

STURMANITE, A FERRIC IRON, BORON ANALOGUE OF ETTRINGITE

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ABSTRACT

Sturmanite, $\text{Ca}_6(\text{Fe}^{3+}_{1.5}\text{Al}_{0.3}\text{Mn}^{2+}_{0.2})_{\Sigma 2.0}(\text{SO}_4)_{2.3}\{\text{B}(\text{OH})_4\}_{1.2}(\text{OH})_{12}\cdot 25\text{H}_2\text{O}$, is a ferric iron, boron-containing analogue of ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$. Sturmanite occurs on hematite and barite as flattened dipyrarnidal crystals at the Black Rock mine, Republic of South Africa. The probable space group is $P31c$, a 11.16(3), c 21.79(9)Å, $Z=2$. It is bright yellow and has one perfect cleavage on $\{10\bar{1}0\}$. The density is 1.847 g/cm³ (obs.), 1.855 g/cm³ (calc.). Optically sturmanite is uniaxial (+), with $\omega=1.500$, $\epsilon=1.505$, but some crystals have a core that is optically (-), with $\epsilon=1.497$, $\omega=1.499$. It is weakly dichroic with O pale green and E pale yellow green. The principal X-ray-diffraction lines [d in Å (intensity)(hkl)] are: 9.67(100)(100), 5.58(70)(110), 3.89(70)(114), 2.774(50)(304), 2.582(60)(216), 2.215(50)(226, 320). Sturmanite is named in honor of B. Darko Sturman, mineralogist at the Royal Ontario Museum.

Keywords: sturmanite, ettringite group, new mineral species, sulfate, Republic of South Africa.

SOMMAIRE

La sturmanite, $\text{Ca}_6(\text{Fe}^{3+}_{1.5}\text{Al}_{0.3}\text{Mn}^{2+}_{0.2})_{\Sigma 2.0}(\text{SO}_4)_{2.3}\{\text{B}(\text{OH})_4\}_{1.2}(\text{OH})_{12}\cdot 25\text{H}_2\text{O}$, est un analogue ferrique et borifère de l'ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$. La sturmanite se présente en cristaux dipyrarnidaux aplatis sur l'hématite et la barite à la mine Black Rock, république de l'Afrique du Sud. Le groupe spatial probable est $P31c$; a 11.16(3), c 21.79(9)Å, $Z=2$. Le minéral est jaune clair et possède un clivage parfait selon $\{10\bar{1}0\}$. La densité mesurée est 1.847 (obs), 1.855 (calc.). La sturmanite est optiquement uniaxe (+), $\omega=1.500$, $\epsilon=1.505$, mais certains cristaux ont un coeur uniaxe (-), avec $\epsilon=1.497$, $\omega=1.499$. Le minéral est faiblement dichroïque, avec O vert pâle, et E vert jaunâtre pâle. Les principales raies de diffraction des rayons X [d en Å (intensité)(hkl)] sont: 9.67(100)(100), 5.58(70)(110), 3.89(70)(114), 2.774(50)(304), 2.582(60)(216), 2.215(50)(226, 320). La sturmanite est dédiée à B. Darko Sturman, minéralogiste au Royal Ontario Museum.

(Traduit par la Rédaction)

Mots-clés: sturmanite, groupe de l'ettringite, nouvelle espèce minérale, sulfate, république de l'Afrique du Sud.

INTRODUCTION

The mineral described herein was brought to our attention by Dr. Richard V. Gaines of Pottstown, Pennsylvania, who recognized it as being uncommon and worthy of further investigation. Preliminary X-ray powder-diffraction and optical examination indicated that the mineral is related to ettringite, but with substantial differences. Qualitative chemical tests indicated the presence of significant ferric iron and the near-absence of aluminum. We therefore proceeded on the assumption that it is a new mineral species related to ettringite; this assumption was borne out by subsequent studies.

We take pleasure in naming this new mineral *sturmanite* in honor of B. Darko Sturman of the Department of Mineralogy and Geology, Royal Ontario Museum, Toronto. His contributions to systematic mineralogy, and in particular, his studies of phosphate minerals from the Yukon, together with his refinement of methods used in optical mineralogy, reflect his devotion to mineralogy. The mineral and the name were approved by the Commission on New Mineral Names, I. M. A., prior to publication. Holotype material is preserved at the Smithsonian Institution under catalogue number 148261. Cotype and metatype specimens are preserved both in the Smithsonian Institution and the Royal Ontario Museum.

