

# MINERALOGY OF CONCRETIONS FROM PITTSBURGH COAL SEAM, WITH SPECIAL REFERENCE TO ANALCITE<sup>1</sup>

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## ABSTRACT

Four concretions were found in the Pittsburgh coal bed at Pursglove, Monongalia County, West Virginia, and were collected for study to obtain a better understanding of acid formation in the mine. Three of the concretions were mainly pyrite and the fourth was mainly dolomite. Associated with one or more of these concretions were these minerals: analcite, brammallite, calcite, dolomite, kaolinite, melanterite, pyrite, and an unknown mineral. The Pittsburgh coal bed is of Pennsylvanian age, and the base of the Monongahela formation. Analcite has been found in sedimentary rocks, identified as a constituent of boiler scale, and synthesized under hydrothermal conditions. In all cases it has been formed under alkaline conditions; it is decomposed by acid. It is supposed that alkaline solutions containing sodium reacted with clay to form analcite. Acids in the coal bed could have been neutralized by ground water passing through a limestone bed a few feet above the coal.

Analcite was synthesized at atmospheric pressure and 90°C. by allowing NaOH solution to react on kaolinite for 29 days. Only a small amount was formed; most was unidentified material.

## INTRODUCTION

In connection with studies relating to acid formation in coal mines, four concretions, supposedly of the sulfur-ball type, were obtained. Determination of the minerals in these concretions seemed desirable to provide a better basis for understanding their origin, even though such information may not apply directly to the acidity of mine water. Acid conditions are closely connected with decomposition of the pyritic minerals, which are commonly predominant in concretions of this general character.

## SOURCE AND GENERAL DESCRIPTION OF SAMPLES

These samples were collected from the Pittsburgh coal bed at the Pursglove No. 15 mine of the Pursglove Coal Mining Company, Pursglove, Monongalia County, West Virginia. This region, known as the Scotch Run Area, is just west of the Monongahela River and about five miles south of the Pennsylvania state line.

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The specimens were about 15 to 20 cm. in the longest dimension and weighed approximately 1 to 2 kg.

#### MINERAL ASSOCIATION IN THE CONCRETIONS

All of the minerals were identified by  $\alpha$ -ray diffraction; the identification of those minerals of particular interest was confirmed by petrographic methods. The minerals are tabulated in Table 1 and were identified either as a part of the concretion or associated with it.

TABLE 1. MINERALS FOUND IN THE SPECIMENS

Constituent	Concretion No. 1	Concretion No. 2	Concretion No. 3	Concretion No. 4
Major	Pyrite	Pyrite	Pyrite	Dolomite
Other Minerals	Kaolinite Unknown	Analcite Calcite Melanterite Unknown	Calcite Dolomite	Pyrite Calcite Brammallite

As shown in Table 1, three of the concretions were sulfur balls, and the fourth was mainly dolomite, resembling the coal-ball type in its woody cellular structure, although it was not typical of this type of concretion. No typical coal balls are known from the Appalachian coal field.

#### DESCRIPTIVE MINERALOGY

*Analcite*.—Analcite was found adjoining concretion No. 2, filling in a series of parallel cleat joints of the coal and adhering to the concretion. These joint fillings made a very intimate contact with the pyrite nodule but did not seem to extend into it. The analcite was white and was accompanied by a trace of calcite. Microscopically, it occurred in thin plates and was either isometric or weakly birefringent and uniaxial negative; in both cases the index of refraction was  $1.485 \pm 0.003$ . The spacings and intensities of its  $\alpha$ -ray diffraction lines are listed in Table 2.

*Brammallite*.—Brammallite,<sup>4</sup> a high-sodium illite, has been described only recently. It occurred as a white inclusion in concretion No. 4. A semi-quantitative spectrographic analysis showed several per cent of sodium, calcium, aluminum, iron, and silicon. Microscopically it had undulatory extinction and was biaxial negative with parallel extinction, and positive elongation. The indices were:  $\alpha = 1.55^+$ ,  $\gamma = 1.57^+$ . The

<sup>4</sup> Bannister, F. A., Brammallite (sodium illite), a new mineral from Llandebie, South Wales: *Mineral. Mag.*, **26**, 304-307 (1943).

axial angle is uncertain but may be small. *X*-ray data are given in Table 3. This is the second sodium-bearing mineral found in these concretions.

*Calcite*.—Traces of calcite were found in concretions Nos. 2 and 4. It was abundant in a joint crack outside concretion No. 3, in places inside the ball, and in surface depressions as a reddish or brownish material associated with dolomite.

*Dolomite*.—A little reddish or brownish dolomite was associated with calcite in concretion No. 3 in surface depressions. Brown dolomite was the major constituent of concretion No. 4.

