THE AMERICAN MINERALOGIST, VOL. 52, NOVEMBER-DECEMBER, 1967

FLUORITE IN CRYSTAL-LINED VUGS IN THE MAQUOKETA SHALE AT VOLGA, CLAYTON COUNTY, IOWA

C. ERVIN BROWN,[1] *U. S. Geological Survey, Washington, D. C.*

ABSTRACT

Near Volga, Iowa, vugs lined with small but well-formed crystals of calcite, color-zoned fluorite, sphalerite, and pyrite are in the lowermost phosphatic sediments of the Maquoketa Shale. The association of calcite, pyrite, and sphalerite and their paragenesis, crystal habits, minor element content, and fluid inclusions, suggest a genetic relation to the ores of the upper Mississippi Valley zinc-lead district, only 20 miles to the east. The occurrence of fluorite is anomalous, however, because only one minor occurrence of fluorite is known even though 60 other mineral species are identified in the ores of the district.

Most of the chemical elements necessary to form this crystal assemblage at Volga are common constituents of the enclosing phosphatic rock. However, rare earth elements, present in the phosphatic wall rock, are not found in the fluorite even though fluorite at many places commonly contains traces of them. This notable deficiency suggests that the crystals did not result from a reorganization of chemical elements freed by a breakdown of the surrounding carbonate-fluorapatite.

INTRODUCTION

Fluorite-bearing vugs occur in the lowermost phosphatic and dolomitic sediment of the Maquoketa Shale of Late Ordovician age which fills the corrosion-pitted and hollowed top limestone bed of the underlying Dubuque Shaly Member of the Galena Dolomite of Middle Ordovician age. The flat lying strata of the Dubuque Member form the bed of the Volga River just upstream from an abandoned damsite in Volga, Iowa. The east bank of the river for several hundred feet above the damsite is a bluff of Maquoketa Shale that has been studied and illustrated previously because it is a particularly fine exposure of Calvin's (1906) Elgin Shaly Limestone Member of the lower Maquoketa. The fringe of the fluorite-bearing layer extends out onto the river bed at the foot of this shale and limestone bluff. Reports on the geology of Clayton County by A. G. Leonard (1906, Fig. 32) and by A. J. Feulner (1953, Fig. 19) have photographs of the riverbank outcrop but neither photograph shows the fluorite-bearing bed because it was under water. In the summer of 1965, when the author visited the outcrop, the river was very low and the mineralized bed was exposed.

The presence of fluorite at Volga was previously noted in an unpublished thesis by R. W. Rall (1950) who studied the ostracods from the basal phosphatic zone of the Maquoketa Shale. In his detailed description of the section at Volga he mentions calcite, fluorite, and pyrite

---

[1] Publication authorized by the Director, U. S. Geological Survey.

intimately associated with the phosphatic and fossiliferous material filling pits and pockets in the top bed of the Dubuque.

This occurrence of fluorite, in association with sphalerite, is noteworthy because of its proximity to the western edge of the extensive upper Mississippi Valley zinc-lead mining district (Fig. 1) which is essentially fluorite-free. Heyl and others (1959, p. 84), in a thorough study of the district ores, list 60 mineral species, but fluorite was not found. Recently, however, Philip M. Blacet (written commun., 1966) identified a few minute fluorite grains in ore from the Grayville Mine near Mineral Point, Wisconsin. Bradbury (1961) does not report fluorite in the part of the lead-zinc district in Illinois, and does not know of any fluorite occurrences in northwestern Illinois (written commun., 1967).

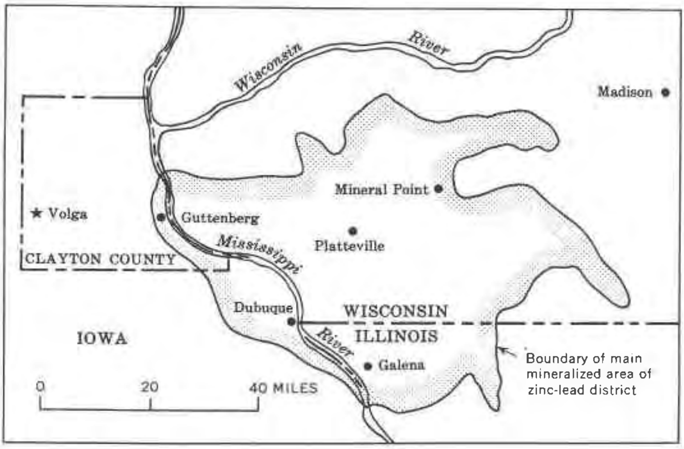

FIG. 1. Location of Volga, Iowa, and boundary of the main mineralized area of the Upper Mississippi Valley zinc-lead district.

A few minor occurrences of fluorite have been reported in the surrounding region of northeastern Iowa and southern Wisconsin. Fluorite, with calcite and galena, occurs in the Galena Dolomite more than 100 miles northeast of the district at Neenah, Wisconsin (Bagg, 1918), and with calcite, barite, and sphalerite, in rocks of Devonian age 40 miles southwest of Volga at Raymond, Iowa (Pratt and Menzel, 1965).