OCCURRENCE

Sturmanite has been observed in two parageneses on specimens reported to have come from the Kuruman district in the Republic of South Africa. We acquired the type specimen from Dr. Gaines, who obtained it from a mineral dealer in Johannesburg, Republic of South Africa. The exact mine from which these specimens were recovered was not specifically recorded, but both assemblages have abundant barite, which is known in quantity only from the Black Rock mine, then under operation by

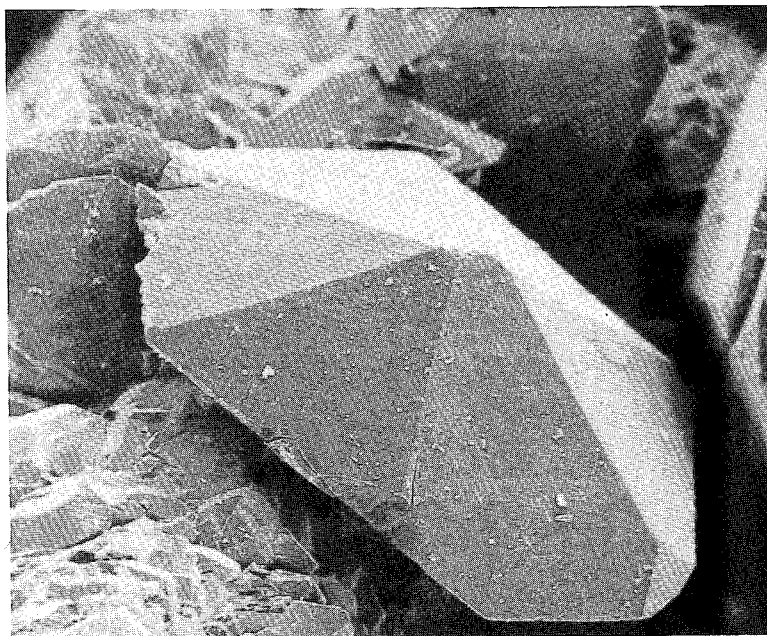


FIG. 1. Scanning electron photomicrograph of a sturmanite crystal (80x).

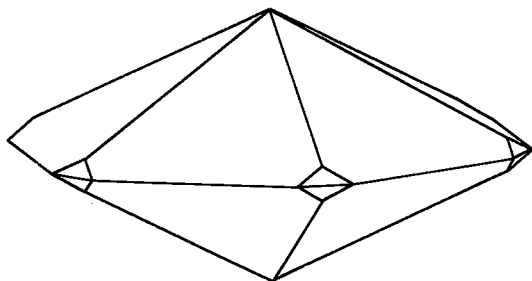


FIG. 2. Clinographic projection of a sturmanite crystal. The dominant form is $\{10\bar{1}4\}$, and the less prominent form is $\{11\bar{2}4\}$.

courtesy of Dr. E. A. J. Burke of the Vrije University in Amsterdam, The Netherlands; a collector had obtained these in the Republic of South Africa. On these specimens, sturmanite crystals of identical habit to those on the holotype specimen encrust druse barite which, in turn, encrusts massive hematite. Barite is also found as inclusions in these specimens of sturmanite. Also acquired from Dr. Burke are brown opaque pseudomorphs after sturmanite. These are composed predominantly of gypsum, with remnant sturmanite inferred to be present from weak X-ray-diffraction lines attributable to an ettringite-group mineral. These pseudomorphous crystals encrust massive barite and mimic sturmanite morphologically in all but one detail, the absence of the smaller dipyrmaid. On all observed specimens, sturmanite is the last phase to form.

MORPHOLOGICAL, PHYSICAL, AND OPTICAL DESCRIPTION

Associated Manganese Mines of South Africa, Ltd. Details of the mineralogy of the mines in the Kalahari manganese field have been summarized by Wilson & Dunn (1978), who provided abundant references to the geology of the area.

The holotype specimen consists of yellow euhedral sturmanite crystals encrusting black, opaque hematite ore. Barite is abundant as inclusions in the sturmanite crystals; sturmanite with especially abundant barite inclusions is turbid. Most observed material is transparent.

