Canadian Mineralogist
Vol. 21, pp. 697-703 (1983)

THE OCCURRENCE OF WURTZITE POLYTYPES IN EASTERN OHIO*

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ABSTRACT

The examination of several showings of sedimentary wurtzite in the Pennsylvanian of eastern Ohio has led to the discovery of one new *natural* polytype, 18*R*, and of another one, 21*R*, that is new to North America. The wurtzite occurs in the septa of siderite concretions that are associated with carbonaceous black shales. The stratigraphic range of wurtzite now includes about 70 m of strata of the Vanport Limestone (Allegheny Group), to be added to the Brush Creek Shale (Conemaugh Group). At Negley (eastern Columbiana County), crystals of 4*H*, 6*H*, 15*R*, 18*R* and 21*R* wurtzite have been obtained from the Columbiana Shale; at Steubenville (Jefferson County), the same polytypes save 21*R* occur in the Brush Creek Shale. The two hexagonal polytypes are most abundant, with 6*H* dominant. Among the rhombohedral ones, 15*R* is relatively common, but 18*R* and 21*R* are rare. Hexagonal cell-dimensions for the 18*R* wurtzite are: *a* 3.82(1), *c* 56.2(1) Å.

Keywords: concretions, new mineral species, polytype, Ohio, Pennsylvanian, wurtzite.

SOMMAIRE

L'examen de plusieurs gîtes de wurtzite sédimentaire d'âge pennsylvanien dans la partie orientale de l'état d'Ohio (E.-U.) a mené à la découverte du polytype 18*R*, espèce nouvelle, et du polytype 21*R*, trouvé pour la première fois en Amérique du Nord. La wurtzite se trouve dans les septa de concrétions de sidérite associées à des shales noirs carbonacés. Ces découvertes rattachent 70 m du calcaire de Vanport (groupe d'Allegheny) au shale de Brush Creek (groupe de Conemaugh), accroissant ainsi l'intervalle stratigraphique qui contient la wurtzite. A Negley (partie Est du Comté de Columbiana), les polytypes 4*H*, 6*H*, 15*R*, 18*R* et 21*R* caractérisent le shale de la formation Columbiana; à Steubenville (comté de Jefferson), on les trouve tous sauf 21*R* dans le shale de la formation Brush Creek. Les deux polytypes hexagonaux sont les plus abondants, et 6*H* prédomine. Parmi les rhomboédriques, 15*H* est assez fréquent, mais 18*R* et 21*R* sont rares. Les paramètres réticulaires de la wurtzite 18*R* (maille hexagonale) sont: *a* 3.82(1), *c* 56.2(1) Å.

(Traduit par la Rédaction)

Mots-clés: concrétions, espèce nouvelle, polytypes, Ohio, Pennsylvanien, wurtzite.

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INTRODUCTION

Wurtzite, the hexagonal polymorph of sphalerite, is relatively rare, but superb small crystals have been collected during the past few years in eastern Ohio. Wurtzite structures are characterized by either hexagonal ($P6_3mc$) or rhombohedral ($R3m$) symmetry. Wurtzite crystals, which are steeply pyramidal, appear morphologically either as hexagonal pyramids or trigonal pyramids. Several polytypes, which are distinguished by the slopes of pyramidal faces, exist in both space-groups. Smith (1955) discussed the system of notation for the polytypes.

Single crystals of wurtzite have been described previously from several localities in the United States and Europe. For example, in western Pennsylvania and eastern Ohio, crystals of the 4*H*, 6*H* and 15*R* polytypes have been reported by Frondel & Palache (1948, 1950), Seaman & Hamilton (1950) and Seaman (1977). Evans & McKnight (1959) observed 6*H*, 8*H* and 10*H* polytypes at Joplin, Missouri. Myer (1962) noted crystals of 6*H* wurtzite at Thomaston Dam, Connecticut. In northwestern Germany, crystals of 2*H*, 4*H*, 6*H*, 9*R*, 12*R*, 15*R* and 21*R* polytypes were recorded by Haussühl & Müller (1963).