In the general area of the Upper Mississippi Valley lead-zinc district the zone including the basal beds of the Maquoketa Shale and the Upper beds of the Dubuque Shaly Member of the Galena Dolomite at most places are lightly mineralized with disseminated pyrite, marcasite, and calcite. Barite crystals commonly occur in widely scattered vugs in these rocks near Dubuque, Iowa, and locally sphalerite, galena, and smithsonite also are found (Brown and Whitlow, 1960, p. 59). Although mineral occurrences are not unusual in this zone, the occurrence of fluorite-bearing vugs at Volga, Iowa, is unique.

OCCURRENCE

The Dubuque Shaly Member of the Galena Dolomite at Volga is pale-yellowish-brown fine-grained, irregularly bedded limestone that contains finely comminuted fossils, mainly crinoid segments. The upper slabby beds are separated by thin shaly partings. The 2- to 3-inch limestone bed at the upper contact is deeply corroded, probably by phosphate-rich water of the initial Late Ordovician Maquoketa sea. Pits and cavities are filled with a dark grayish-brown mixture of dolomite rhombs, phosphatic pellets, nodules, shell debris, and interstitial brown clay. The crystal-lined vugs in the specimens that the author collected are all enclosed by this filling of dark brown phosphatic and dolomitic material (Figs. 2 and 3).

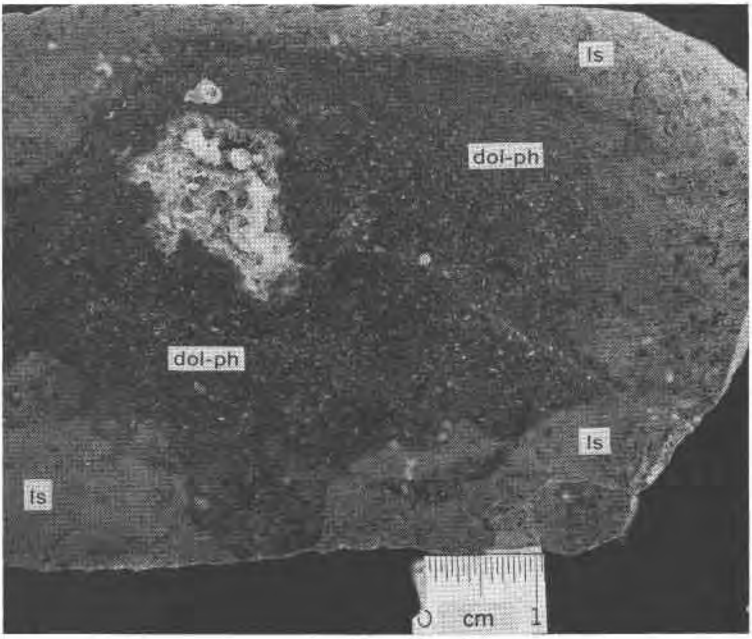

FIG. 2. Crystal-lined vug enclosed in phosphatic and dolomitic detritus (dol-ph) that fills hollow in corroded crinoidal limestone (ls). Top of picture is top of bedding.

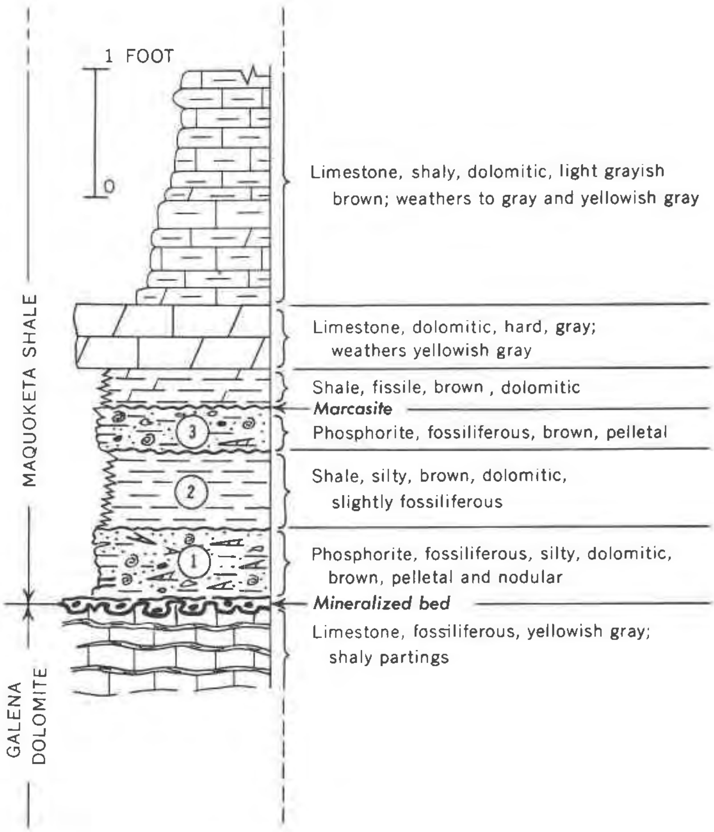

FIG. 3. Stratigraphic section showing the basal beds of the Maquoketa Shale, the contact with the Galena Dolomite, and the mineralized bed at Volga, Iowa. Channel sample CEB-65-11 (table 2) is from beds 1 and 3, and sample CEB-65-12 is from bed 2.

The vugs are irregular in shape, range from $\frac{1}{2}$ to 4 inches across, and although generally scattered are locally crowded within inches of one another. The vugs show no evidence of collapse or distortion of their shape because of compaction from above. Wedging outward from a few of the cavities are thin calcite veinlets that interconnect vugs or die out within a few inches. The thin calcite veins and crystal-lined cavities are wholly within the phosphatic material of the mineralized bed and were not observed along bedding surfaces. Apparently the only open spaces available during mineralization were these small cavities and fine fractures.

