

FRIEDELITE, SCHALLERITE, AND RELATED  
MINERALS

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The problem of the isomorphism of friedelite and a number of other minerals similar in crystallographic and optical properties, and related chemically, has attracted several investigators. New chemical and physical data recently determined on some minerals of this group by the authors and others, have led to a review of the problem.

The main object of this paper is to point out the isomorphism of friedelite and schallerite, two minerals that occur at Franklin, New Jersey. Friedelite has also been found at other localities. In the course of this study it was found desirable to examine some other probable members of the group and the results of such work are also presented.

## GENERAL CHARACTERISTICS OF THE FRIEDELITE GROUP

The following species are accepted by the authors as members of the friedelite group: friedelite, pyrosmalite, schallerite, and molybdophyllite. These minerals have physical properties common to the group, the most marked of which is the perfect basal cleavage. The optical orientation of all the members of the group is identical, i.e.,  $\alpha = \epsilon = c$ . Friedelite and some others of the group exhibit an anomalous biaxial character sometimes, although they are normally uniaxial and negative. The axial angle, however, never exceeds a few degrees. The members of the group are rhombohedral hemimorphic, as determined by crystallographic and X-ray<sup>5</sup> methods. No crystallographic data are available for schallerite, which has been found only in the massive form.

The general formula for the group may be expressed as:  $R_8[(\text{SiO}_3)_x(\text{OH,Cl})_y(\text{As}_2\text{O}_5)_z] + n\text{H}_2\text{O}$ , where  $R = \text{Mn}$  and  $\text{Fe}$ . (In molybdophyllite  $R = \text{Mg}:\text{Pb} = 1:1$ .)  $x = 6$  (in Molybdophyllite  $x = 4$ ),  $y$  and  $z$  are variable to make up the valency requirements.  $n = 3$ . The  $\text{H}_2\text{O}$  is variable to a certain extent, probably due to water of crystallization.

TABLE I contains analyses of friedelite and schallerite, made by the senior author and others. TABLE II is a list of the physical properties of the analyzed material of the preceding table, and other values taken from various sources, as noted.

TABLE I.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
SiO <sub>2</sub>	34.45	35.36	34.69	33.99	36.35	34.73	31.44	31.82	32.42	32.76
MnO	51.48	55.80	48.00	50.73	46.67	54.80	44.70	50.20	49.21	51.68
MgO	1.54		0.98	1.45	0.05		2.19		0.71	
FeO	0.68		1.45	0.54	5.27		2.12		0.62	
CaO			0.63		trace		0.36			
ZnO	1.43		1.05	0.77	0.32		0.54		trace	
Cl	0.29		3.43	2.32	3.08	3.42	0.08		0.60	
As <sub>2</sub> O <sub>3</sub>				1.15			12.24	12.25	7.50	9.01
Al <sub>2</sub> O <sub>3</sub>	present				0.03				1.59	
H <sub>2</sub> O	9.74	8.84	+9.08 -1.94	9.40	8.86	7.82	6.55	5.73	7.24	6.55
	99.61	100.00	101.25	100.35	100.63	100.77	100.22	100.00	99.89	100.00
O=Cl	0.06		0.77	0.52	0.69	0.77	0.02		0.13	
Total	99.55		100.48	99.83	99.94	100.00	100.20		99.86	

1. Low-chlorine friedelite—Franklin, L. H. Bauer, analyst. Cat. No. 34826.
2. Chlorine-free friedelite—calculated composition.
3. Friedelite—Buckwheat Mine, Franklin, W. T. Schaller, analyst. Cat. No. 87123.
4. Friedelite—Franklin, L. H. Bauer analyst.
5. Friedelite—Taylor Mine, Franklin, R. B. Gage, analyst.
6. Friedelite—calculated composition.
7. Schallerite (type material) Franklin, Reanalysis, L. H. Bauer, analyst.
8. Schallerite—calculated composition (type I).
9. Schallerite—Franklin, L. H. Bauer, analyst (type II).
10. Schallerite—calculated composition (type II).