We obtained additional specimens through the

Sturmanite occurs as hexagonal dipyramidal crystals, tabular on $\{0001\}$, with a width-to-height ratio of approximately 3:1. Figure 1 is a SEM photomicrograph of a typical sturmanite crystal, and Figure 2 is a projection of an idealized crystal. The crystals are composed of dipyramids; the dominant one is $\{10\bar{1}4\}$, and $\{11\bar{2}4\}$ is present as small truncations. Both forms have equivalent vitreous luster.

There is no epitaxy with associated minerals. Sturmanite does exhibit parallel growth, with successive individuals stacked parallel to {0001}. Maximum observed size of the crystals is 2.0 mm. All specimens seen consist of euhedral crystals.

Sturmanite has one perfect cleavage, parallel to {10 $\bar{1}$ 0} and easily produced. Sturmanite is exceedingly brittle. The streak is light yellow. The luster is vitreous on cleavage surfaces and vitreous to slightly greasy on fracture surfaces. The Mohs hardness is approximately 2½. The density, measured with heavy liquids and pycnometer, is 1.847 g/cm³, compared with the calculated value of 1.855 g/cm³, determined using the formula with 25H₂O and unit-cell parameters. Sturmanite does not fluoresce in ultraviolet radiation, and there is no cathodoluminescence under excitation by the electron-microprobe beam.

Sturmanite is bright yellow in fresh unaltered material. Optically, sturmanite is uniaxial (+), with indices of refraction ω 1.500 and ϵ 1.505. It is weakly dichroic with *O* pale green and *E* pale yellowish green; absorption *E* > *O*. Some sturmanite crystals are optically zoned; a uniaxial (–) core has indices of refraction ω 1.499 and ϵ 1.497. Absorption and dichroism in these sectors are similar to those of the optically positive material. Calculation of the Gladstone–Dale relationship using the constants of Mandarino (1976) yields a value K_C of 0.275 for the chemical composition, compared with a value K_P of 0.272 for physical properties. These provide excellent agreement using the compatibility relationship proposed by Mandarino (1979).

X-RAY CRYSTALLOGRAPHY

Single crystals studied using Weissenberg and precession techniques show that sturmanite is hexagonal, *a* 11.16(3), *c* 21.79(9) Å. These final parameters were obtained by least-squares refinement of powder-diffraction data obtained from a 114.6-mm-diameter Gandolfi-camera photograph of a polycrystalline specimen with Si as an internal standard, and CuK α X radiation. The powder data are listed in Table 1.

The diffraction data are similar to those of members of the ettringite group. In particular, there is a very pronounced subcell having parameters *A* = *a* and *C* = *c*/2; i.e., all reflections having *l* = 2*n* + 1 are very weak. Extinctions are present for reflections *hhl*, *l* = 2*n* + 1, as consistent with a glide plane. As all reflections having *l* = 2*n* + 1 are extremely weak (most are not observable even on photographs obtained with long exposures), the assignment of the glide plane is more problematical than is the usual case. Moore & Taylor (1970) determined the crystal structure of ettringite and concluded that the true space-group is *P*31*c*. They noted that

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR STURMANITE

hk \bar{l}	<i>d</i> (calc.)	<i>d</i> (obs.)	I/I ₀
100	9.66	9.67	100
110	5.58	5.58	70
112	4.97	4.97	15
104	4.75	4.75	20
114	3.90	3.89	70
204	3.615	3.612	20
212	3.463	3.447	20
300	3.222	3.223	20
304	2.773	2.774	50
008	2.724	2.725	1
216	2.575	2.582	60
224	2.483	2.485	5
314	2.405	2.404	15
226	2.212	2.215	50
320	2.217		
316	2.157	2.161	40
410	2.109	2.110	5
324	2.054	2.053	10
334	1.760	1.759	2
424	1.732	1.732	5
1.1.12	1.727		
418	1.668	1.668	15
600	1.611	1.612	5
		1.578	2
		1.526	5
		1.301	2
		1.261	1

ettringite commonly shows diffraction relations consistent with space group *P*6₃/*mmc*, but that this is caused by either twinning or disorder. As our observations for sturmanite are compatible with space group *P*6₃/*mmc* (and *P*6₂*c* or *P*6₃*mc*), and because sturmanite is isostructural with ettringite, we conclude that the probable space-group for sturmanite is *P*31*c*; crystals are either twinned or disordered to produce the apparent higher symmetry, by analogy with ettringite.