The areal extent of mineralization is unknown because only a few hundred square feet of the mineralized layer is exposed along the east side of the river. Other exposures of this bed were not seen in the vicinity of Volga. The author, while sampling this stratigraphic zone for its phosphate content, carefully examined the zone at numerous localities in Clayton County. Except for sparsely scattered small clots of calcite and disseminated pyrite, mineralization in vugs such as at Volga was not seen.

The origin of the cavities is not obvious. The wedge-like veinlets extending outward from the cavities suggest fractures resulting from shrinkage of the clayey, phosphatic debris toward the periphery of the limestone shell during lithification. They also might be simply small solution cavities. One vug has a narrow zone of fine-grained material surrounding it which could be insoluble residues remaining after dissolution of the rock. None of the other specimens show this phenomenon.

MINERALOGY

The minerals in the vugs are calcite, fluorite, pyrite, and sphalerite. Calcite and fluorite, in that order, are the most common minerals. Pyrite and sphalerite are present in minor quantities, and minute shiny black globules that are residues of hydrocarbons speck some of the crystal surfaces. The paragenesis of the minerals is shown in Figure 4.

Calcite. Calcite has grown in three stages each of which has a different crystal habit. Stage 1 calcite forms an equigranular crust that is a few

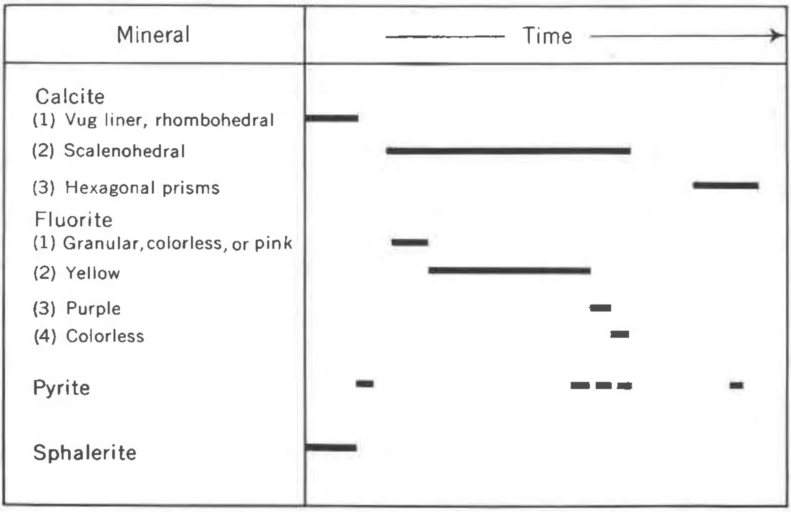

FIG. 4. Diagram showing paragenesis of the minerals in the vugs at Volga, Iowa.

millimeters in thickness and completely lines the wall of each vug. This calcite is fairly clear and does not have inclusions of other minerals. The small crystal units appear to terminate in stubby flattened forms, probably rhombohedrons; however, actual crystal terminations have not been observed. Calcite of stage 1 has a whitish fluorescence, the other two stages do not fluoresce.

The thin cavity lining of stage 1 calcite is overgrown by pyrite, fluorite, and second-stage calcite which is milky appearing and forms scalenohedrons that are generally 5 to 15 mm long. Some scalenohedrons, however, are more than an inch long and nearly fill the central part of cavities. One crystal in the author's collection is about 3 inches long. The second-stage calcite in a few of the vugs is in the form of "butterfly twins" (Fig. 5), *i.e.*, scalenohedral crystals twinned on planes parallel to either the positive or negative rhombohedrons. Most scalenohedrons have minute included pyrite crystals close to their outer surfaces.

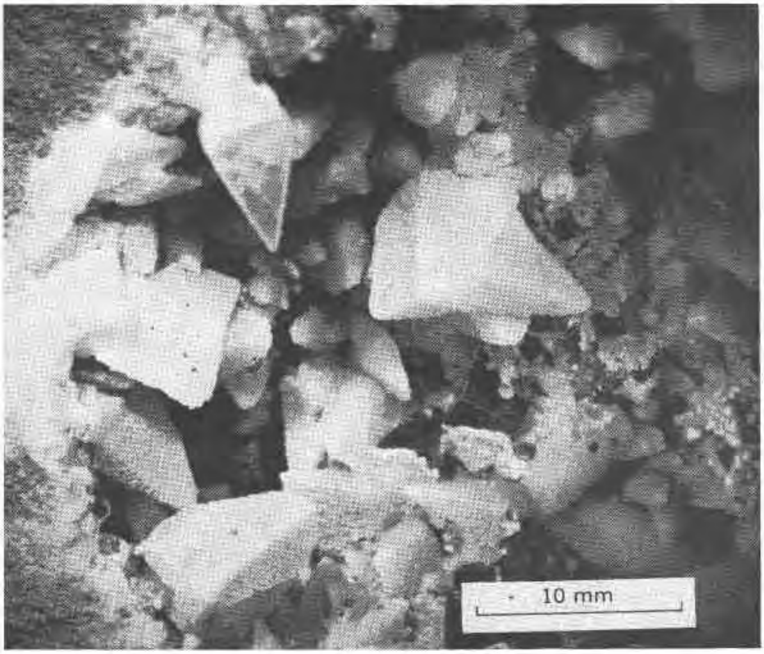

Fig. 5. Twinned scalenohedral stage 2 calcite. Rough surface is caused by overgrowth of stage 3 calcite.

