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Dolomitic limestones of the Middle Devonian Cedar Valley Formation are exposed at Pint's Quarry. The mineralized vugs contain well developed crystals of barite, calcite, fluorite, galena, marcasite, quartz, pyrite, and sphalerite.

INDEX DESCRIPTORS: Vugs, barite, calcite, fluorite, galena, marcasite, quartz, pyrite, sphalerite.

Welp and McCarten, Inc. operate "Pint's Quarry," just north of Raymond, Iowa in SE1/4, Sec. 36, T.89N., R.12W. of Black Hawk County. This quarry is a favorite locality for mineral collectors (Anderson, 1972). Good crystals of barite, calcite, fluorite, galena, marcasite, pyrite, quartz, and sphalerite can be found in the lower levels of the quarry in the Solon Member of the Cedar Valley Formation (Pratt, 1965 and Menzel, 1968).

Diagenesis is a striking feature of the rocks at Pint's Quarry. Recrystallization of calcite and dolomitization of the original limestone is extensive and few beds in the quarry have escaped it. Silicification, although less abundant, is pervasive (Kettenbrink, 1972). Vugs, ranging from one-half inch to six inches (1 to 15 cm) in diameter and lined with calcite crystals, are conspicuous throughout the quarry. In addition, these vugs may be mineralized with barite, fluorite, galena, marcasite, pyrite, quartz, and sphalerite.

I collected minerals in vugs at Pint's Quarry and also examined other collections. The minerals were identified by different methods including x-ray diffraction. This paper describes the crystal forms, x-ray diffraction data and paragenesis of minerals in Pint's Quarry.

Although I examined several specimens identified by collectors as chalcopyrite and wurtzite, they proved to be pyrite and sphalerite respectively.

Secondary iron oxide is present in the exposed vugs. These oxides formed by the weathering of marcasite and pyrite when they were exposed to air.

I did not find chalcopyrite, geothite, limonite, and wurtzite, which were reported by Horick (1974).

BARITE

Barite occurs as tabular crystals which are usually found in radiating aggregates (Figure 1). It is usually very pale yellow, tabular on (001) which means the c-axis is perpendicular to the tabular face (Figure 2).

CALCITE

Calcite is the most abundant mineral in the vugs. There are three different forms of rhombohedral calcite. Figure 3 shows the first type of rhombohedron f$\{02\bar{2}1\}$ calcite. This crystal form is diagrammed in Figure 4. The second type of rhombohedron is r$\{10\bar{1}1\}$. The third type of rhombohedron is e$\{01\bar{1}2\}$. Figure 5 shows a tabular calcite crystal. The c-axis is perpendicular to the flat face (0001). This crystal form is diagrammed in Figure 6. A combination of rhombohedron and pinacoid crystal form in calcite is shown in Figure 7. This crystal form is diagrammed in Figure 8. Figure 9 shows a white scalenohedron v$\{21\bar{3}1\}$ crystal form of calcite which grows on the surface of stained calcite. This crystal form is diagrammed in Figure 10. Figure 11 shows the calcite that grows as a combination of scalenohedron v$\{21\bar{3}1\}$ and prism m$\{10\bar{1}0\}$ crystal forms.

FLUORITE

Fluorite in Pint's Quarry is always found as cubes. The color usually is yellow, though some pale brown crystals were noted. Purple and white fluorite are rare. The size of crystals varies from 1 mm to 4 cm. The x-ray diffraction data on fluorite (Table 1) from Pint's Quarry were comparable with the powder diffraction file (JCPDS, 1974). The calculated axial unit, a_0, is 5.46_3 A which was obtained by using graphical extrapolation (Azaroff, 1968).

GALENA

Galena is very rare, indicating that the quarry may have lacked lead. Only two pieces of galena have been found to date; one belongs to Mr. Ed Hix, and the other belongs to Mrs. Muriel Menzel. The x-ray diffraction data of galena were comparable with the powder diffraction file (Table 2). The calculated axial unit, a_0, is 5.93_5 Å.

