Three new wurtzite-type polymorphs of ZnS have been found along shrinkage cracks in clay-ironstone concretions a few feet above the Brush Creek limestone horizon of the Conemaugh Formation near Etna, Allegheny County, Pennsylvania. Two of them, wurtzite-4H and wurtzite-6H, have been noted at this horizon over an area of fifty square miles in western Pennsylvania and eastern Ohio. The third, wurtzite-15R, is reported in only four crystals from the Etna locality. The geology and mineralogy are described for the known occurrences of these polymorphs.

INTRODUCTION

Three new polymorphous forms of ZnS are described by Dr. Clifford Frondel and Dr. Charles Palache of Harvard University in the current issue of the American Mineralogist. It is at their suggestion that this brief accompanying paper has been prepared describing somewhat more fully the geology and mineralogy of the occurrences.

The original locality was found on a very bright afternoon, August 10, 1946, while the authors were on a fossil collecting trip to the Brush Creek limestone horizon, one half mile northwest of Shelocta, Indiana County, Pennsylvania, along U. S. Route 422. In his search for fossils the junior author happened to break open a clay-ironstone concretion from a layer about ten feet above this limestone. To his surprise, he noted some tiny brownish red crystals embedded in white, platy barite in the center of the concretion. The crystals would undoubtedly have been missed if it had not been for the brilliant, mirror-like reflections from the tiny crystal faces. The first crystals found were less than one millimeter in length and barely visible to the naked eye.

Viewing them under a microscope at the museum it was noted that they were steep pyramidal crystals with hexagonal-hemimorphic development. In the belief that they might be wurtzite, several crystals were sent to Dr. Frondel of Harvard University for verification. Wurtzite had not previously been reported from western Pennsylvania. This first polymorph proved to be wurtzite-6H of their study. Additional material from the Shelocta locality revealed another new polymorph, wurtzite-4H.

* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 310.
Subsequent collecting from a number of localities yielded a third new wurtzite polymorph at the Wittmer locality near Etna, Pennsylvania, of rhombohedral (trigonal) crystallization, wurtzite-15R. Only four specimens of this polymorph have been found, all at the Brush Creek limestone horizon at the Wittmer locality. The two hexagonal forms, wurtzite-4H and wurtzite-6H, have been found together at fifteen different localities: thirteen in western Pennsylvania and two in eastern Ohio.

**Geology**

The polymorphous wurtzites occur in clay-ironstone concretions in concretionary layers at various distances above the Brush Creek limestone of the lower Conemaugh Formation of the Pennsylvanian period. The concretions themselves are usually oval in shape and from two to four or five inches in length, and up to two inches in thickness with their long dimension in the plane of stratification. Sometimes the concretions form an almost unbroken layer, end to end, in black, carbonaceous shale. The Brush Creek limestone is a nodular, black, fossiliferous limestone ranging from one foot to two feet in thickness occurring some one hundred and twenty-five feet above the Upper Freeport Coal which marks the lower boundary of the Conemaugh Formation. A few tiny wurtzites of the 4H and 6H types have been found in similar concretions one foot above the Pine Creek limestone, which is also found at the Wittmer locality some ninety feet above the Brush Creek limestone.

**Mineralogy of Concretions**

The minerals of the concretions are found along shrinkage cracks. Most of the wurtzites occur in radiating groups of single crystals side by side, like small sunbursts, with the acute pyramidal terminations pointing towards the center of the radiations. The associated minerals are usually platy barite or granular calcite, in which the wurtzites are embedded. Platy and curved sphalerite is often intimately associated with the wurtzites, with crystalline pyrite and chalcopyrite common at some localities. There appears to be no particular mineral which indicates the presence of the wurtzites in the concretions other than the usually accompanying sphalerite. The wurtzites may be found alone or with any of the above mentioned minerals. If calcite is present, there is no barite, and vice versa. These two minerals are never found in the same concretions though both are present at the Wittmer locality. Here the barite-bearing concretions seem to be confined to the southern end of the cut and the calcite concretions to the center and northern end.

The size of the seam or crack is also not indicative of the presence or absence of the wurtzites in the concretions, for they have been noted in
very narrow fractures often coating most or nearly the entire surfaces in radiating crystal growths, as at the Wittmer locality. Larger crystals up to two and one half millimeters in length have been found in the wider shrinkage cracks, for here the crystals had more space in which to grow.

Figure 1 shows the area around Shelocta, Pennsylvania, the original locality of the polymorphous wurtzites. Figure 2 is a photograph taken at this locality. Figure 3 shows the geological section at the Shelocta locality. Figure 4 shows the location of all the polymorphous wurtzite localities within a fifty mile radius of Pittsburgh. Fourteen localities are shown: the one near Glouster, Athens County, Ohio, being omitted as it is some one hundred and twenty-five miles southwest of Pittsburgh.

**Localities**

The following is a list of all the localities so far found where the wurtzites occur. They are listed from east to west beginning with the Shelocta locality and ending with the Glouster, Ohio, locality. Their positions may be noted on the map, Figure 4.
1. One half mile northwest of Shelocta, Indiana County, Pa., along U. S. Route 422.
3. Railroad cut along the main line of the Pennsylvania Railroad just east of the small station of Donohoe, about four miles east of Greensburg, Westmoreland County, Pa.
4. Along the old William Penn highway about one quarter of a mile west of Murrysville, Westmoreland County, Pa.
5. Along a branch line of the Pennsylvania Railroad about two miles south of the William Penn highway (U. S. Route 22) at Aber Creek about eight miles east of Wilkinsburg, Allegheny County, Pa.