All calcite of stage 2 is covered by a crystallographically oriented overgrowth of crystals of stage 3 calcite forming a crust 1 to 2 mm thick which grades from milky white to clear (Fig. 6). Individual crystals of stage 3 calcite are 1 to 2 mm long and are beautifully formed first order hexagonal prisms terminated by positive rhombohedral faces. The prisms are evenly distributed on and oriented to the underlying stage 2 scalenohedral crystals. When magnified, their regular pattern reminds one of tiles on a roof. Each scalenohedron is tipped by a single overgrown hexagonal prism. Megascopically, their oriented prism faces give a sheen to the calcite surfaces (Fig. 7). Near the bottom of some vugs, single or intergrown groups of millimeter-sized hexagonal prisms, in contrast to the oriented overgrowths, are found in little clusters and piles attached to the upward facing fluorite and stage 2 calcite crystal faces. These crystals apparently nucleated in the solution and settled to the floor of the vug. They are neither crystallographically oriented to the underlying crystal nor to each other. Some of the unoriented calcite crystals are shown in Figures 6 and 7. In a few small vugs which contain very little stage 2 calcite, the stage 3 calcite crystals are rhombohedrons without the hexagonal prism faces.

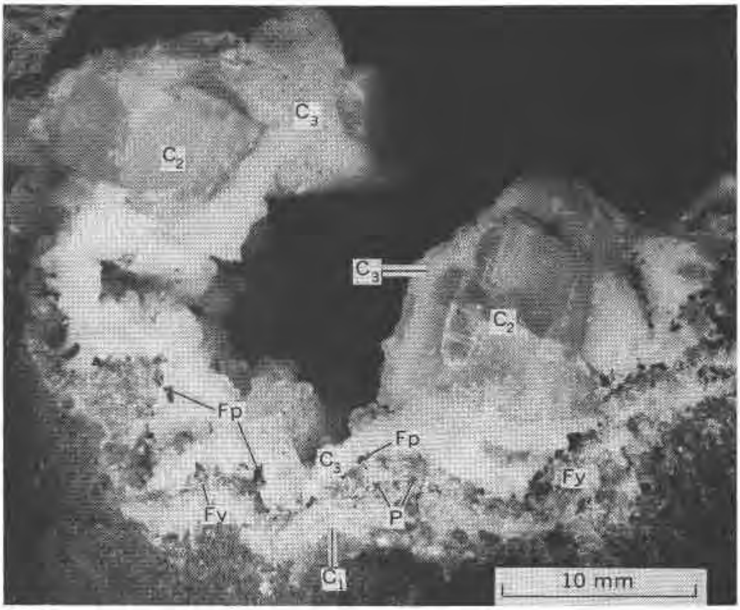

FIG. 6. Drusy vug showing overgrowth of stage 3 calcite and paragenetic relations of other minerals. Calcite stages (C_1, C_2, C_3); pyrite (P); yellow and purple fluorite (Fy, Fp).

Fluorite. Fluorite crystals are color-zoned cubes as large as 5 mm on a side. Under magnification, a slight rounding of the corners of some crystals by minute hexoctahedral faces is visible.

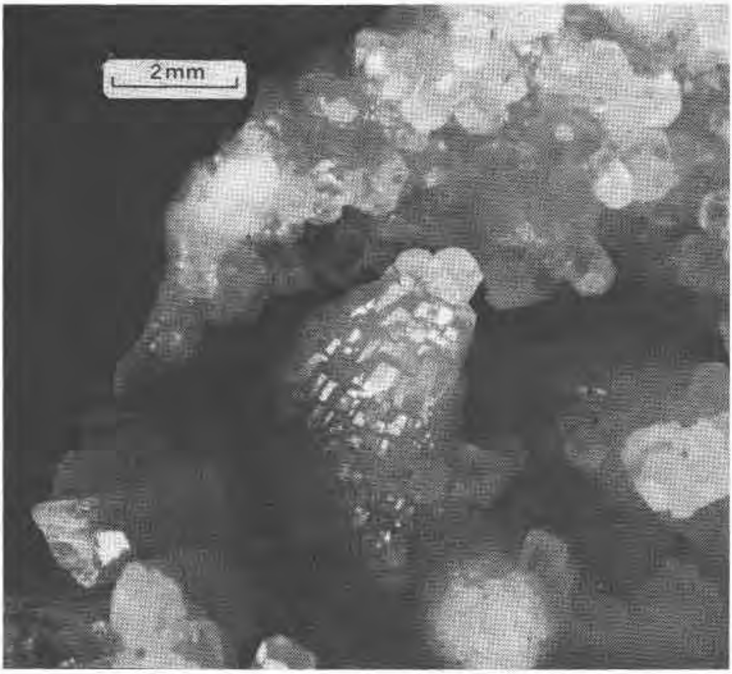

FIG. 7. Hexagonal prisms of stage 3 calcite overgrown on a stage 2 calcite scalenohedron.

Fluorite crystallized contemporaneously with stage 2 calcite and developed in 4 stages mainly distinguished by color (Fig. 8). The initial stage consists of fine, clear, colorless to very pale pink granules attached to the surface of stage 1 calcite or to pyrite crystals that are deposited on calcite 1. These granules coalesce into large, clear crystal units and grade upward to pale yellow fluorite which forms the bulk of most crystals (Fig. 9). Small fluorite crystals commonly do not show the yellow color. Under ultraviolet light the yellow fluorite has a faint yellowish fluorescence.