MARCASITE

Figure 13 shows a typical crystal of marcasite found in the quarry. It is bronze-yellow, tabular on (010). A hair-like needle of marcasite which capillary along c-axis is shown in Figure 14. An isolated crystal of marcasite is shown in Figure 15. Other crystals occur as rosette, tabular rose, and tabular needle.

PYRITE

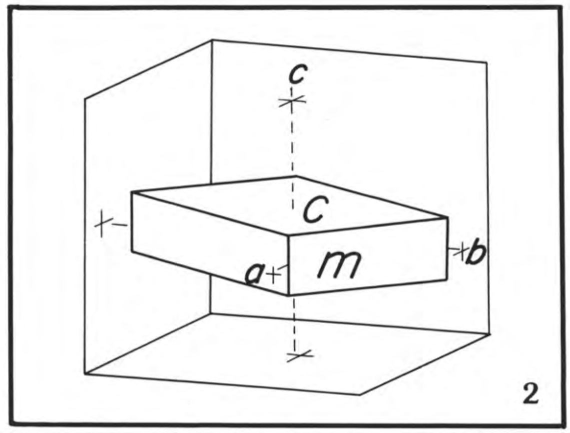
Pyrite is usually found in cubic or octahedral form. The pyrite crystals shown in Figure 17 are a combination of the cube a$\{100\}$ and octahedron o$\{111\}$ crystal forms. This type of crystal form is diagrammed in Figure 18. The pyrite crystal shown in Figure 19 has five faces surrounding one point. This indicates a combination of octahedron o$\{111\}$ and pyritohedron e$\{210\}$ crystal forms. This crystal form is diagrammed in Figure 20. The x-ray diffraction data of pyrite were comparable with x-ray diffraction file (Table 3). The calculated axial unit, a_0, is 5.41_8 Å. Sometimes, the color of tarnished pyrite is blue. When the tarnished pyrite is placed in hydrochloric acid, it will return to a brass-yellow color.

Plate 1.

Figure 1. Barite in Pint's Quarry. Scale = 2 cm.
Figure 2. Barite crystal forms: basal pinacoid c$\{001\}$ and m$\{210\}$.
Figure 3. Rhombohedron f$\{02\bar{2}1\}$ of calcite. Scale = 3 cm.
Figure 4. Calcite crystal form: rhombohedron f$\{02\bar{2}1\}$.
Figure 5. Calcite which shows pinacoid $\{0001\}$ crystal form. Scale = 2 cm.
Figure 6. A combination of pinacoid $\{0001\}$ and prism m$\{10\bar{1}0\}$ crystal form.
Figure 7. Calcite shows a combination of rhombohedron f$\{02\bar{2}1\}$ and pinacoid $\{0001\}$ crystal form. Scale = 1 cm.
Figure 8. A combination of rhombohedron f$\{02\bar{2}1\}$ and pinacoid $\{0001\}$ crystal form.

2 CM

1



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3 CM

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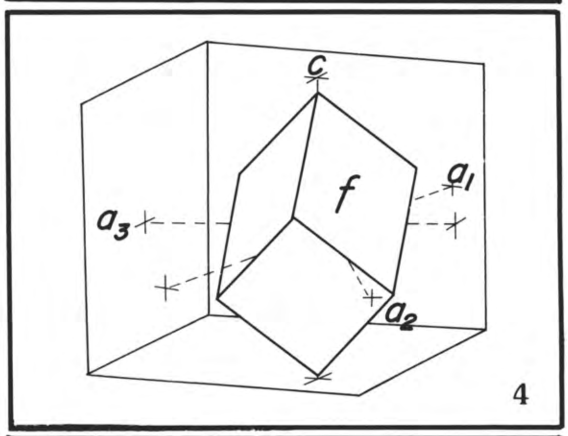

