.

X-ray diffraction study

A sample of caswellsilverite was scraped out from a polished thin section, after the grain had

been analyzed by electron microprobe techniques, and was studied by X-ray diffraction techniques, using a 114.6 mm Debye-Scherrer camera and Ni-filtered Cu radiation. The X-ray powder pattern contains a few weak lines due to unknown material coexisting with caswellsilverite, but most lines agree well with those of synthetic NaCrS_2 and the standard X-ray powder data for NaCrS_2 (Table 2). According to Boon and Mac Gillavry (1942) and Rüdorff and Stegemann (1943), NaCrS_2 has a NaHF_2 -type hexagonal rhombohedral structure (space group $R\bar{3}m$), consisting of hexagonal Na-, Cr- and S-layers, where Cr-layers are separated from each other by two S-layers and one Na-layer. Lattice parameters of caswellsilverite from the Norton County enstatite achondrite are $a = 3.55\text{\AA}$ and $c = 19.5\text{\AA}$, based on a hexagonal unit cell, and are consistent with the data for synthetic NaCrS_2 of $a = 3.51\text{\AA}$ and $c = 19.57\text{\AA}$ (Boon and Mac Gillavry, 1942) and $a = 3.534\text{\AA}$ and $c = 19.49\text{\AA}$ (Rüdorff and Stegemann, 1943), obtained by single crystal structure analysis. The small amounts of Ti in caswellsilverite (Table 1) may be present in the Cr position, because NaTiS_2 has the same NaHF_2 -type structure as NaCrS_2 (Rüdorff, 1965). There are no crystallographic data available for sodium-manganese sulfide. However, Parant *et al.* (1971) synthesized NaMnO_2 which has a distorted NaFeO_2 - (or NaHF_2) type structure, and NaCrO_2 is structurally of the NaFeO_2 -type (Rüdorff and Becker, 1954). Thus, the small amounts of Mn in caswellsilverite (Table 1) may occupy the Cr position without causing a deformation of the lattice.

Comparison of the physical properties of caswellsilverite and synthetic NaCrS_2

Chemical composition and the X-ray powder pattern of caswellsilverite agree well with those of synthetic NaCrS_2 . For the purpose of further confirmation and comparison, the optical properties and reflectivity were measured for synthetic NaCrS_2 . Two polished sections were prepared of synthetic NaCrS_2 crystals mounted, respectively, parallel to $\{0001\}$ and parallel to the c -axis, for the purpose of measuring the optical properties, reflectance and micro-indentation hardness. Synthetic NaCrS_2 exhibits a metallic luster and a yellowish green tint in obliquely incidental light. In reflected light, it looks bright—slightly greenish on the section parallel to $\{0001\}$ and more yellowish on that parallel to the c -axis. Bireflectance is strong, and reflection pleochroism in air is: O = pale yellow with greenish tint,

Table 2. X-ray powder diffraction pattern of caswellsilverite from the Norton County enstatite achondrite

Caswellsilverite		Synthetic NaCrS ₂		NaCrS ₂ (ASTM 10-292)	
d (Å)	I/I ₀ *	d (Å)	I/I ₀ *	d (Å)	I/I ₀
6.49	7	6.46	8	6.46	7
		3.24	1	3.22	1
		3.04	2	2.99	2
2.90	4	2.89	1	2.91	1
2.66**	2,B				
2.60	10	2.60	10	2.58	10
2.07	8	2.07	6	2.05	6
1.910	8	1.910	9	1.89	9
1.779	8	1.781	9	1.76	9
1.750**	4				
1.713	2	1.717	4	1.70	4
				1.64	2
1.625	1	1.623	4,B	1.62	5
				1.55	1
1.537	2	1.537	5	1.54	6
1.465	6	1.470	6	1.46	8
				1.36	1
1.347	1	1.348	3	1.34	4
1.302	4	1.302	6	1.294	8
		1.270	2	1.280	2
1.200	4	1.200	6	1.200	1
				1.195	8
1.160	1	1.160	4	1.159	4
1.134	6	1.134	7	1.133	10
1.079	2	1.076	2	1.080	1
1.049	6	1.049	7	1.055	4
				1.043	10

*Visually estimated.

**Unknown lines

B Broad

and E' = grayish white. In oil, O remains rather bright but looks more greenish than in air, and E' becomes much darker gray. The optical anisotropy is very strong, both in air and in oil. Internal reflection was not observed in air or in oil. Reflectance of synthetic NaCrS₂ was measured in air at 20 nm intervals and at standard wavelengths in the visible region of the spectrum (Table 3). R_O and R_{E'}, throughout the visible spectrum indicate that NaCrS₂ (uniaxial) has a negative optic sign. It was difficult to obtain reliable reflectance data of caswellsilverite, because of the thinness of the bireflecting lamellae and the poor polishing quality of the monoreflecting areas. Non-principal reflectances measured on a well-polished area containing three bireflecting lamellae of caswellsilverite range from 24 to 28% in the middle of the visible spectrum. These values fall between R_O and R_{E'} of synthetic NaCrS₂ (Table 3). The Vickers hardness number of synthetic NaCrS₂ at 15 gram load is ~17–45, based on four measurable indentations. Indentations on the {0001} plane are perfect or nearly so, and those on sections parallel to the c-axis are asymmetric with respect to the trace of {0001}. Such indentations are largely developed on one side of the {0001} trace and only fractionally developed on the other, as if the