A sharply bounded dusky purple zone about 1 mm thick overlies the yellow fluorite and imparts a deep purple color to the entire crystal. It fluoresces in a bright whitish-yellow. On top of the thin purple zone is a shell of clear colorless fluorite generally less than 1 mm thick.

The proportions of the four stages of fluorite vary from vug to vug so that on some fluorite crystals the outer colorless zone is hardly visible. One vug in the collection has yellow crystals on which the purple zone is so thin that it is only visible when viewed on edge under a magnifier, and the clear outer shell is completely missing as in Figure 9.

Pyrite. Pyrite was deposited in at least three periods during the mineralization of the vugs. The earliest pyrite formed millimeter-sized cubes and aggregates of complexly modified pyritohedrons that locally form a discontinuous crust on first-stage calcite (Fig. 6). This early pyrite apparently grew alone since it is not found included in other crystals as are later pyrite crystals. The late pyrite crystals, which are included in the outer part of both fluorite and calcite crystals, formed octahedrons, cubes, and pyritohedrons, some grown together like beaded rods a few millimeters long. In some cases pyrite crystals protrude through the crystal faces of fluorite causing a sharply studded appearance under magnification. Pyrite crystals generally are included in calcite 2 near the boundary with calcite 3, and rarely are also in calcite 3.

Sphalerite. Sphalerite, one of the earliest minerals deposited in the vugs, occurs in grains as large as 5 mm intergrown with the first calcite stage. The sphalerite is very dark, and thin fragments are smoky yellow. Crystal form is not readily apparent; however, two minute broken crystals, both spinel twins, were found.

Marcasite. Marcasite is not present in the vugs but does occur at the Volga outcrop as crystalline aggregates and as a replacement of fossils

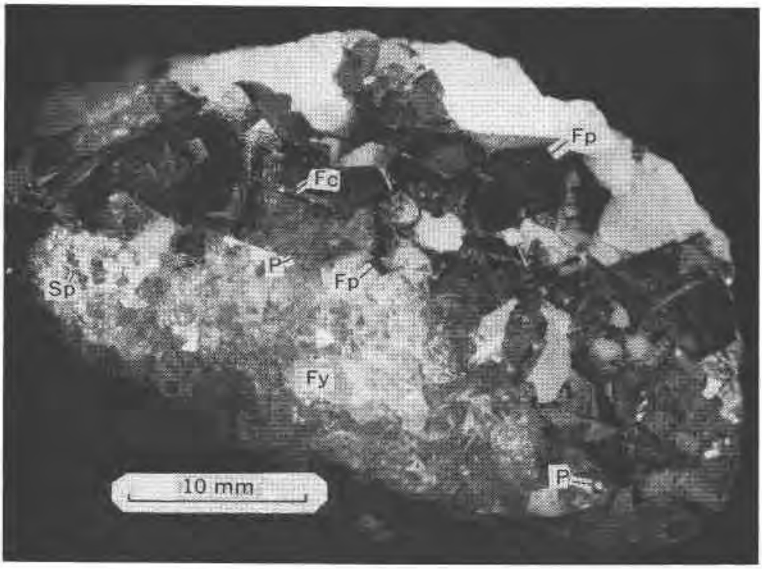

FIG. 8. Crystals showing 3 stages of fluorite, minute pyrite inclusions, and sphalerite. Yellow, purple, and late colorless fluorite (Fy, Fp, Fc); pyrite (P); sphalerite (Sp).

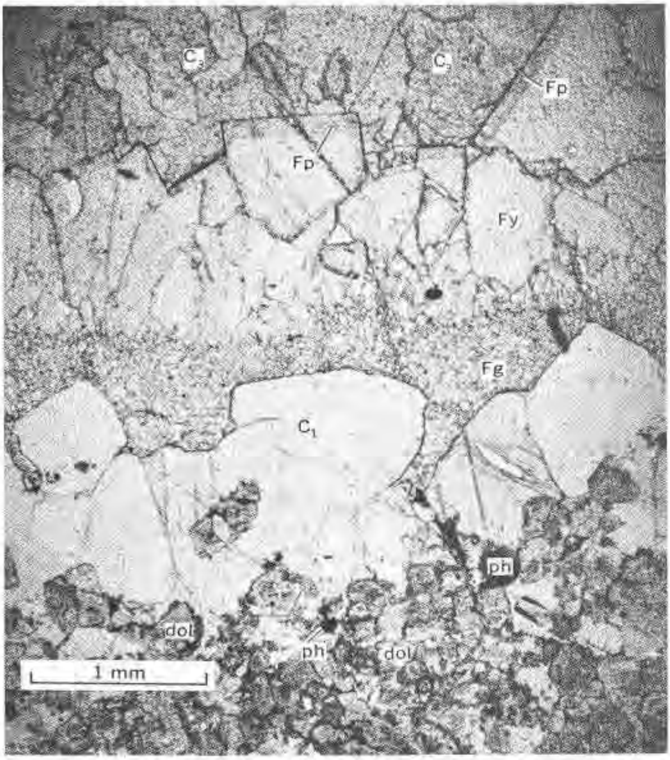

FIG. 9. Photomicrograph of crustified minerals on phosphatic dolomite of wallrock. Stages 1 and 3 calcite (C_1, C_3); colorless granular, yellow, and purple fluorite (Fg, Fy, Fp); dolomite (dol); phosphatic pellet (ph). Ordinary light.

and matrix in the upper part of the upper phosphorite bed, about 1.5 feet above the fluorite-bearing layer (Fig. 3).

