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THE OCCURRENCE OF TWO RARE POLYTYPES OF WURTZITE, 4*H* AND 8*H*, AT MONT SAINT-HILAIRE, QUEBEC

GEORGE Y. CHAO[1]

Ottawa–Carleton Geoscience Centre, Department of Earth Sciences, Carleton University, Ottawa, Ontario K1S 5B6

ROBERT A. GAULT[2]

Research Division, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

Abstract

The rare 4*H* and 8*H* polytypes of wurtzite have been identified on the basis of single-crystal X-ray diffraction from sodalite xenoliths in the nepheline syenite in the Poudrette Quarry, Mont Saint-Hilaire, Quebec. They are hexagonal, space group $P6_3mc$, *a* 3.8277(3), *c* 12.521(8) Å for wurtzite-4*H* and *a* 3.8286(3), *c* 25.041(8) Å for wurtzite-8*H*. Wurtzite-4*H* may be distinguished from the other polytypes by the presence of the 2.596, 1.997, 1.382 and 1.2283 Å lines and by the strong intensity of the 3.203 Å line in the powder-diffraction pattern. Wurtzite-8*H* is distinguished by the presence of the moderately strong 3.082 Å line and the weak 2.766, 1.876, 1.666 and 1.341 Å lines and by the increased intensity of the 3.129 and 1.633 Å lines. The mineral occurs as pale green or reddish brown irregular grains with an adamantine to slightly waxy luster and as well-formed, hexagonal, short prismatic to tabular crystals with pedial terminations. Electron-microprobe analyses show the 4*H* polytype to be almost pure ZnS, with a metal:sulfur ratio of 1, whereas the 8*H* polytype shows minor substitution of Fe and Mn for Zn, and is metal-deficient with respect to sulfur.

Keywords: wurtzite-4*H*, wurtzite-8*H*, polytypes, X-ray diffraction, Mont Saint-Hilaire, Quebec.

Sommaire

Les polytypes 4*H* and 8*H* de la wurtzite, très rares, ont été identifiés par diffraction X sur cristal unique dans des xénolithes à sodalite provenant de syénite néphélinique dans la carrière Poudrette, au mont Saint-Hilaire, Québec. Ils sont hexagonaux, groupe spatial $P6_3mc$, *a* 3.8277(3), *c* 12.521(8) Å pour la wurtzite-4*H*, et *a* 3.8286(3), *c* 25.041(8) Å pour la wurtzite-8*H*. On distingue la wurtzite-4*H* des autres polytypes par la présence des raies à 2.596, 1.997, 1.382 et 1.2283 Å et par la forte intensité de la raie à 3.203 Å dans le spectre de diffraction sur poudre. On distingue la wurtzite-8*H* par la présence de la raie à 3.082 Å, d'intensité relativement intense, et les faibles raies à 2.766, 1.876, 1.666 et 1.341 Å, ainsi que par l'intensité accrue des raies à 3.129 et 1.633 Å. La wurtzite se présente en cristaux vert pâle à brun rougeâtre de forme irrégulière, ayant un éclat adamantin ou légèrement cireux, et en cristaux hexagonaux bien formés en prismes trappus ou tabulaires, avec terminaisons pédiales. D'après les analyses à la microsonde électronique, la composition du polytype 4*H* est le pôle ZnS presque pur, avec un rapport métal à S égal à 1, tandis que le polytype 8*H* contient de faibles teneurs en Fe et Mn à la place du Zn, et montre un léger déficit en métaux par rapport au soufre.

(Traduit par la Rédaction)

Mots-clés: wurtzite-4*H*, wurtzite-8*H*, polytypes, diffraction X, mont Saint-Hilaire, Québec.