Several sites for wurtzite have been discovered by the writers in eastern Ohio. It is the purpose of this paper to give the general character of the occurrences and to describe the Negley locality (Columbiana County), which is the most important. New data are provided, also, for the Steubenville locality (Jefferson County), which was described originally by Seaman & Hamilton (1950).

OCCURRENCE

The wurtzite occurs in siderite concretions in the Pennsylvanian shales of eastern Ohio (Fig. 1). With the addition of several new sites, the stratigraphic range of wurzite has been expanded to include a thickness of approximately 70 m in the Allegheny and Conemaugh groups. Within the Allegheny Group, wurtzite-bearing concretions occur in shale above the Vanport Limestone at site 1 (Hollenbaugh 1979), above the Lower Kittanning Coal at sites 2

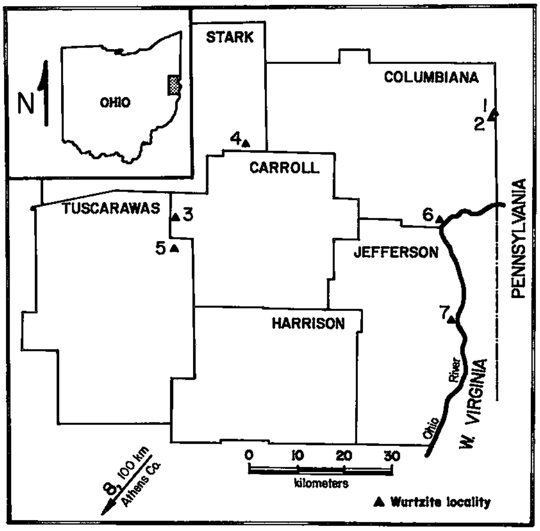

FIG. 1. Wurtzite localities in eastern Ohio.

(Hollenbaugh 1979) and 3 (Carlson 1977), associated with the Middle Kittanning Coal at sites 4 (Rice, in Seaman & Hamilton 1950) and 5 (Carlson 1977) and above the Lower Freeport Coal at site 6 (Hollenbaugh 1979). In the overlying Conemaugh Group, wurtzite-bearing concretions are found in the Brush Creek Shale at sites 7 and 8 (Seaman & Hamilton 1950). Although it seems likely that other wurtzite-bearing horizons will be found in the region, only the shales above the Lower Kittanning Coal (site 2) and the Brush Creek Shale (site 7) have provided abundant wurtzite thus far.

Most of the concretions are ellipsoidal and range from 1 cm to over 35 cm in diameter. They are flattened along the bedding planes of the shales, thus forming discontinuous bands. Some concretions are fossiliferous, but the majority contain no fossils. The bodies of the concretions are dark grey to dark brown and fine grained, consisting chiefly of siderite with minor amounts of quartz, calcite and carbonaceous compounds. Whereas some of the concretions are barren of mineralization, others contain septa that presumably formed by shrinkage during diagenesis. It is within these septa that the wurtzite and associated minerals are found. The shales that are associated with the mineralization invariably are grey to black and carbonaceous.

Wurtzite was discovered near Negley (site 2) by one of the authors (D.H.) in 1976. The first coal-pit, located approximately 0.2 km southwest of Ohio Route 154 on the north side of Columbiana County Road 1026, has been in operation intermittently since 1929. The second pit, located approximately 0.8 km further west on County Road 1026, has been mined intermittently since the early sixties. The wurtzite-bearing concretions are restricted to the Columbiana Shale, which lies approximately 2–3 m above the top of the Lower Kittanning Coal. The Lower Kittanning Coal is found generally near the base of the highwall in both pits. The occurrence of wurtzite at a given exposure is erratic. At one spot, almost every mineralized concretion may contain wurtzite, whereas several metres away little or no wurtzite may be found.

The Steubenville locality (site 7) is a roadcut on the east side of Ohio Route 7, about 2 km north of Steubenville and just north of the intersection with Ohio Route 213. The wurtzite-bearing horizon occurs about 1 m above the Brush Creek Coal at an elevation of about 6 m above the highway. About one out of every four mineralized concretions is wurtzite-bearing.