COMPARISON WITH MINERALS OF THE UPPER MISSISSIPPI VALLEY ZINC-LEAD DISTRICT

The paragenesis, fluid inclusions, and minor elements of the minerals at Volga are compared below to those of the minerals in the upper Mississippi Valley zinc-lead district to determine the similarities and differences.

Paragenesis and crystal habit. Heyl and others studied the sequence of mineralization in the nearby zinc-lead mining district (1959, p. 97–101). Although fluorite is very rare and many more mineral species occur with the ores than at Volga, the chronologic order of crystallization of sphalerite, pyrite, and particularly the several crystal habits of calcite is similar. In the mining district, however, iron sulfide as pyrite or marcasite grew before and during the growth of sphalerite as well as forming crystal aggregates on the surface of crustiform sphalerite. The last stage of mineralization yielded four distinct types of calcite which occur in the same order throughout the district. They are in general as follows (Heyl and others, 1959, p. 100):

> Type I, milky to pale pink rhombohedrons with inclusions of marcasite and other sulfide minerals; type II, slightly cloudy, sharp, etched scalenohedrons with small marcasite crystals on the surfaces; type III, scalenohedrons modified by rhombohedral faces; and type IV, clear, unetched rhombohedrons as oriented overgrowths on the scalenohedrons.

The early growth of sphalerite, and the similarity of crystal form of calcite types III and IV of the district to calcite stages 2 and 3 at Volga, are possibly important in relating the vug mineralization with that of the mining district.

Fluid inclusions. Fluid inclusions in the Volga fluorite were examined by Edwin Roedder, who is also studying inclusions in the ore minerals of the other Mississippi Valley lead-zinc districts. His preliminary findings show that the liquid in the primary inclusions of the fluorite is a very concentrated saline solution and he estimates that the bubbles were filled at a relatively low temperature, certainly below 80°C (oral commun., 1966). Hall and Friedman (1963) found that fluid inclusions in ore minerals from the upper Mississippi Valley zinc-lead district are very concentrated sodium-calcium-chloride brines. Therefore, the saline solutions in the inclusions in fluorite at Volga possibly are similar to those of the nearby mining districts.

A. J. Erickson, Jr. (1965) studied fluid inclusions to determine the temperatures of calcite deposition for the upper Mississippi Valley zinc-lead district and found the following temperature ranges (uncorrected for pressure):

(1) Type II calcite, 51.0 to 74.0°C
(2) Type III calcite, 46.5 to 62.5°C
(3) Type IV calcite, 46.2 to 56.0°C
(4) All minerals, 46.2 to 121°C

In general, temperature of deposition is less in the younger calcite types.

Because the fluorite at Volga and the scalenohedral stage 2 calcite grew contemporaneously, and calcite 2 appears correlative with type III calcite of the zinc-lead district, a relatively cool temperature at deposition as estimated by Roedder for fluorite at Volga should be expected.

TABLE 1. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF ROCKS AND MINERALS FROM VOLGA, IOWA, AND TWO CALCITES FROM NEW DIGGINGS, WISCONSIN J. L. Harris, analyst

Laboratory No.	165668	165676	166006	166008	162723	162726	166004	166003	166002	W-16618	166005
Field No. and/or Name	CEB-65-11 Phosphorite (Fig. 4)	CEB-65-12 Phosphatic shale (Fig. 4)	Stage 2 calcite	Stage 3 calcite	Type III calcite[b]	Type IV calcite[b]	Early colorless fluorite	Yellow fluorite	Purple fluorite	Early pyrite	Sphalerite
Minor elements (in weight percent)[c]											
Si	[a]	[a]	0.001	0.015	0.003	0.0007	0.001	0.003	0.05	0.15	0.07
Al	[a]	[a]	<0.001	< .001	0.002	0.0007	0.001	<0.001	0.05	<0.001	<0.001
Fe	[a]	[a]	0.05	0.2	0.002	0.001	0.0	0	0.03	M	1.5
Mg	[a]	[a]	0.2	0.05	0.03	0.07	0.03	0.02	0.005	0	0.07
Ca	[a]	[a]	M	M	M	M	M	M	M	2.0	0.7
Ti	[a]	[a]	0	0	0	0	0	0	0	0.01	0
Mn	[a]	[a]	0.03	0.07	0.05	0.03	0	0	0	0	0.03
Ag	0	0	0	0	0	0	0	0	0	0	≤0.0001
B	0	0.003	0	0	0	0	0	0	0	0	0
Ba	0.02	0.02	0	0.0003	0.03	0.0003	0	0	0	0	0.003
Ce	0.03	0	0	0	0	0	0	0	0	0	0
Co	0.001	0	0	0	0	0	0	0	0	0	0
Cr	0.007	0.005	0	0.002	0	0	0	0	0.002	0	0.0007
Cu	0.003	0.002	0.0005	0	0	0	0	0	0.0005	0.02	0.1
Ga	0.0007	0.0007	0	0	0	0	0	0	0	0	0.01
La	0.01	0.007	0	0	0	0	0	0	0	0	0
Mo	0.0003	0	0	0	0	0	0	0	0	0.0015	0
Nb	0	0	0	0	0	0	0	0	0	0.005	0
Nd	0.03	0	0	0	0	0	0	0	0	0	0
Ni	0.005	0.003	0	0	0	0	0	0	0	0.01	0
Pb	0.007	0.0005	0	0	0	0	0	0	0	0.02	0.05
Sc	0.0007	0.0005	0	0	0	0	0	0	0	0	0
Sr	0.03	0.05	0.007	0.002	0.01	0.007	0.007	0.007	0.007	0	0
V	0.003	0.003	0	0	0	0	0	0	0	0	0
Y	0.01	0.007	0	0	0	0	0	0	0	0	0
Yb	0.0005	0.0005	0	0	0	0	0	0	0	0	0
Zn	0	0	0	0	0	0	0	0	0	0.007	M
Zr	0.003	0.015	0	0	0	0	0	0	0	0.01	0