*Kaolinite*.—Large amounts of kaolinite were found in concretion No. 1 as light-colored inclusions in the surface and inside.

*Melanterite*.—A small amount of melanterite coated concretion No. 2; it was also found inside on some partings.

*Pyrite*.—Pyrite was the major constituent of concretions Nos. 1, 2, and 3; a trace was also present in No. 4. Marcasite was not found. Pyrite tends to form at a higher *pH* than marcasite. Two of the three sulfur balls oxidized rapidly and disintegrated while standing in the laboratory; the third was relatively inert. Bain<sup>5</sup> reported that pyrite that weathers easily has a high electrical conductivity, while more stable pyrite has only a low conductivity; however, all three of these samples were of a uniformly low conductivity.

*Unknown*.—An unknown mineral was found. It was most abundant as a thin coating on concretion No. 2; smaller amounts were found on No. 1. Further studies to identify this mineral are in progress.

#### DISCUSSION OF FORMATION OF ANALCITE

Since analcite has been found only occasionally in sedimentary mineral deposits and has not previously been reported in coal deposits, the following discussion relates particularly to its occurrence and formation.

The Pittsburgh coal bed forms the base of the Monongahela series of the Upper Pennsylvanian. Deposition continued on into Permian time, when there was an uplift, and Monongalia County has been above sea level ever since. Approximately 1400 to 1500 ft. of strata now remain above the Pittsburgh coal<sup>6</sup> in Monongalia County. Undoubtedly other strata were deposited and completely eroded, but the geological consensus is that the temperature of the coal never far exceeded 100°C., due to depth of burial.

According to Schopf,<sup>7</sup> the concretions in coal are generally formed

<sup>5</sup> Bain, G. W., Pyrite oxidation: *Econ. Geol.*, **30**, 166–169 (1935).

<sup>6</sup> Hennen, R. V., and Reger, D. B., *West Virginia Geol. Sur. County Report*: Marion, Monongalia, and Taylor Counties pp. 90–94 (1913).

<sup>7</sup> Schopf, James M., Paleobotanist, Coal Constitution Laboratory, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa. Personal communication.

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR ANALCITE SAMPLE COMPARED WITH PUBLISHED DATA  
(Ni-filtered Cu radiation. Camera radius=203 mm. Calibration against quartz, pyrite, and kaolinite.)

Analcite in Concretion No. 2		Analcite <sup>2</sup> (Mo radiation)	
Interplanar spacing, A	Estimated intensity <sup>1</sup>	Interplanar spacing, A	Intensity <sup>1</sup>
5.8	vs	5.59	.8
4.95	m	4.85	.4
		3.82	.1 <sup>3</sup>
3.67	m	3.65	.2 <sup>3</sup>
3.43	vs	3.43	1.0
		3.27	.1 <sup>3</sup>
		3.04	.1 <sup>3</sup>
2.93	vs	2.93	.8
2.81	m	2.79	.4 <sup>3</sup>
2.68	s	2.69	.6
2.50	s	2.50	.6
2.43	m	2.42	.3
2.23	m	2.22	.4
2.17	w		
2.12	w	2.11	.05 <sup>3</sup>
		2.08	.05 <sup>3</sup>
2.02	w		
1.94	vw		
1.90	s	1.90	.5
1.87	m	1.86	.4
1.83	vw		
1.74	s	1.74	.6
1.71	m	1.717	.1 <sup>3</sup>
1.69	m	1.681	.1 <sup>3</sup>
1.66	w		
1.63	vw		
1.62	w	1.615	.05 <sup>3</sup>
1.60	m	1.597	.1 <sup>3</sup>
1.50	w	1.503	.1 <sup>3</sup>
1.480	m	1.477	.1 <sup>3</sup>
1.465	w		
1.445	w	1.444	.05 <sup>3</sup>
1.415	m	1.415	.4 <sup>3</sup>
1.390	vw		
1.380	w		
1.360	m	1.358	.4 <sup>3</sup>
1.310	w	1.309	.1 <sup>3</sup>
1.285	m	1.285	.1 <sup>3</sup>
1.265	w	1.260	.1 <sup>3</sup>
1.245	vw		
		1.238	.05 <sup>3</sup>
1.220	m		

<sup>1</sup> vs=very strong; s=strong; m=medium; w=weak; vw=very weak.

<sup>2</sup> First Supplementary Card File of X-ray Diffraction Data, 1944. Compiled and published by joint committee of A.S.T.M., American Society for X-ray and Electron Diffraction, and Institute of Physics of London.

<sup>3</sup> Not given by all sources.

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR BRAMMALLITE SAMPLE COMPARED WITH PUBLISHED DATA ON BRAMMALLITE AND ILLITE

(Ni-filtered Cu radiation. Camera radius=203 mm. Calibration against dolomite, pyrite, and talc.)