MINERAL ASSEMBLAGE

At Negley, much of the wurtzite is attached loosely to the matrix of siderite or to other minerals, and wurtzite crystals of exceptional quality are found. The wurtzite occurs as small, reddish brown, euhedral crystals up to 2 mm long, averaging about 1 mm in length and 0.25 mm in breadth. Chemical analyses of the crystals, owing to their small size, could not be obtained with the equipment available to the writers. The polytypes that have been identified include *4H, 6H, 15R*, 18*R* and 21*R*, with hexagonal types being dominant. In a random sample of about 200 hexagonal crystals, *6H* polytypes were found to exceed *4H* by a 5:2 margin. The *R* polytypes, which are comparatively rare, were identified by the rotation method from the dimension of the *c* axis (Fig. 2A, B). Of the crystals examined, ten are 15*R*, two are 18*R* and four are 21*R*. The 15*R* crystals are characterized by large, dull faces that give poor signals on the optical goniometer. Many similar crystals were recognized during the microscope study but were not identified. The crystals of 18*R* and 21*R* wurtzite, on the other hand, are characterized by bright faces and are extremely rare. The 18*R* polytype had not been recognized previously in nature; work on its structure is in progress. The unit-cell dimensions for 18*R* wurtzite (hexagonal setting), *a* 3.82(1), *c* 56.2(1) Å, were determined from *c*-axis rotation and zero-level Weissenberg photographs. The 21*R* polytype had not been reported previously from North America. A rotation photograph for 21*R* wurtzite yielded a value of 65.7(1) Å for the *c* axis. These last crystals were not examined further by X-ray methods. The wurtzite occurs either as isolated crystals or in radial groups in which the apices of individual crystals point inward (Fig. 3A).

The crystal forms for each of the polytypes are given in Table 1. With few exceptions, the crystals