[a] Chemical analyses on Table 2.

[b] From Thompson-Temperley Mine, New Diggings, Wisconsin; collected by Allen V. Heyl, Jr.

[c] Results are reported in percent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc., which represent approximate midpoints of group data on a geometric scale. The assigned group for semi-quantitative results will include the quantitative value about 30 percent of the time.

M = major constituent—greater than 10 percent

0 = looked for but not found.

These elements also were looked for but not found: As, Au, Be, Bi, Cd, Ge, Hf, Hg, In, Li, Pd, Pt, Re, Sb, Sn, Ta, Te, Th, Tl, U, W, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu.

Minor element content. Semi-quantitative spectrographic analyses (Table 1) were made on the individual minerals from the Volga occurrence for comparison with similar analyses of minerals from the upper Mississippi Valley zinc-lead district and the Illinois-Kentucky fluorspar district. Allen V. Heyl and Wayne E. Hall are studying the minor element distribution in the many mineral phases of the mining districts and kindly furnished their unpublished data (Heyl, written commun., 1965).

In general, calcite, pyrite and sphalerite at Volga contain similar quantities of elements such as silicon, aluminum, iron, magnesium, and manganese, to those in the same minerals in the upper Mississippi Valley mining district. However, some elements which are characteristically present in significant quantities at one place are present in very minor amounts or completely absent at the other. Thus, differences in minor element suites in the minerals are conspicuous. Nevertheless, a significant match of minor element suites exists between stage 2 and 3 calcite of Volga and Type III and IV calcite of the mining district (Table 1). As mentioned previously, these calcites also match closely in crystal habit. The match of minor elements in the late stages of calcite is mainly due to a lack of yttrium, ytterbium, and silver which consistently appear in analyses of the earlier Types I and II calcite of the upper Mississippi Valley mining district.

Pyrite at Volga is dissimilar in several respects from that of the district. It contains 100 ppm zirconium and 50 ppm niobium; analyses of 2 pyrites from the zinc-lead district show only 7 ppm zirconium, and niobium is absent. Also, pyrite from the zinc-lead district carries as much as 1 percent nickel and cobalt, about 1/2 percent zinc, and a few ppm of silver, arsenic, barium, strontium, and manganese. In contrast the pyrite at Volga contains only 100 ppm nickel, 70 ppm zinc, and silver, cobalt, arsenic, barium, strontium, and manganese are absent (Table 1).

Minor element content of sphalerite from Volga, likewise, has more distinct differences from, than similarities to the sphalerite of the zinc-lead district. Cadmium, cobalt, germanium, and vanadium, which are consistently present in the sphalerite of the district, are absent in the Volga sphalerite. As much as 100 ppm silver is present in sphalerite of the district, but at Volga less than 1 ppm is present. On the other hand, sphalerite at Volga contains more chromium, copper, and gallium than its counterpart in the district.

Despite the differences in minor element suites of several mineral types, the author believes the near match of both crystal habit and minor element suites of calcite types III and IV of the district and calcite stages 2 and 3 at Volga is indicative of a genetic relationship.

TABLE 2. CHEMICAL ANALYSES OF PHOSPHORITE AND PHOSPHATIC SHALE FROM BASAL BEDS OF MAQUOKETA SHALE AT VOLGA, IOWA[a]

Constituent	CEB-65-11[b] Phosphorite	CEB-65-12[b] Phosphatic Shale
SiO_2	5.5	45.8
Al_2O_3	1.2	7.0
Fe_2O_3	1.5	0.79
FeO	0.20	0.92
MgO	1.2	5.8
CaO	47.0	15.1
Na_2O	0.24	0.14
K_2O	0.45	3.4
H_2O-	0.43	0.42
H_2O+	0.87	2.0
TiO_2	0.12	0.53
P_2O_5	19.7	3.8
MnO	0.05	0.19
CO_2	17.2	12.0
F	1.95	0.62
S as SO_3	2.9	1.1
Total	100.51 percent	99.61 percent

[a] Analyzed by Paul Elmore, S. Botts, L. Artis, H. Smith, G. Chloe, J. Glenn, D. Taylor, using methods described in *U. S. Geol. Survey Bull.* **1144-A**, supplemented by atomic absorption methods.

[b] See Figure 4, this paper, for stratigraphic position of analyzed beds.