Fig. 2. Brush Creek limestone (center) near Shelocta, Pennsylvania.
OCCURRENCE OF POLYMORPHOUS WURTZITE

6. Along a secondary road one and one half miles southwest of Murraysville, Westmoreland County, Pa.
7. Old brickyard quarry at Valley Camp, Westmoreland County, Pa.

10. Along Route 28 about a half mile north of Springdale, Allegheny County, Pa.
11. Baltimore & Ohio Railroad cut at Wittmer, about two miles north of Etna, Allegheny County, Pa., and along Route 8.
12. West end of Sewickley bridge opposite from Sewickley, Allegheny County, Pa.
14. Stanton Park along Route 7 about a mile and a half north of Steubenville, Jefferson County, Ohio.
15. Old Glouster Brick quarry, one third of a mile south of Glouster, Athens County, Ohio.

The wurtzite-bearing concretions range from a layer one foot above the Brush Creek limestone at the Sewickley and Wittmer localities to from fifteen to twenty feet above this limestone at the Creighton and Valley Camp localities. All of the strata are essentially horizontal in this area with the exception of those at the Donohoe locality which dip from east to west at about an angle of thirty-five degrees. The wurtzites are extremely rare at some localities as at Sewickley, Creighton and Glassmere, Pennsylvania. About one in ten concretions show them at the Wittmer locality and about one in four concretions at the Donohoe locality. Peculiar expanded bulb-like terminations at the opposite end of the pyramidal terminations occur on the polymorphous wurtzites at Donohoe, Pennsylvania. A few tiny tetrahedral sphalerite crystals have been found embedded in the platy barite in the concretions at the Sheblocta locality and at locality number 13 northwest of Sewickley. Chalcopyrite in tiny crystals has been noted as an associated mineral at Valley Camp. At the Wittmer locality near Etna, the Brush Creek limestone occurs about three feet above the lower bench in the railroad cut, and the Pine Creek limestone about the same distance above the upper bench separated vertically by about ninety feet of black, carbonaceous shales.
The wurtzite-bearing concretions are found in layers about one foot above both limestones in this deep cut. Here as at Donohoe, the wurtzites are usually found embedded in granular calcite which may be readily dissolved by placing the specimens in a solution of cold, dilute hydrochloric acid which makes the crystals stand out brilliantly against the clay-ironstone matrix. The dilute acid does not visibly affect the polymorphs in this short period treatment.

Paragenesis of Minerals

The paragenesis of the minerals found in the concretions appears in general to be as follows. The polymorphous wurtzites were formed first; all three types occur side by side in rudely radiated aggregates of single crystals, indicating simultaneous crystallization; then followed curved and radiating, platy sphalerite. The wurtzites have been noted at several localities, as at Valley Camp, with their steep pyramidal terminations penetrating the sphalerite plates showing that they had formed before the sphalerite. Pyrite or chalcopyrite may be next as they have been found as coatings over the previously formed minerals. Finally barite or calcite has been deposited, but not in the same concretions for all the previously formed minerals have been found embedded in one or the other at numerous localities. However the wurtzites may occur alone without any associated minerals, or with several of them, as with curved and platy sphalerite, pyrite, and calcite at Wittmer, or with curved and platy sphalerite, chalcopyrite, and barite at Shelocta.

A very interesting specimen showing tiny polymorphous wurtzites deposited between the septa of a small straight cephalopod fossil was found at the Brush Creek limestone horizon at Wittmer in June, 1947. The solutions which deposited the wurtzites no doubt filled the open siphuncle in this fossil which was about a quarter of an inch in diameter and about an inch in length. This suggests that they formed during the diagenesis of the sediment, at the time the fossil was enclosed in the concretion on the ocean floor, and not as a later introduction. The association of polymorphous wurtzites with fossils in other concretions, though not within the fossils themselves, at a number of other localities leads to the same conclusion.

Certain of the concretions at Wittmer when broken reveal round or oval-shaped siderite centers with the tiny wurtzites and other associated minerals deposited completely around them as a very thin layer. These nuclei often break free and separate like nuts from a shell when the concretions are opened. This may indicate that these minerals were formed shortly after the first deposition of clay-ironstone forming the core of the concretions, and before the final growth of these concretions was
completed. All the minerals are thought to have formed under essentially ordinary conditions of temperature and pressure at the time of formation of the concretions during sedimentation. The finding of the polymorphous wurtzites and other associated minerals in clay-ironstone concretions in clay or shale rich in carbonaceous material suggests that this type of environment was very favorable to the deposition of these minerals.

An occurrence of what appears to the writers to be tiny crystals of either wurtzite-4H or wurtzite-6H, has been noted in shrinkage cracks in clay-ironstone concretions of from four to ten inches in diameter from clay below the number six (Middle Kittanning) coal, of the Richard Immel Mine southwest of Alliance, Stark County, Ohio. This stratum is near the middle of the underlying Allegheny Formation, or some three or four hundred feet below the Brush Creek limestone horizon of the Conemaugh Formation. This occurrence was reported by W. A. Rice of Mount Union College in a paper presented May 7, 1948, before the Ohio Academy of Science meeting at the University of Toledo. It should prove very interesting should polymorphous wurtzites be found at other geological horizons within the Pennsylvanian system in other areas outside of eastern United States.

CONCLUSION

It is the writers' belief that polymorphous wurtzites will be found with careful search at most of the outcrops of the Pine Creek and Brush Creek limestone wherever the accompanying clay-ironstone concretions are encountered. A fifty square mile area in western Pennsylvania and eastern Ohio is now known where they have been noted. Since they have been found near Glouster, Ohio, some one hundred and twenty-five miles southwest of Pittsburgh, it seems likely that they will be found by careful search at localities between these two points. A diligent search should also be made of the known outcrops of these two limestones in Maryland and West Virginia.