Introduction

The rare natural occurrence of the wurtzite polytypes 4*H*, 6*H* and 15*R* was first reported from clay-ironstone concretions in western Pennsylvania and eastern Ohio by Seaman & Hamilton (1950). Morphological and single-crystal X-ray-diffraction data and crystallographic, physical and chemical properties of these polytypes were given by Frondel & Palache (1950). Calculated X-ray powder-diffraction patterns for wurtzite polytypes 2*H*, 4*H*, 6*H*, 9*R*, 15*R*, 21*R* and 3*C* were presented graphically by Smith (1955). Later, wurtzite polytypes 6*H*, 8*H* and 10*H* were found in the Zig Zag mine, Joplin, Missouri, and were described by Evans & McKnight (1959). Powder-diffraction data of wurtzite-4*H* and wurtzite-6*H* are, however, not

[1] Present address: 2031 Delmar Drive, Ottawa, Ontario K1H 5P6.
[2] *E-mail address*: rgault@mus-nature.ca

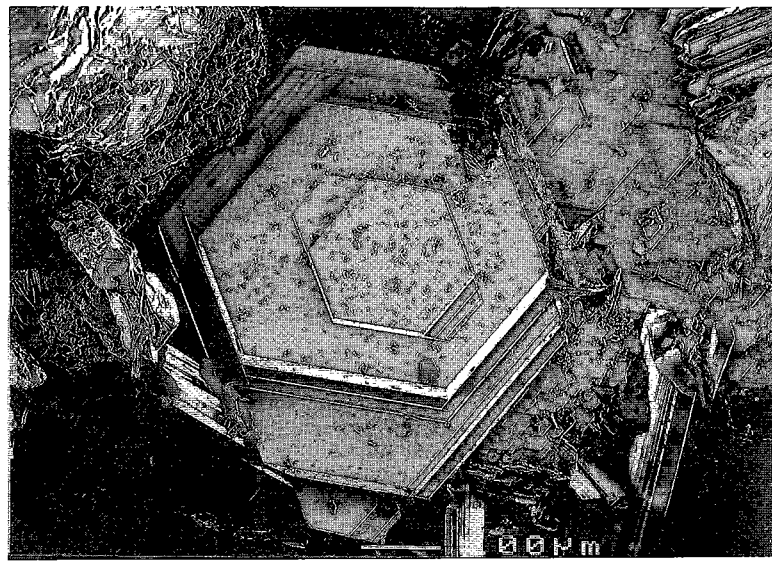

FIG. 1. Scanning electron photomicrograph of wurtzite-4*H* from Mont Saint-Hilaire, Quebec. Scale bar: 100 μm.

available in the literature. Only X-ray powder-diffraction data for the wurtzite polytypes 2*H*, 8*H* and 10*H* are included in the JCPDS Mineral Powder Diffraction File. However, the data presented for the 8*H* and 10*H* polytypes refer to a mixture of 8*H* and 10*H* reported by Evans & McKnight (1959). In the current study, we show that the wurtzite from the sodalite xenoliths in nepheline syenite at Mont Saint-Hilaire, Quebec, reported in Horváth & Gault (1990), consists of the polytypes 4*H* and 8*H* on the basis of single-crystal X-ray diffraction. In view of the rarity of these two polytypes, we deem it worthwhile to document this first Canadian occurrence, and in particular the diffraction pattern of wurtzite-4*H*, to facilitate its identification.

OCCURRENCE

Both wurtzite-4*H* and 8*H* polytypes were found in a very restricted area (25 m^2) in sodalite xenoliths in nepheline syenite in the southeastern corner of the Poudrette quarry, Mont Saint-Hilaire, Quebec. The description and mineralogy of the xenoliths may be found in Mandarino & Anderson (1989) and in Horváth & Gault (1990). Only sphalerite and wurtzite-2*H* have been identified from beyond this area of the quarry. The 4*H* and 8*H* polytypes are indistinguishable except by X-ray diffraction. In one xenolith, these polytypes occur as pale green grains with an adamantine to slightly waxy luster, associated with sodalite, terskite, rhabdophane, gmelinite, sérandite, aegirine, a sodic amphibole, a 1*M* mica and wurtzite-2*H*, the most common polytype at Mont Saint-Hilaire. Most grains in this association are anhedral, with only one small crystal being observed with a short hexagonal prism and pedial termination. This specimen gives a bright yellow-green fluorescence in both short- and long-wavelength ultraviolet light. In another xenolith, wurtzite occurs as irregular, pale green grains and reddish brown, tabular crystals (Fig. 1) in association with sodalite, analcime, microcline, albite, natrolite, sérandite, aegirine, eudialyte, sidorenkite, lintisite, vuonnemite and steenstrupine. These specimens are non-fluorescent in short- and long-wavelength ultraviolet light.