CHEMISTRY

An emission-spectrograph analysis of sturmanite by D. C. arc showed very strong lines of calcium, strontium and barium, strong lines of boron and aluminum, and lines of moderate intensity for iron, manganese and silicon. Qualitative electron-microprobe scans also showed significant Ca, Fe and S, with minor amounts of Al and Mn. Fluorine and phosphorus were found to be present in amounts less than 0.1 and 1.0 wt.%, respectively.

Sturmanite is readily soluble in cold 3*N* hydrochloric acid with the evolution of CO₂, resulting in an insoluble residue of 25 wt.%, which was subsequently identified as barite. No significant barium or strontium was found in the soluble fraction. Optical examination also revealed, in addition to barite, the presence of fluid inclusions contain-

TABLE 2. CHEMICAL ANALYTICAL DATA FOR STURMANITE

	<u>1.</u>	<u>2.</u>	<u>3.</u>	<u>4.</u>	<u>5.</u>	<u>6.</u>	<u>7.</u>	<u>8.</u>
CaO	24.8	22.5			24.4	25.6		25.62
Fe ₂ O ₃	8.09	7.45	7.22	7.18	7.62	8.84		9.11
MnO	0.90	0.87				1.30		1.16
Al ₂ O ₃	1.0	0.8				1.13		1.08
SO ₃				13.7 (16.9)*	12.2 (14.2)*			14.02
B ₂ O ₃			2.82 (3.5)*	2.6 (3.2)*				3.18
H ₂ O							46.7	45.83

- 1974 µg (impure), includes soluble BaSO₄ and soluble CaCO₃ and liquid inclusions.
- 4360 µg (impure), includes soluble BaSO₄ and soluble CaCO₃ and liquid inclusions.
- 2005 µg (impure), includes soluble BaSO₄ and soluble CaCO₃ and liquid inclusions.
- 3980 µg (impure), includes soluble BaSO₄ and soluble CaCO₃ and liquid inclusions.
- 5045 µg soluble material (24.4 percent insoluble).
- 142 µg optically pure material.
- 229 µg optically pure material, Penfield method.
- Theoretical composition for Ca_{6.0}(Fe³⁺_{1.5}Al_{0.3}Mn²⁺_{0.2})(SO₄)_{2.3}{B(OH)₄}_{1.2}(OH)_{12.0} · 25.0 H₂O.

*Values in parentheses are normalized on the basis of precise Fe³⁺ determinations.

ing radial, fibrous aluminum sulfate. Calcite was also a solid contaminant. Optically pure material did not evolve CO₂ when dissolved in acid, indicating that the CO₂ can be ascribed to calcite.

The chemical analysis of cations was done by atomic-absorption spectroscopy with a precision of ±2% of the amount present. Sulfate was determined indirectly using amino perimidine; the precision was ±10% of the amount present. Boron was determined spectrophotometrically using carminic acid. The precision of the boron analysis is approximately ±5% of the amount present. Water was determined using the Penfield method.

The fact that most of the chemical analyses were carried out with impure material caused some difficulty. Accordingly, 142 micrograms of optically pure material were analyzed for iron, calcium, manganese and aluminum. Water was determined on another 229 micrograms of optically pure material. Because of the limited availability of pure material, all other analyses were performed on material with some impurities as described above. Sulfur and boron results provide problems inasmuch as both elements might be present in the fluid inclusions. Because of the scarcity of crystals that lack fluid inclusions, we cannot give more accurate analytical data at this time. The values for Ca in columns 1 through 5 (Table 2) are high owing to soluble inclusions of calcite. Measured SO₃ and B₂O₃ values in columns 3, 4 and 5 (Table 2) are "as determined" values, coupled (in parentheses) with values corrected by normalization, based on the Fe₂O₃ values of 8.84% by weight, obtained on optically pure material. Because these S and B values are subject to a greater standard error than the values obtained for other elements, interpretation of these data

is tentative pending a crystal-structure determination. The paucity of material precluded determinations of the oxidation state of Mn. Although the presence of Fe³⁺ and Al suggests that the Mn might be present as Mn³⁺, the absence of the typical color absorption of Mn³⁺ and the effects of Jahn-Teller distortions suggest that Mn³⁺ is not present. Inasmuch as jouravskite, an isostructural phase, has Mn⁴⁺ reported, manganese in this oxidation state might be a possibility in sturmanite, but that is speculative. We have tentatively assigned the Mn to Mn²⁺.