Brammallite in Concretion No. 4		Brammallite <sup>2</sup> (Fe radiation)		Illite <sup>2</sup> (Mo radiation)	
Interplanar spacing, A	Estimated intensity <sup>1</sup>	Interplanar spacing, A	Intensity	Interplanar spacing, A	Intensity
10	s	10.2	1.0	10.0	1.0
		4.8	.5	4.9	.4
4.45	s	4.4	1.0	4.46	1.0
				4.11	.2
		3.6	.5	3.64	.2
				3.4	.2
				3.33	.7
3.19	vs	3.2	1.0	3.2	.2
				2.98	.4
		2.81	.5	2.83	.3
		2.69	.2		
2.54	m	2.54	.9	2.56	1.0
		2.43	.7	2.44	.4
		2.34	.7	2.37	.5
				2.24	.6
		2.15	.5	2.18	.4
				2.12	.4
		1.95	.5	1.99	.5
		1.68	.5	1.65	.3
		1.64	.7	1.64	.5
1.488	m	1.49	1.0	1.50	.9
				1.38	.4
				1.35	.2
1.285	w	1.28	.6	1.30	.5
		1.26	.2	1.25	.4
		1.24	.5		

<sup>1</sup> vs=very strong; s=strong; m=medium; w=weak.<sup>2</sup> First Supplementary Card File of X-ray Diffraction Data, 1944. Compiled and published by joint committee of A.S.T.M., American Society for X-ray and Electron Diffraction, and Institute of Physics of London.

early in the peat stage; the coal around them is later compressed, but the concretions are not altered materially by such diagenetic and low-pressure metamorphic adjustments. Possibly initial deposition of the pyrite may be associated with bacterial decomposition in the peat.

The joint cracks in the coal were formed after the coal was indurated, much later than the formation of the concretions.<sup>7</sup> They were probably formed by tangential stresses on the bed during the Appalachian revolution.

Sedimentary analcite has been reported twice in this country; in both cases volcanic ash fell into a mineralized lake, probably alkaline, and the dissolved salts reacted to form analcite.<sup>8,9</sup> Bradley<sup>9</sup> also refers to two German occurrences of sedimentary analcite, one associated with a clay ironstone (argillaceous siderite) concretion in a clay formation.

Analcite was discovered by Powell<sup>10</sup> as a constituent of boiler scale, where the boiler-water temperature was 290°C. He refers to two papers of interest; one reported the synthesis in 1880 of analcite from sodium aluminate and sodium silicate solutions in a sealed copper tube at 180°C.; the other stated that analcite will form from its components in a closed system between 180° and 430°C. Powell, Carpenter, and Coates<sup>11</sup> report the finding of the silicates analcite, noselite, and natrolite; they were identified both by x-ray diffraction and petrographic analysis. Imhoff and Burkardt<sup>12,13,14</sup> published numerous x-ray diffraction patterns for minerals found in scale deposits, among them analcite.

Noll synthesized analcite under hydrothermal conditions.<sup>15</sup> He used a sodium hydroxide solution, hydrated alumina and silica—mol. ratio NaOH:Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>=1:1:4, at a temperature of 300°C., with a corresponding saturated vapor pressure of 87 atmospheres, and a reaction time of 15 and 24 hours.

Straub<sup>16</sup> also has synthesized analcite. He used sodium silicate solution, various amounts of water, and solid sodium aluminate in a bomb at

<sup>8</sup> Ross, Clarence S., Sedimentary analcite: *Am. Mineral.* **26**, 627–629 (1941).

<sup>9</sup> Bradley, W. H., The occurrence and origin of analcite and meerschaum beds in the Green River formation of Utah, Colorado, and Wyoming: *U. S. Geol. Sur. Prof. Paper No. 158A* (1930), pp. 1–7.

<sup>10</sup> Powell, Sheppard T., A critical study of boiler scales and advanced methods of analyses and identification: *Combustion*, **5**, 15–19 (Sept. 1933).

<sup>11</sup> Powell, Sheppard T., Carpenter, Lewis V., and Coates, John J., Complex silicate scales in high pressure boilers: *Combustion*, **11**, 18–24 (Aug. 1939).

<sup>12</sup> Imhoff, C. E., and Burkardt, L. A., X-ray fingerprints scale deposits: *Power*, **86**, 10–12 (Jan. 1942).

<sup>13</sup> Imhoff, C. E., and Burkardt, L. A., X-ray diffraction methods in the study of power plant deposits: *Proc. Am. Soc. Testing Mater.*, **43**, 1276–1288 (1943).