CHEMICAL COMPOSITION

Wurtzite-4*H* and 8*H* were analyzed on a Cambridge Microscan MK5 electron microprobe (wavelength-dispersion mode) with an operating voltage of 15 kV and a beam current of 0.30 μA, using the correction program EMPADR VII developed by Rucklidge & Gasparrini (1969), modified by D. Marshall and P. Jones. A series of synthetic Zn-, Fe-, Mn- and Cd-bearing sphalerite compositions were used as standards. They are: for Zn and S, ZnS; for Fe, $Zn_{0.40}Fe_{0.60}S$; for Mn, $Zn_{0.80}Mn_{0.20}S$ and for Cd, $Zn_{0.95}Cd_{0.05}S$. Indium was sought but not detected. The results of the electron-microprobe analyses (Table 1) show that the wurtzite-4*H* is nearly pure ZnS, whereas an average of 2.04 wt.% Fe and 0.71 wt.% Mn is present in the 8*H* polytype. The results also indicate a metal deficiency in the 8*H* polytype.

X-RAY CRYSTALLOGRAPHY

Single-crystal precession photographs of the 4*H* and 8*H* wurtzite polytypes show that the symmetry and the systematic extinctions are consistent with those for $P6_3mc$, the space group for all hexagonal polytypes of wurtzite. The *c* parameter for the 4*H* polytype, measured from the precession photographs, is 12.521 Å, and that for the 8*H* polytype is 25.041 Å, twice and four times the *c* value of the 2*H* polytype (6.260 Å), respectively, thus confirming that the designations 4*H* and 8*H* for the wurtzite from this particular occurrence at Mont Saint-Hilaire are correct. The X-ray powder-diffraction data were recorded with a 114.6-mm Gandolfi camera using Cu*K*α radiation (λ 1.5418 Å), and are presented in Table 2, along with data for the most common polytype, wurtzite-2*H*, for comparison. The intensities were visually estimated. The cell parameters of the Mont Saint-Hilaire material refined by a least-squares method using the Gandolfi-derived diffraction data are: for wurtzite-4*H*, *a* 3.8277, *c* 12.521(8) Å, in good agreement with the values (*a*, *c*) 3.806, 12.46 and 3.814, 12.46 Å for the wurtzite-4*H* from western Pennsylvania and eastern Ohio, respectively (Frondel & Palache 1950); for wurtzite-8*H*, *a* 3.8286(3), *c* 25.041(8) Å, in good agreement with the values 3.82 and 24.96 Å for the wurtzite-8*H* from the Zig Zag mine, Joplin, Missouri (Evans & McKnight 1959).

TABLE 1. CHEMICAL COMPOSITION OF WURTZITE-4*H* AND WURTZITE-8*H* FROM MONT SAINT-HILAIRE, QUEBEC

wt%	1	2	3	4	5	6
Zn	66.92	67.15	67.24	63.25	63.13	64.37
Fe	0.00	0.00	0.00	2.05	1.93	2.14
Cd	0.00	0.01	0.00	0.00	0.00	0.00
Mn	0.00	0.01	0.01	0.70	0.69	0.73
S	32.89	32.84	32.83	33.61	33.07	34.15
Total	99.81	100.01	100.08	99.61	98.82	101.39
			metal:sulfur ratio			
	0.998	1.003	1.005	0.970	0.980	0.973