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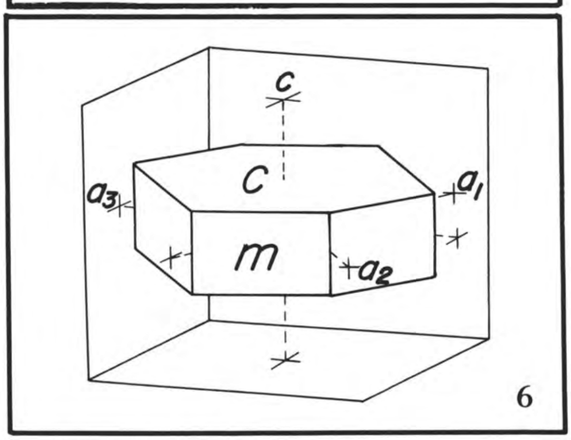

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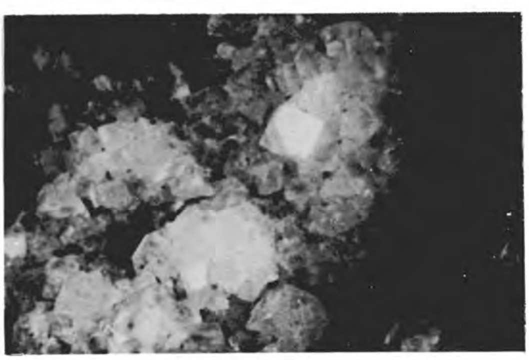

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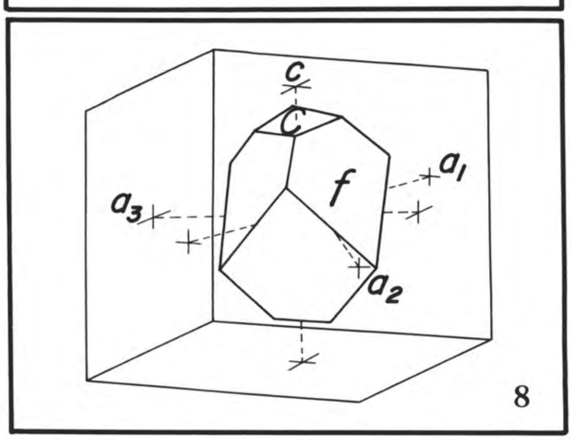

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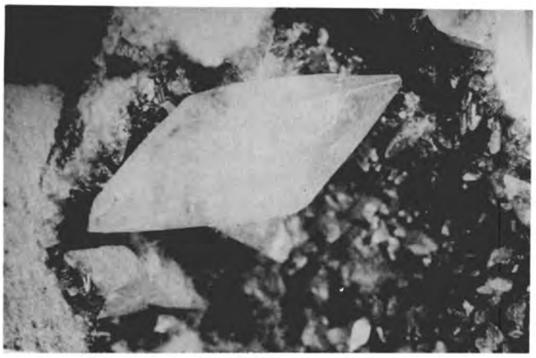

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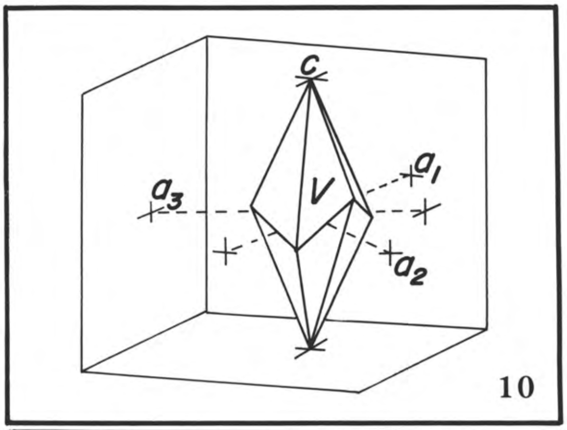