Bioclastic phosphorite in the Phosphoria Formation locally has veinlets of secondary fluorite that are apparently produced by a chemical reorganization of elements in the surrounding calcium and fluorine-rich rocks (R. A. Gulbrandsen, written commun., 1966; Sheldon, 1963, p. 144). This process could also account for the vug minerals at Volga because the surrounding rocks probably contain all the elements found in the vug minerals. Zinc, although indicated as not present in Table 1, may be there in quantities less than about 0.01 percent because that is its limit of detection in semi-quantitative spectrographic analysis. The complete lack of rare earth elements in the Volga fluorite seems to refute this mode of origin because fluorite commonly contains small quantities of rare earths and at Volga they are available in the enclosing phosphorite. Heinrich (1948) notes the widespread geochemical association of rare-earth elements in fluorite, however, most of the examples he cited are from pegmatites. R. D. Allen (1952), reporting only elements occurring in quantities greater than 50 ppm, found yttrium in 24 of 34 fluorites from several different geologic environments and a few of these fluorites also contain lanthanum and europium. Dunham (1952) shows that many fluorites from England commonly contain yttrium and traces of other rare earths, and a dark-purple fluorite from Hicks Dome, Illinois, contains several rare earths in notable quantities (W. E. Hall, written commun., 1965). The wallrock phosphorite of the Volga vugs contains a total of more than 800 ppm cerium, lanthanum, neodymium, scandium, and yttrium (Table 1). The absence of these elements in the Volga fluorite implies an origin other than from chemical breakdown of carbonate-fluorapatite in the surrounding phosphorite.

CONCLUSIONS

Although the chemical elements needed to form the assemblage of minerals in the vugs at Volga are available locally, the minerals' similarity in paragenesis, composition, temperature of formation of fluid inclusions, crystal habits and minor element content of calcites to late-formed calcites of the upper Mississippi Valley zinc-lead district, suggests a common origin.

The lack of rare earths, particularly yttrium, in the Volga fluorite argues against a derivation from the surrounding rocks because fluorite elsewhere commonly contains these elements, and at Volga rare earths are available in the enclosing phosphorite host rock.

The occurrences of fluorite in the outlying areas such as Volga and Raymond, Iowa, and Mineral Point and Neenah, Wisconsin, and the virtual lack of fluorite in the central part of the upper Mississippi Valley zinc-lead district, suggests that the mineral might be part of a paragenetically late, outward fringe of mineralization.

ACKNOWLEDGMENTS

The writer appreciates the many helpful suggestions and criticisms offered by Robert M. Grogan, R. A. Gulbrandsen, Allen V. Heyl, G. I. Smith, and Ralph Van Alstine. John Creel was of great assistance in taking the photographs of minerals. The author also acknowledges the fine work of Robert W. Banks and Jane Martin in preparing the illustrations for this paper.

REFERENCES

ALLEN, R. D. (1952) Variations in chemical and physical properties of fluorite. *Amer. Mineral.* **37,** 910–930.

BAGG, R. M. (1918) Fluorspar in the Ordovician limestone of Wisconsin. *Geol. Soc. Amer. Bull.* **29,** 393–398.

BRADBURY, J. C. (1961) Mineralogy and the question of zoning, north-western Illinois zinc-lead district. *Econ. Geol.* **56,** 132–148.

BROWN, C. ERVIN, AND JESSE W. WHITLOW (1960) Geology of the Dubuque South quadrangle, Iowa-Illinois. *U. S. Geol. Surv. Bull.* **1123**-A.

CALVIN, SAMUEL (1906) Geology of Winnesheik County [Iowa]. *Iowa Geol. Surv. Ann. Rep.* **16,** 39–146.

DUNHAM, K. C. (1952) Fluospar. *Great Brit. Geol. Surv. Mem.* **4,** 1–143.

ERICKSON, A. J., JR. (1965) Temperatures of calcite deposition in the upper Mississippi Valley lead-zinc deposits. *Econ. Geol.* **60,** 506–528.

FEULNER, A. J. (1953) *Ground water resources of Clayton County, Iowa.* Iowa State Univ., M.S. thesis.

HALL, W. E., AND IRVING FRIEDMAN (1963) Composition of fluid inclusions, Cave-in-Rock fluorite district, Illinois, and upper Mississippi Valley zinc-lead district. *Econ. Geol.* **58,** 886–911.

HEINRICH, E. WM. (1948) Fluorite-rare earth mineral pegmatites of Chaffee and Fremont Counties, Colorado. *Amer. Mineral.* **33,** 64–75.

HEYL, A. V., JR., A. F. AGNEW, E. J. LYONS, AND C. H. BEHRE, JR. (1959) Geology of the upper Mississippi Valley zinc-lead district. *U. S. Geol. Surv. Prof. Pap.* **309.**

LEONARD, A. G. (1906) Geology of Clayton County [Iowa]. *Iowa Geol. Surv. Ann. Rep.* **16,** 217–319.

PRATT, MARILYN, AND MURIEL MENZEL (1965) Iowa has something for everyone. *Gems Minerals Mag. Calif. Fed. Mineral. Soc.* **334,** (July), 14–19.

RALL, RAYMOND W. (1950) *Ostracods from the depauperate zone of the Maquoketa Shale.* Univ. Illinois, M.S. thesis.

SHELDON, RICHARD P. (1963) Physical stratigraphy and mineral resources of Permian rocks in western Wyoming. *U. S. Geol. Surv. Prof. Pap.* **313**-B.

Manuscript received, March 20, 1967; accepted for publication, September 20, 1967.