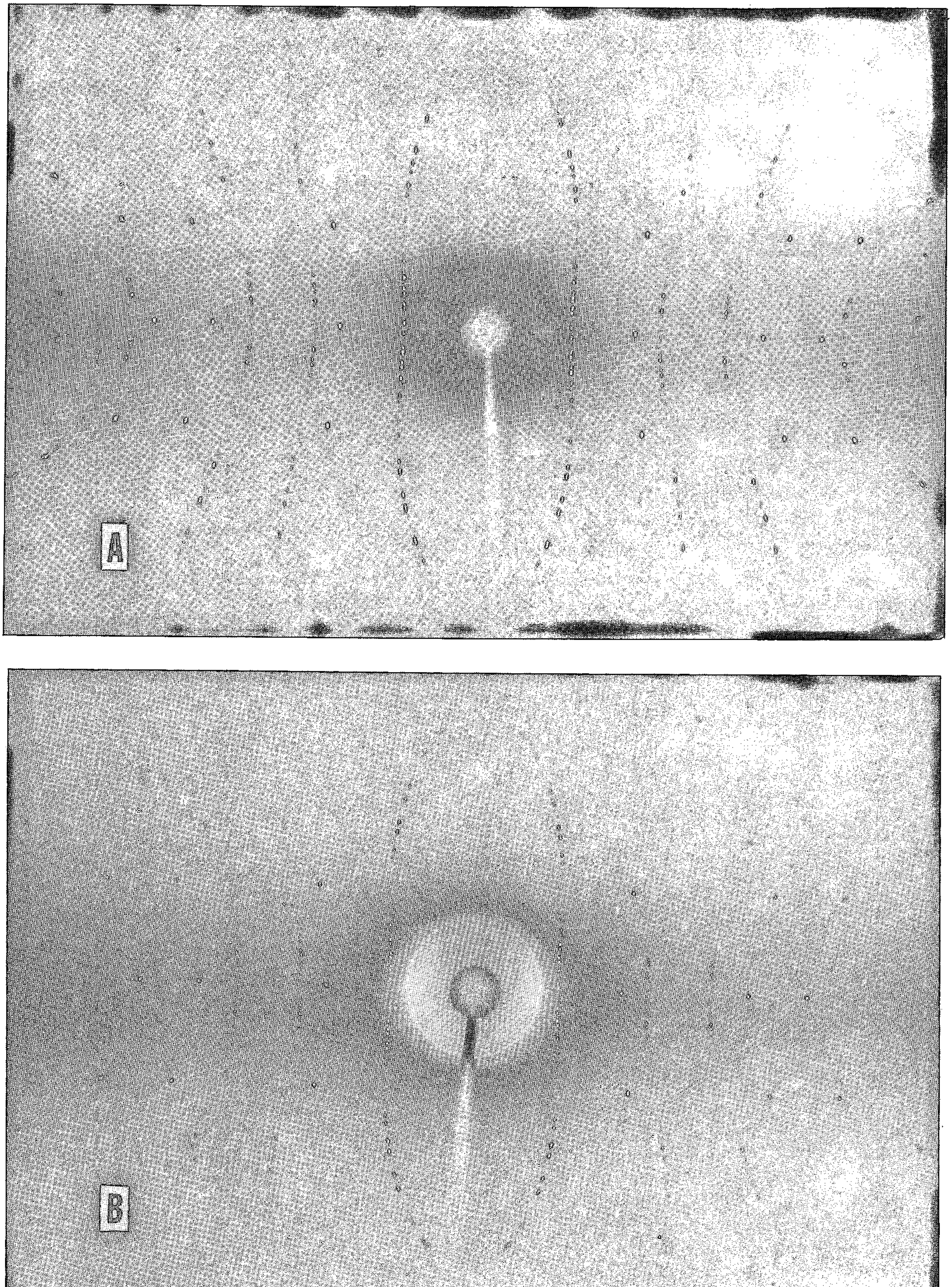

FIG. 2. Rotating-crystal photographs of wurtzite. Rotation axis is *c*. Cu*K*α radiation. A) 18*R* wurtzite. B) 21R wurtzite.