<sup>14</sup> Imhoff, C. E., and Burkardt, L. A., Crystalline compounds observed in water treatment: *Ind. Eng. Chem.*, **35**, 873–882 (1943).

<sup>15</sup> Noll, W., The conditions for formation of kaolinite, montmorillonite, sericite, pyrophyllite, and analcite: *Mineral. Petrog. Mitt.*, **48**, 210–247 (1936).

<sup>16</sup> Straub, Frederick G., Analcite, preparation and solubility between 182° and 282°C.: *Ind. Eng. Chem.*, **28**, 113–114 (Jan. 1936).

282°C. for 46 hours. The vapor pressure for pure water at 282°C. is 960 lbs. per sq. in. The calculated hydrostatic pressure at the coal bed is 650 lbs. per sq. in. for the 1500 ft. of rock now remaining. The pressure is of the right order of magnitude for the formation of analcite.

It is evident that analcite needs alkaline conditions for its formation. It is destroyed by acid, and yet acid conditions are more probable in a consolidating coal bed.

The analcite with the sulfur balls may have formed directly from its components, or again sodium in alkaline solution, possibly in connate waters, reacted with clay-like minerals to form the analcite. The analcite was reported to be in thin plates and may be a pseudomorph of a clay mineral. Since the analcite was found in a joint crack, it apparently did not form until after the joint cracks had formed, which would allow a freer circulation of the ground waters.

In order to account for the alkaline conditions which are necessary for the formation of analcite, it is necessary to consider the geological column above the Pittsburgh coal.<sup>17</sup> Immediately above the coal are usually several feet of shale. Directly above is the Upper Pittsburgh sandstone; this is developed east of the Monongahela River and is about 25 ft. thick. However, west of the Monongahela, where the analcite occurs, it is largely replaced by limestone. Above is the Redstone limestone 5 to 15 ft. thick. Calcium bicarbonate solutions originating at various times in these limestones could have percolated down to the coal bed and neutralized the acids, allowing the analcite to form. The presence of pyrite instead of marcasite also suggests alkaline conditions.

The juxtaposition of the analcite and the concretion may be entirely fortuitous. Or this concretion may have mechanically blocked water circulation in the joints, and the stagnant region may have favored mineral deposition.

#### SYNTHESIS OF ANALCITE AT ATMOSPHERIC PRESSURE

An attempt was made to synthesize analcite from clay and an alkaline solution containing sodium in order to study the formation of analcite. A solution of 10 gm. of sodium hydroxide of A.R. grade in 100 ml. distilled water was put in a bottle with 7 gm. of kaolinite from Langley, S. C., placed in a drying oven at 90°C., and agitated occasionally. Samples were taken at 11 and 29 days.

The 11-day sample when examined microscopically appeared much like the kaolinite, but the mean index was 1.50. An x-ray diffraction pattern indicated sodalite, a sodium aluminum silicate containing chlorine.

<sup>17</sup> Hennen, R. V., and Reger, D. B., Work cited in footnote 6, pp. 262-265.

Since no chlorine was present in the original solution this might be a hydroxyl-sodalite, as some replacement of chlorine by water has been reported.<sup>18</sup> A chemical analysis showed a trace of chlorine and a loss on ignition of 14.6 per cent. The 29-day sample contained mostly spherulites of a mean index of 1.49. *X*-ray diffraction showed a small amount of analcite and a large amount of an unidentified material.

In a second test sodium chloride was substituted for sodium hydroxide. Both petrographic and *x*-ray diffraction methods showed unchanged kaolinite at 11 days and 29 days.

In a third test sodium chloride and sulfuric acid were substituted for the sodium hydroxide. Microscopically the 11-day sample looked like unchanged kaolinite, except the refractive index was  $1.455 \pm 0.005$ . About 5 per cent had a higher index. Small amounts of kaolinite and anatase were identified by *x*-ray diffraction. The 29-day sample was similar microscopically, except the mean index was  $1.460 \pm 0.005$ . The *x*-ray diffraction showed no kaolinite, a small amount of anatase, and a trace of sodium chloride. Also doubtfully identified were  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and diaspore. The anatase probably was an inclusion in the kaolinite.

#### SUMMARY

Three sulfur balls and one other concretion collected from the Pittsburgh coal seam in West Virginia were examined by petrographic and *x*-ray diffraction methods. The following minerals were identified: analcite, brammallite, calcite, dolomite, kaolinite, melanterite, and pyrite. A discussion on the occurrence and formation of analcite is included. The presence of analcite indicates that waters penetrating the joint cracks of the juvenile coal bed were alkaline in their reaction.

<sup>18</sup> Dana, E. S., *The System of Mineralogy*, 6th Ed. (1914), John Wiley & Sons, Inc., p. 1134.