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2 CM

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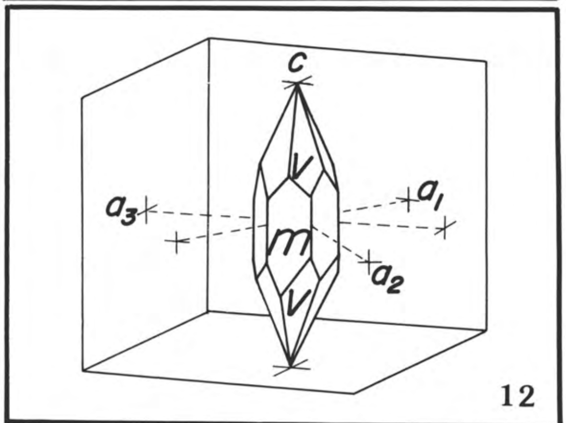

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3 CM

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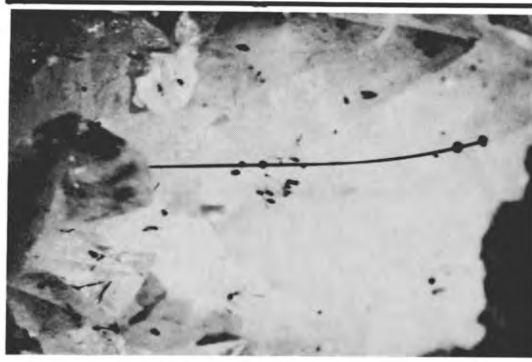

1 CM

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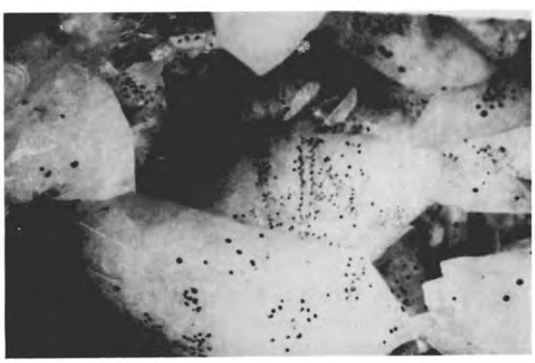

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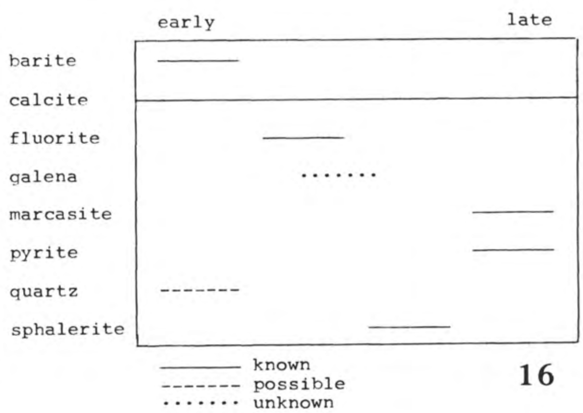


16

QUARTZ

Quartz is present as combined prism m{10$\bar{1}$0}, and pyramids r{10$\bar{1}$1} and z{01$\bar{1}$1} from Pint's Quarry (Figure 21). This crystal form is diagrammed in Figure 22.

SPHALERITE

Figure 23 shows sphalerite with many triangular faces, indicating that it is composed of tetrahedrons o{111}. This crystal form is diagrammed in Figure 24. The color is very dark, probably indicating a high iron content. The x-ray diffraction data of sphalerite were comparable with powder diffraction file (Table 4). The calculated axial unit, a_O, is 5.40_7 Å.