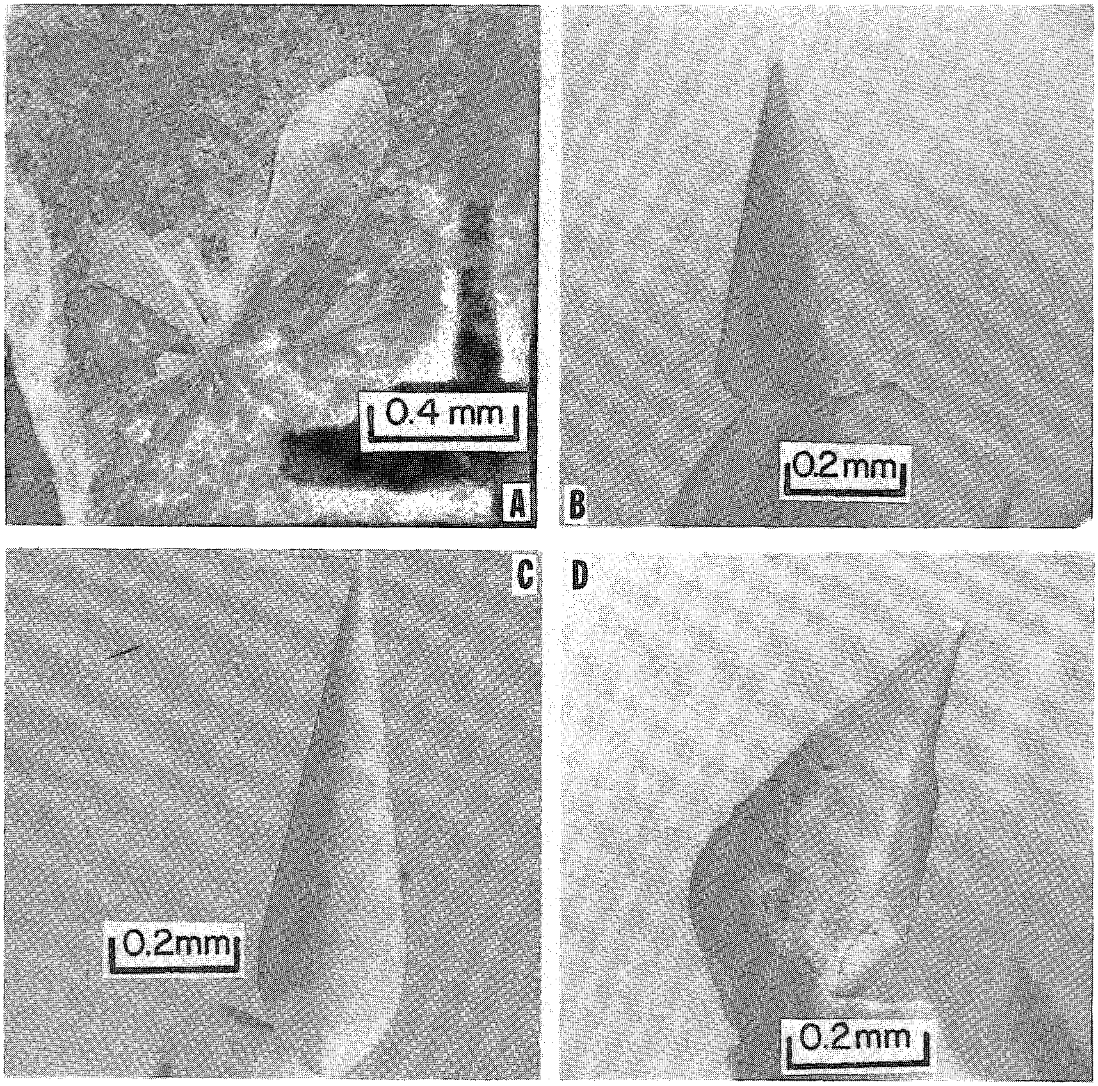

FIG. 3. Scanning-electron photomicrographs of wurtzite. A) Radiating group of typical 6*H* crystals, Negley. B) Crystal of 4*H* wurtzite displaying the characteristic $\{10\bar{1}1\}$ and $\{000\bar{1}\}$ forms, Negley. C) Crystal of 6*H* wurtzite with prominent $\{10\bar{1}1\}$ pyramid and a combination of lower pyramids that have curved faces, Steubenville. D) Barrel-like crystal of 6*H* wurtzite with prominent $\{10\bar{1}1\}$ spire, Negley.

are distinguished by a single, steeply inclined upper pyramid and either a basal pedion or a combination of lower pyramids, with the latter commonly displaying curved faces. The 4*H* wurtzite invariably displays a dominant $\{10\bar{1}1\}$ pyramid and a basal pedion (Fig. 3B) and may have subordinate combinations of lower pyramids. Crystals of 6*H* wurtzite show three diverse habits. The most common type consists of the $\{10\bar{1}1\}$ pyramid and a complex combination of lower pyramids (Fig. 3C). A second 6*H* habit consists of a spire-like $\{10\bar{1}1\}$ pyramid that rests on a barrel-shaped, oscillatory growth of horizontally striated pyramids (Fig. 3D). A third habit, the rarest of the three, is characterized by an unusual pagoda-like combination of $\{10\bar{1}1\}$ and $\{10\bar{1}5\}$ pyramids that taper upward and a broad basal pedion (Fig. 4A). For the last two types of 6*H* wurtzite, X-ray data are identical for both the upper and lower portions of individual crystals; these results confirm that both habits are formed by single crystals and not parallel intergrowths of different polytypes. The radial groups invariably are dominated by individuals of