DISCUSSION

The data for sturmanite indicate that it is a member of the ettringite group, which includes, for example, ettringite Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O and bentonite Ca₆(Cr,Al)₂(SO₄)₃(OH)₁₂·26H₂O. The latter was recently discovered in the "Mottled Zone" in Israel (Gross 1980).

Taylor (1973) reviewed the crystal chemistry of the ettringite group. He noted that the structure consists of columns (parallel to *c*) of Al octahedrally coordinated by hydroxyl ions, alternating with groups of 3 Ca ions co-ordinated by four hydroxyl and four H₂O. These columns have the composition Ca₆{Al(OH)₆}₂·24H₂O. The eight-co-ordinated Ca may be replaced by ions such as Pb²⁺, and octahedrally co-ordinated Al replaced by Fe, Mn, etc. Channels between the columns are occupied by anionic groups such as (SO₄)²⁻ and (CO₃)²⁻ or by 2H₂O. There are four anion-sites per 6 Ca. These may be occupied by combinations of various anionic groups or H₂O that must sum to four (or less) per 6 eight-fold co-ordinated ions such as Ca. The repeat distance along a column is *C* = *c*/2, the prominent

translation of the substructure, with the superstructure being due to ordering of anionic groups in the sites between columns.

The chemical formula for sturmanite was calculated using the following weight percentages, as derived from the chemical compositions in Table 2: CaO 25.6, Fe₂O₃ 8.84, Al₂O₃ 1.13, MnO 1.30, B₂O₃ 3.2, SO₃ 14.2, H₂O 46.7, sum = 101.0%. This analysis yields, on the basis of 6 Ca atoms: Ca_{6.0}(Fe³⁺_{1.5}Al_{0.3}Mn²⁺_{0.2})_{Σ2.0}(SO₄)_{2.3}{B(OH)₄}_{1.2}(OH)_{12.0}•25.7H₂O.

As noted previously, the analytical values for S and B are subject to a greater error than those for other elements. We were able to obtain a precise value for Fe₂O₃ on optically pure material (specimen #6, Table 2). Accordingly, we normalized the S and B values of specimens 3, 4 and 5 based on values required to correct the low Fe values of specimens 3, 4 and 5 to the precise value of composition 6. We have chosen the lower normalized values (14.2% SO₃ and 3.2% B₂O₃) for use in calculation of the formula, in part because the higher values would lead to an excessively high wt.% summation.

Sturmanite can therefore be characterized as the Fe³⁺ and B analogue of ettringite, with the octahedrally co-ordinated sites in the columns occupied primarily by Fe³⁺ in the type material, and also by Al and Mn. Although substitution of a boron anionic group for (SO₄)²⁻ is uncommon, we note that B was described in an ettringite-like mineral from Franklin, New Jersey, by Hurlbut & Baum (1960). The Franklin material is presently under re-investigation; it has a S:B ratio very similar to that of sturmanite and is likely the Al-analogue of sturmanite.

An idealized formula for sturmanite is tentative, in part owing to some ambiguity in the number of S and B atoms. The formula is provisionally given as Ca₆(Fe³⁺, Al, Mn²⁺)₂(SO₄)_{2.3}{B(OH)₄}_{1.2}(OH)_{1.2}•25H₂O. The assignment of B to a B(OH)₄ group *i.e.*, to tetrahedral co-ordination, is not based on direct evidence. This anionic group was specified because: (1) it is consistent with overall charge-balance requirements, (2) it is in agreement with the total H₂O determined, and (3) it is reasonable by analogy with other boron minerals. The total H₂O is less than the 26 in the idealized formula, consistent with the crystal-structure relations of the et-

tringite group. The ideal 26H₂O are composed of 24 within the columns of the structure, plus two from the channels between the columns. We propose an excess of SO₄ and B(OH)₄ in those channels. This is compensated for, in part, by a deficiency of H₂O. In addition, we recognize the difficulty of H₂O determinations on such a highly hydrated mineral and note that part of the variance in H₂O can be due to analytical error.

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