Table 1. *X-ray diffraction data of fluorite and powder diffraction file 4-0864.*

hkl	fluorite (Pint's Quarry) d (Å)	fluorite (Pint's Quarry) I(visual)	fluorite (JCPDS file 4-0864) d (Å)	fluorite (JCPDS file 4-0864) I/I₁
111	3.12_2	9	3.153	94
220	1.92_0	10	1.931	100
311	1.64_1	7	1.647	35
400	1.36_1	2	1.366	12
331	1.24_9	2	1.253	10
422	1.11_3	4	1.1150	16
511	1.050	1	1.0512	7
440	0.965	1	0.9657	5
531	0.923	1	0.9233	7
600			0.9105	1
620	0.863	1	0.8637	9
533	0.833	0	0.8330	3
	0.789	0		

$a_O = 5.46_3$ Å $a_O = 5.4662$ Å

PARAGENESIS

I examined many specimens in order to determine the paragenetic sequence. Calcite grew continuously. A pyrite crystal grew on the surface of a sphalerite crystal and a sphalerite grew on the surface of a fluorite crystal. A fluorite crystal was found growing on the surface of a barite crystal. These minerals probably have the following paragenetic sequence from earliest to latest; barite, fluorite, sphalerite, pyrite. Marcasite grew at the same time pyrite grew. A fluorite crystal was found growing on the surface of a quartz crystal. Quartz is therefore older than fluorite. Only two pieces of galena have been found in the quarry up to now and its paragenetic relationship is unknown. It is very hard to determine the paragenesis of all the minerals in the vugs. Figure 16 shows a suggested paragenesis of the minerals in Pint's Quarry.

Table 2. *X-ray diffraction data of galena and powder diffraction file 5-0592.*

hkl	galena (Pint's Quarry) d (Å)	galena (Pint's Quarry) I(visual)	galena (JCPDS file 5-0592) d (Å)	galena (JCPDS file 5-0592) I/I_1
111	3.40_7	6	3.429	84
200	2.95_3	10	2.969	100
220	2.09_2	6	2.099	57
311	1.78_5	5	1.790	35
222	1.71_1	4	1.714	16
400	1.48_2	3	1.484	10
331	1.36_0	4	1.362	10
420	1.32_6	7	1.327	17
422	1.21_0	7	1.212	10
511	1.14_1	4	1.1424	6
440	1.048	3	1.0489	3
531	1.002	3	1.0034	3
600	0.989	3	0.9893	6
620	0.938	3	0.9386	4
533	0.905	2	0.9050	2
622	0.894	2	0.8952	4
444	0.857	1	0.8568	1
711	0.831	3	0.8312	3
640	0.823	3	0.8232	3
	0.794	10		
	0.773	10		

$a_O = 5.93_5$ Å $a_O = 5.9362$ Å

Plate 2.

Figure 9. Calcite showing a scalenohedron crystal form. Scale = 2 cm.

Figure 10. A scalenohedron v{21$\bar{3}$1} calcite.

Figure 11. Calcite showing a combination of scalenohedron and prism forms. Scale = 2 cm.

Figure 12. A combination of scalenohedron v{21$\bar{3}$1} and prism m{10$\bar{1}$0} forms.

Figure 13. A typical crystal of marcasite from Pint's Quarry. Scale = 3 cm.

Figure 14. A hair-like needle of marcasite from Pint's Quarry. The small round grains on the top of needle are marcasite. Scale = 1 cm.

Figure 15. Round, isolated crystals of marcasite from Pint's Quarry. Scale = 3 cm.

Figure 16. A paragenetic diagram of the minerals in Pint's Quarry.

Plate 3.

Figure 17. Pyrite crystals showing a combination of cubic and octahedral crystal forms. Scale = 3 cm.

Figure 18. Pyrite crystal forms: cube a{100}, octahedron o{111}.

Figure 19. Pyrite crystal showing a combination of the octahedral and pyritohedral crystal forms. Scale = 2 cm.

Figure 20. Pyrite crystal forms: octahedron o{111}, pyritohedron e{210}.