TABLE 1. GONIOMETRIC DATA FOR WURTZITE

Polytype	a:c Ratio	Calculated ρ angle*	Form indices	Observed frequency of form; average of measured angles: Negley	Observed frequency of form; average of measured angles: Steubenville
4H	1:3.268**	75°09'	$\{10\bar{1}1\}$	8; 74°32'	1; 74°08'
		90°00'	$\{10\bar{1}0\}$	1; 90°00'	0; --
		110°01'	$\{80\bar{8}\cdot\bar{11}\}$	1;109°31'	0; --
		117°55'	$\{10\bar{1}\bar{2}\}$	1;118°26'	0; --
		124°49'	$\{80\bar{8}\cdot\bar{21}\}$	1;125°01'	0; --
		180°00'	$\{000\bar{1}\}$	4;180°00'	0; --
6H	1:4.902**	48°33'	$\{10\bar{1}5\}$	2; 47°48'	0; --
		79°59'	$\{10\bar{1}1\}$	19; 79°50'	12; 79°53'
		90°00'	$\{10\bar{1}0\}$	0; --	2; 90°00'
		107°11'	$\{40\bar{4}\bar{7}\}$	0; --	1;107°58'
		119°52'	$\{40\bar{4}\cdot\bar{13}\}$	0; --	1;119°41'
		121°44'	$\{20\bar{2}\bar{7}\}$	1;120°50'	2;122°16'
		126°54'	$\{40\bar{4}\cdot\bar{17}\}$	1;127°01'	0; --
		130°00'	$\{40\bar{4}\cdot\bar{19}\}$	1;130°34'	2;129°40'
		131°27'	$\{10\bar{1}\bar{5}\}$	1;131°31'	2;130°56'
		134°11'	$\{20\bar{2}\cdot\bar{11}\}$	2;134°13'	0; --
		136°40'	$\{10\bar{1}\bar{6}\}$	1;135°54'	0; --
		180°00'	$\{000\bar{1}\}$	1;180°00'	4;180°00'
15R	1:12.24**	70°31'	$\{10\bar{1}5\}$	1; 70°58'	0; --
		85°57'	$\{10\bar{1}1\}$	4; 85°56'	2; 85°53'
		113°00'	$\{10\bar{1}\bar{6}\}$	1;113°30'	0; --
		119°30'	$\{10\bar{1}\bar{8}\}$	1;119°54'	0; --
		136°42'	$\{10\bar{1}\cdot\bar{15}\}$	1;136°17'	0; --
		180°00'	$\{000\bar{1}\}$	2;180°00'	0; --
18R	1:14.71***	73°35'	$\{01\bar{1}5\}$	1; 72°50'	0; --
		83°17'	$\{10\bar{1}2\}$	2; 83°04'	1; 82°58'
21R	1:17.15****	75°50'	$\{01\bar{1}5\}$	4; 75°34'	0; --
		78°35'	$\{10\bar{1}4\}$	3; 78°33'	0; --
		133°48'	$\{01\bar{1}\cdot\bar{19}\}$	2;134°09'	0; --
		180°00'	$\{000\bar{1}\}$	1;180°00'	0; --

* ρ = (hkil) ∧ (0001). ** Frondel & Palache (1950). *** This study. **** Haussühl & Müller (1963).

6H wurtzite that show the first and second types of habit. The *15R* crystals typically display a $\{10\bar{1}1\}$ pyramid and a basal pedion (Fig. 4B). Both *18R* crystals examined are characterized by $\{10\bar{1}2\}$ pyramids and broken basal surfaces; owing to insufficient material, a scanning-electron photomicrograph could not be obtained. A typical *21R* crystal exhibits a dominant $\{10\bar{1}4\}$ pyramid, a subordinate $\{01\bar{1}5\}$ pyramid and a lower $\{01\bar{1}.\bar{1}\bar{9}\}$ pyramid (Fig. 4C).

At the Steubenville locality, well-formed crystals of wurtzite are abundant, being embedded mostly in a matrix of siderite or other minerals that fill the septa. A calcite matrix, however, is present in the core area of some concretions and can be etched to free the wurtzite, yielding scores of unbroken crystals. The crystals measure up to 2 mm in length and average slightly less than 1 mm and 0.20 mm in width. In several concretions, crystals of *4H*, *6H*, *15R* and *18R* wurtzite were identified, with *6H* wurtzite dominant. The most common habit for *6H* wurtzite is a $\{10\bar{1}1\}$ pyramid and a complex combination of lower pyramids (Fig. 3C). The radial groups, which are abundant at Steubenville, are characterized by *6H* crystals of this type. During a casual count of about 60 crystals that were freed by etching, only one *4H* was observed. The rarity of *4H* wurtzite at Steubenville may be more apparent than real, however, since the sample may not be representative of the locality. The crystal that was observed was distinguished by a $\{10\bar{1}1\}$ pyramid. Several rhombohedral crystals were recognized during microscopic examination, with six being identified as *15R* polytypes. The *15R* crystals, which invariably display large, dull faces, are distinguished by a prominent $\{10\bar{1}1\}$ pyramid and a basal pedion. One crystal of *18R* wurtzite displays a $\{10\bar{1}2\}$ pyramid. The forms that are present for each polytype are given in Table 1.