1-3 wurtzite-4*H*
4-6 wurtzite-8*H*

DISCUSSION

Although the X-ray powder-diffraction patterns of wurtzite-2*H*, 4*H*, 8*H* and 10*H* are similar, the 4*H* polytype can be distinguished from the others by the

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR WURTZITE-4*H* AND 8*H* FROM MONT SAINT-HILAIRE, QUEBEC

4*H*				8*H*[1]				2*H*[2]		
hkl	$d_{calc.}$	$d_{obs.}$	*I*	*hkl*	$d_{calc.}$	$d_{obs.}$	*I*	*hkl*	$d_{obs.}$	*I*
100	3.3148	3.313	20	100	3.3169	3.309	<5	100	3.311	100
101	3.2044	3.203	100	102	3.2062	3.206	50			
004	3.1301	3.129	80	008	3.1289	3.129	100	002	3.129	84
				103	3.0823	3.082	60			
102	2.9295	2.928	80	104	2.9307	2.929	10	101	2.927	87
				105	2.7651	2.766	10			
103	2.5957	2.596	20	106	2.5963	2.599	10			
104	2.2758	2.275	20	108	2.2760	2.275	10	102	2.273	28
105	1.9980	1.997	40	10·10	1.9980	1.998	20			
110	1.9138	1.913	90	110	1.9150	1.916	90	110	1.910	81
				10·11	1.8764	1.876	30			
106	1.7659	1.765	70	10·12	1.7658	1.766	15	103	1.764	54
200	1.6574	1.657	5					200	1.654	11
				10·13	1.6652	1.666	10			
201	1.6430	1.643	10							
114	1.6328	1.633	70	118	1.6333	1.634	90	112	1.630	47
202	1.6022	1.602	30	204	1.6031	1.602	<5	201	1.599	12
107	1.5741	1.575	20	10·14	1.5738	1.572	5			
								004	1.564	2
203	1.5404	1.541	10							
204	1.4647	1.465	10					202	1.463	6
								104	1.414	1
205	1.3821	1.3820	20	20·10	1.3825	1.3820	10			
				20·11	1.3402	1.3407	15			
206	1.2978	1.2978	40	20·12	1.2981	1.2981	5	203	1.296	15
				20·13	1.2566	1.2572	5			
109	1.2827	1.2830	5							
211	1.2466	1.2479	20					210	1.251	6
212	1.2285	1.2283	20	214	1.2296	1.2290	5	211	1.226	9
118	1.2115	1.2118	10	11·16	1.2115	1.2124	5	114	1.210	2

1. Sphalerite lines 2.713, 1.355 and 1.243 Å are present in the pattern of the 8*H* polytype.
2. Synthetic wurtzite-2*H*, JCPDS card # 36-1450.

presence of lines at 2.596, 1.997, 1.382 and 1.2283 Å and by the strong intensity (I = 100) of the 3.203 Å line. This line is absent in the patterns of the 2*H*, 6*H* and 10*H* polytypes and is very weak in that of the 8*H* polytype. The 8*H* polytype is distinguished by the presence of the moderately strong 3.082 Å line, the weak 2.766, 1.876, 1.666 and 1.341 Å lines, and the increased intensity of the 3.129 and 1.633 Å lines.

Scott & Barnes (1972) concluded from their studies of the system Zn–Fe–S that the stoichiometry of ZnS is not fixed at a Zn:S ratio of unity, but must vary with sulfur fugacity and temperature. They stated that wurtzite must be sulfur-deficient relative to sphalerite. However, in their studies of the Zn–Fe–Ga–S system, Ueno *et al.* (1996) found that the wurtzite phase appears in the sulfur-rich portion of the system. The present study supports the findings of Ueno *et al.* in that Zn:S in wurtzite-4*H* is 1:1, the 8*H* polytype is distinctly metal-deficient with respect to sulfur.

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