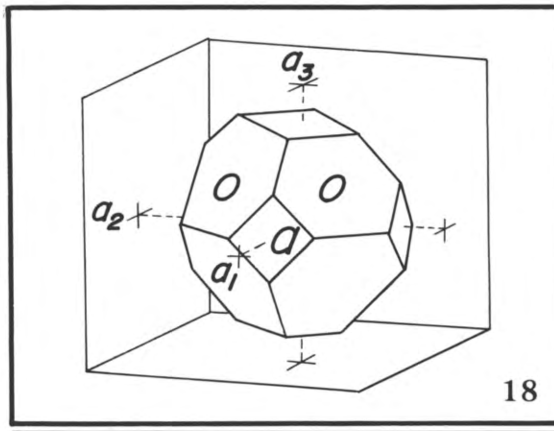
Figure 21. The quartz is prismatic, terminated by two sets of rhombohedrons. Scale = 2 cm.

Figure 22. Quartz crystal forms: prism m{10$\bar{1}$0}, two rhombohedrons r{10$\bar{1}$1} and z{01$\bar{1}$1}.

Figure 23. Sphalerite showing triangular faces. Scale = 1 cm.

Figure 24. Sphalerite crystal form: tetrahedron o{111}.

3 CM 17



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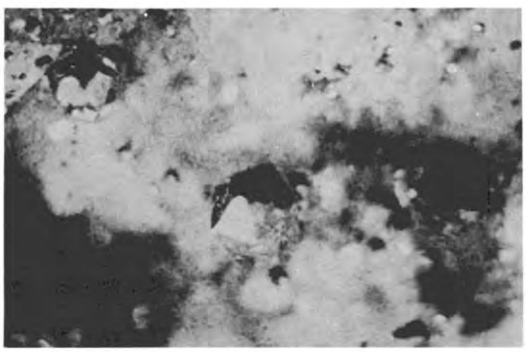
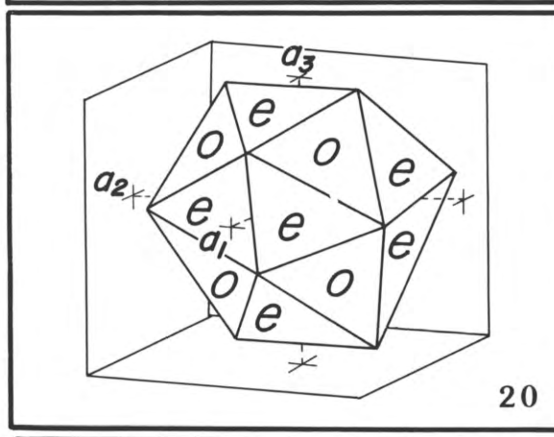


2 CM 19



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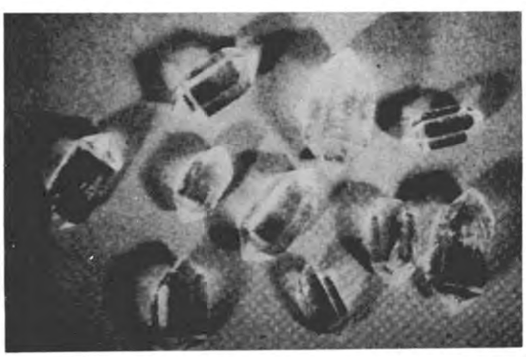

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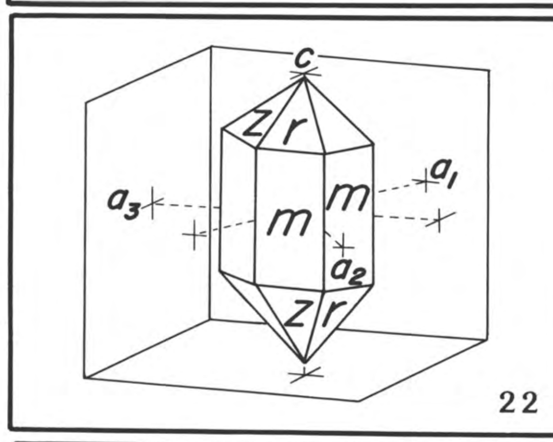