Barite, calcite, chalcopyrite, kaolinite, pyrite and sphalerite also occur in the veinlets that fill the septa. These minerals show poor development, and crystals rarely exceed 3 mm in length. Sphalerite is the most abundant, whereas barite, calcite and pyrite are encountered commonly. Kaolinite and chalcopyrite are relatively rare, being found only at the Negley locality. Sphalerite commonly is present as curved, tabular crystals and coarsely crystalline aggregates, or more rarely as minute crystals. The sphalerite varies from deep reddish brown to black, and contains up to 4 wt.% Fe. Colorless to white barite appears as coarse plates that may contain embedded wurtzite, pyrite and sphalerite. White to tan calcite occurs as fine-grained plates and irregularly shaped masses that may contain embedded sulfide minerals. Pyrite, which may be iridescent, is present typically as small brassy crystals or finely crystalline masses. Kaolinite is found as very finely crystalline white masses and veinlets. Chalcopyrite appears as tiny brass-yellow grains.

Wurtzite appears to be the earliest mineral to form in the septa. It is found either free of matrix or embedded in veinlets of barite, calcite and sphalerite. The wurtzite may be coated by pyrite (Fig. 4D). In some specimens, sphalerite appears to have formed at the same time as the wurtzite, but in others, wurtzite is found penetrating the sphalerite. The sphalerite usually is coated by or embedded in barite, calcite and pyrite. Pyrite occurs as coatings on wurtzite and sphalerite and in turn is embedded in barite and calcite. Chalcopyrite probably formed at about the same time as the pyrite, since it has been found embedded in calcite and barite. In western Pennsylvania, Seaman & Hamilton (1950) found chalcopyrite coating the sphalerite and wurtzite. Calcite, barite and kaolinite, having formed later, usually are found enclosing the sulfides. Vein calcite and barite have not been found in the same concretion.

Discussion

Although wurtzite is commonly believed to be the high-temperature polymorph of sphalerite, recent work indicates that wurtzite may be stable at low temperatures (Scott & Barnes 1972, Scott 1974). These investigators consider that wurtzite is nonstoichiometric and deficient in sulfur relative to sphalerite, with sulfur fugacity being the main factor in determining whether wurtzite or sphalerite forms. Wurtzite, thus, would develop where sulfur fugacity is low, and sphalerite would form where