Vickers pyramid had skidded when it first touched the section. This may indicate that the true maximum VHN of synthetic NaCrS₂ exceeds the observed 45 by some large amount. VHN of caswellsilverite was not measured due to the small grain size of the mineral. Although hardness data could not be directly compared, caswellsilverite and synthetic NaCrS₂ are similar in their polishing properties and qualitative optical properties, and apparently concordant in reflectance in the middle of the visible spectrum. Under a carefully calibrated comparison microscope, homologous areas of caswellsilverite and synthetic NaCrS₂ look alike when viewing both samples side by side.

Discussion

Of the known meteoritic minerals, caswellsilverite is only the second sulfide that contains sodium as a major component, the other being djerfisherite, K₃(Na,Cu)(Fe,Ni)₁₂S₁₄ (Fuchs, 1966). The occurrence of caswellsilverite is further confirmation of the highly reducing conditions under which the Norton County enstatite achondrite formed. Sodium and chromium normally are very strongly lithophile elements in terrestrial, lunar and most meteoritic rocks and become chalcophile only under extremely reducing conditions. The Norton County

Table 3. Reflectance of synthetic NaCrS₂ measured in air at 20 nm intervals and at standard wavelengths*

	R _O	R _{E'}		R _O	R _{E'}
400 nm	26.7%	19.3%	600 nm	32.2%	20.8%
420	26.2	20.1	620	31.4	20.5
440	26.3	21.9	640	30.7	20.5
460	27.4	21.5	660	29.4	20.1
480	30.0	21.7	680	26.7	18.1
500	31.6	22.0	700	28.8	18.0
520	32.3	22.0	At standard wavelengths		
540	32.8	21.8	470	29.6	21.4
560	33.0	21.7	546	32.9	21.8
580	32.5	21.3	589	31.8	21.1
			650	29.1	20.1

*Measured by Dr. B. F. Leonard, U.S. Geological Survey, Denver, Colorado, with a Zeiss MPM microphotometer fitted with a Smith vertical illuminator and a Veril type-S running interference filter whose half-width at half-height is ~10 nm. Objective 16x Po1, N.A. 0.35. Zeiss-calibrated SiC standard no. 052. Mounts press-leveled on plasticine.

enstatite achondrite formed under just such extremely reducing conditions, as is indicated by the occurrence of essentially FeO-free enstatite and olivine, the presence of perryite, $(Ni,Fe)_5(Si,P)_2$, as well as by the chalcophile behavior of other, normally lithophile elements (*e.g.*, Ti in titanite, Mn, Mg in ferromagnesian alabandite, $(Mn,Fe,Mg)S$; Ca in oldhamite, CaS; and Cr in daubréelite, $FeCr_2S_4$; Keil and Fredriksson, 1963; Keil, 1969; Okada *et al.*, 1980, 1981). Thus, we suggest that during the crystallization of the Norton County melt, oxygen fugacities were extremely low, and concentrations of cations that normally combine with sulfur so low (after most of the silicates had crystallized), that some of the sulfur combined with available sodium and chromium to form caswellsilverite.

Textural relationships between caswellsilverite, the dark gray phase, daubréelite and ferromagnesian alabandite suggest complex reactions to have taken place between these phases (*e.g.*, Figs. 1A, B). For example, textural evidence suggests that caswellsilverite may have formed by reaction of, say, an Na_2S -rich melt and daubréelite and/or chromium sulfide component in ferromagnesian alabandite.

Finally, we note that Keil (1968) mentioned the occurrence of sodium-chromium sulfide from the Indarch enstatite chondrite, and Ramdohr (1963, 1964, 1973) described the occurrence of several, apparently heretofore unknown minerals with layer structures from enstatite achondrites and chondrites. He referred to these phases as A, B, I, II and III, but did not completely characterize them so that naming as new minerals was not warranted. However, judging from his descriptions of the optical properties of these phases and their occurrences, it is possible that some correspond to caswellsilverite (and the dark gray phase). Ramdohr (1963, 1964, 1973) noted the occurrence of his phases in many enstatite achondrites and chondrites. Thus, it is likely that the occurrence of caswellsilverite (and the dark gray phase) is not restricted to Norton County but is a widespread, albeit rare, mineral, in other enstatite achondrites and, possibly, enstatite chondrites as well.

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have largely been incorporated into the section entitled "Comparison of the physical properties of caswellsilverite and synthetic $NaCrS_2$ " and Table 3. Quantitative color data for synthetic $NaCrS_2$ are available from Dr. B. F. Leonard.

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