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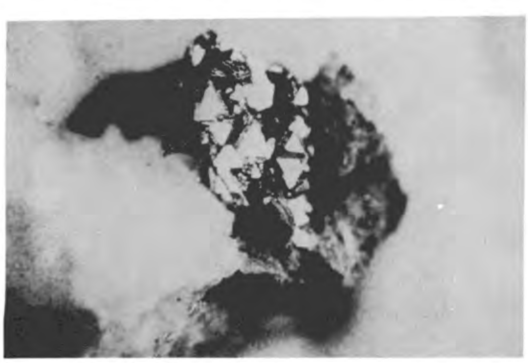

1 CM 23

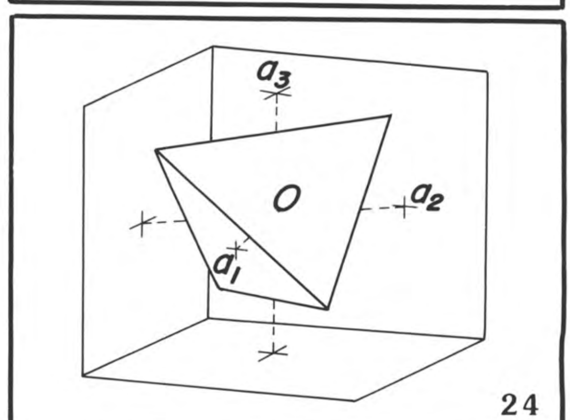

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Table 3. *X-ray diffraction data of octahedral pyrite and powder diffraction file 6-0710.*

hkl	pyrite (Pint's Quarry) d (Å)	pyrite (Pint's Quarry) I (visual)	pyrite (JCPDS file 6-0710) d (Å)	pyrite (JCPDS file 6-0710) I/I_1
111	3.09_5	2	3.128	35
200	2.68_2	8	2.709	85
210	2.40_1	6	2.423	65
211	2.19_8	6	2.2118	50
220	1.90_6	6	1.9155	40
311	1.62_7	10	1.6332	100
222	1.55_8	1	1.5640	14
230	1.49_8	2	1.5025	20
321	1.44_4	2	1.4448	25
331	1.24_0	1	1.2427	12
420	1.20_9	1	1.2113	14
421	1.18_0	1	1.1823	8
332	1.15_3	1	1.1548	6
	1.11_7	1		
422	1.10_4	1	1.1057	6
511	1.041	1	1.0427	25
432	1.005	1	1.0060	8
521	0.989	1	0.9892	6
440	0.958	1	0.9577	12
	0.912	0		
600	0.903	0	0.9030	16
	0.891	0		
611	0.879	0	0.8788	8
620	0.857	0	0.8565	8
533	0.826	0	0.8261	4
622	0.817	0	0.8166	4
	0.808	0		
631	0.799	0	0.7981	6
	$a_0 = 5.41_8$ Å		$a_0 = 5.417$ Å	

Table 4. *X-ray diffraction data of sphalerite and powder diffraction file 5-0566.*

hkl	sphalerite (Pint's Quarry) d (Å)	sphalerite (Pint's Quarry) I (visual)	sphalerite (JCPDS file 5-0566) d (Å)	sphalerite (JCPDS file 5-0566) I/I_1
111	3.10_4	10	3.123	100
200	2.69_3	1	2.705	10
220	1.90_7	9	1.912	51
311	1.62_8	8	1.633	30
222	1.55_9	0	1.561	2
400	1.35_1	1	1.351	6
331	1.24_0	4	1.240	9
420			1.209	2
422	1.10_4	2	1.1034	9
511	1.040	1	1.0403	5
440	0.956	1	0.9557	3
531	0.914	2	0.9138	5
620	0.855	0	0.8548	3
533			0.8244	2
	$a_0 = 5.40_7$ Å		$a_0 = 5.4060$ Å	

ACKNOWLEDGEMENT

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