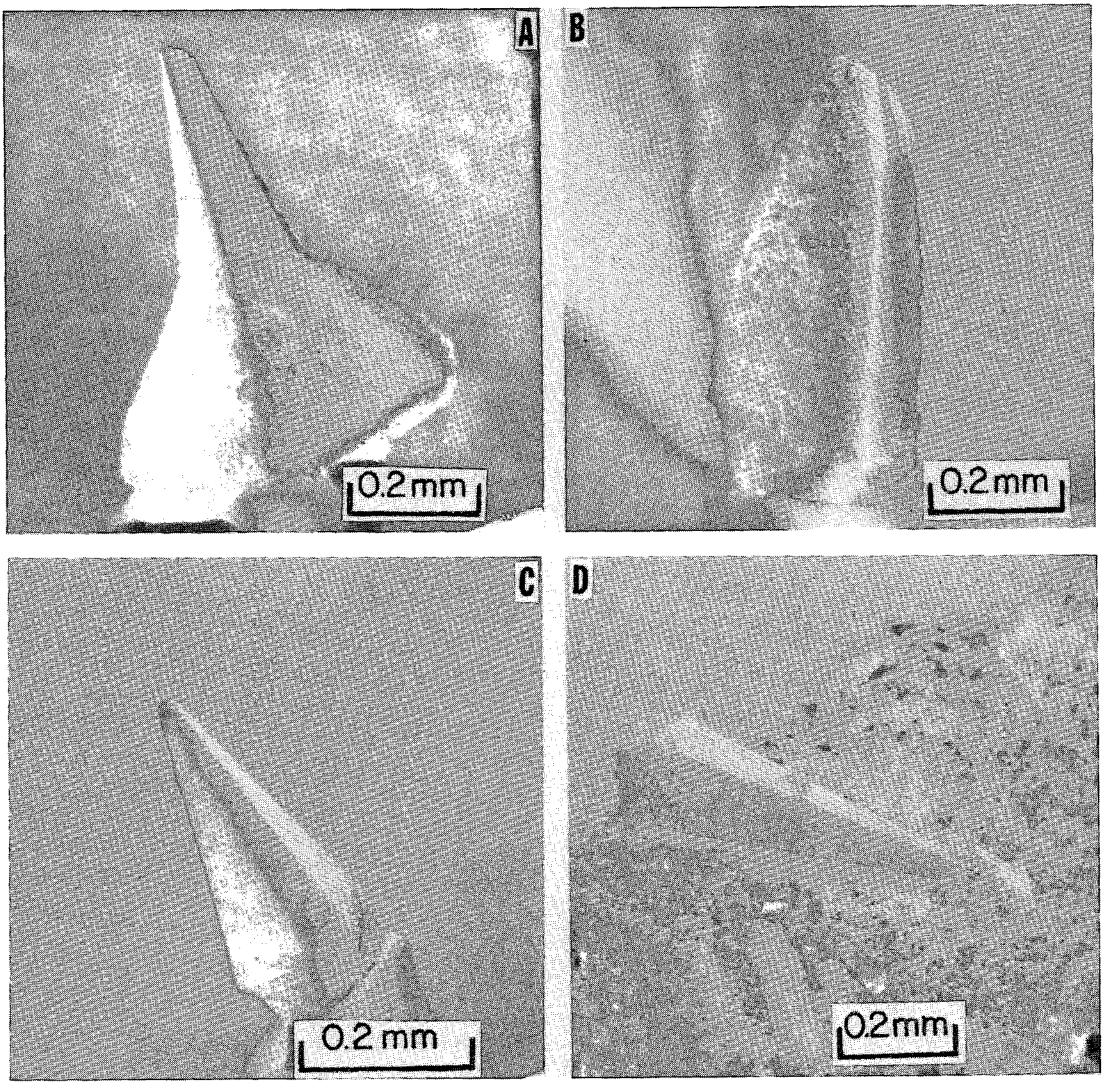

FIG. 4. Scanning-electron photomicrographs of wurtzite. A) Pagoda-like crystals of 6*H* wurtzite displaying {$10\bar{1}1$}, {$10\bar{1}5$} and {$000\bar{1}$} forms, Negley. B) Crystal of 15*R* wurtzite displaying {$10\bar{1}1$}, {$10\bar{1}\bar{6}$} and {$000\bar{1}$} forms, Negley. C) Crystal of 21*R* wurtzite displaying {$10\bar{1}4$}, {$01\bar{1}5$} and {$01\bar{1}\cdot\overline{19}$} pyramids, Negley. D) Ball-shaped mass of pyrite coating the apex of a crystal of 6*H* wurtzite, Negley.

sulfur fugacity is high. In the case of wurtzite, variations in the sulfur fugacity also determine the stability ranges for different polytypes. The presence of sphalerite and different polytypes of wurtzite in the same concretion thus could be explained by a variable fugacity of sulfur. At both the Negley and Steubenville localities, sphalerite and polytypes of 4*H*, 6*H* and 15*R* wurtzite were found together in single concretions. Conversely, the predominance of a single polytype in a sedimentary horizon would indicate uniform levels of sulfur fugacity. Thus the apparent rarity, at Steubenville, of 4*H* wurtzite, a polytype that is common at most localities in eastern Ohio and western Pennsylvania, may be related to local conditions in the sedimentary environment.

This study has shown that well-formed crystals of sedimentary wurtzite, including two polytypes that are new to North America, occur over a broad area in eastern Ohio. Since the wurtzite is found over a wide stratigraphic interval, further mineralogical investigations of this unusual mineral and a search for additional localities could prove rewarding.

ACKNOWLEDGEMENTS

Professor Rodney Feldmann of Kent State University operated the scanning-electron microscope; his assistance is acknowledged gratefully. Cheryl Birkhimer also assisted with some of the SEM photographs. The authors are also grateful to M.E. Fleet and an anonymous referee for constructive comments. The drafting was done by Tom Bjerstedt.

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Received Jan. 31, 1983, revised manuscript accepted April 27, 1983.