TABLE IIa. PHYSICAL PROPERTIES OF THE MEMBERS OF THE FRIEDELITE GROUP AND RELATED MINERALS

	1. Friedelite anal. 3 table I	2. Friedelite anal. 4 table I	3. Schallerite anal. 9 table I	4. Schallerite anal. 7 table I	5. Pyrosmalite	6. Molybdophyllite
Crystal system	rhombohedral	rhombohedral	rhombohedral?	rhombohedral?	rhombohedral	rhombohedral
Cleavage	(0001)	(0001)	(0001)	(0001)	(0001)	(0001)
Optical Character	(-)	(-)	(-)	(-)	(-)	(-)
Optical Orientation	$\epsilon = c$	$\epsilon = c$	$\epsilon = c$	$\epsilon = c$	$\epsilon = c$	$\epsilon = c$
2V = axial angle	0°	0°	0°	0°	0°	0°
$\omega$	1.654	1.656	1.681	1.704	1.675	1.815
$\epsilon$	1.625	1.62	1.643	1.679	1.636	1.761
Birefringence ( $\omega - \epsilon$ )	.029	.03	.038	.025	.039	.054
Specific Gravity	3.041	3.059	3.339	3.339	3.153	4.72

Column 4—reference 6.

Column 5—E. S. Larsen—*Bull. 679 U. S. G. S.*

Column 6—reference 8.

TABLE IIb.

	7. Bementite	8. Hematolite	9. Dixenite type I	10. Dixenite type II	11. Mcgovernite	12. Parsetten- site	13. Errite
Crystal system	Orthorhombic	rhomboidal	rhomboidal?	rhomboidal?	rhomboidal	hexagonal?	hexagonal?
Cleavage	(001)	(0001)	(0001)	(0001)	(0000)	(0001)	(0001)
Optical character	(-)	(-)	(-)	(-)	+	(-)	(-)
Optical orientation	$\alpha = c$	$\epsilon = c$	$\alpha = c$	$\alpha = c$	$\epsilon = c$	$\epsilon = c$	$\epsilon = c$
2V = axial angle	small	0°	small	small	0°	small	small
$\omega$	1.650	1.735	1.96	1.757	1.754	1.576	1.575
$\epsilon$	1.624	1.716		1.735		1.546	1.547
Birefringence ( $\omega - \epsilon$ )	.026	.019			very weak	.030	.028
Specific gravity	2.98 3.20	3.416	4.2	3.485	3.719	2.590	2.681

Column 7—reference 9.

Column 9—reference 12.

Columns 12-13—reference 14.

## FRIEDELITE

The formula of friedelite as given by Groth,<sup>1</sup> Dana,<sup>2</sup> and Palache<sup>3</sup> is in the orthosilicate form. Zambonini,<sup>4</sup> however, in a later paper, prefers the metasilicate form, and Aminoff<sup>5</sup> in a recent paper also considers friedelite as a metasilicate. In a discussion of the probable relation of friedelite and schallerite, in the original description of the latter mineral, Gage, Larsen and Vassar<sup>6</sup> consider them as probably metasilicates. In this paper friedelite and the other members of the group are considered as metasilicates mainly because it seems to simplify the discussion. The formula here adopted for friedelite is:  $Mn_8[(SiO_3)_6(OH,Cl)_4] + 3H_2O$ , derived from the same composition, Column 6, TABLE I, as the orthosilicate formula of Palache.<sup>3</sup> Friedelite seems to vary in its chlorine content, as is shown by the analyses in TABLE I. The analysis in column 1 is that of an almost chlorine free friedelite.

Column 2 gives the calculated composition for the chlorine free variety. In column 4 the friedelite analysis carries a small amount by arsenic trioxide indicating that it is probably a "connecting link" with the related arsenic-bearing schallerite.

Friedelite is rhombohedral hemimorphic, with a perfect basal cleavage showing a pearly luster on the cleavage plane. It is uniaxial negative with a medium birefringence. The mineral exhibits anomalous biaxial character quite frequently, the axial angle, however, does not exceed a few degrees.

#### SCHALLERITE

In columns 7, 8, 9, 10 are given analyses for schallerite and calculated compositions for the formulae suggested. The reanalysis of the type material (column 7) indicates that the arsenic is present as the trioxide rather than the pentoxide as reported in the original description.<sup>6</sup> The method used by the senior author in determining the state of oxidation of the arsenic in the schallerite is identical with that given by him in the description of mcgovernite. The formula here suggested for schallerite is:  $Mn_8[(SiO_3)_6 \cdot (OH)_{1.2}(As_2O_5)_{.7}] + 3H_2O$ , for which the calculated composition is given in column 8. This formula differs from that of friedelite in that part of the hydroxyl and chlorine is replaced by the pyroarsenious acid radical, the total valency values remaining the same.

The optical properties and general physical characteristics of schallerite and friedelite are similar, so much so, in fact, that there is no way of distinguishing them except by physical measurements or chemical examination. Schallerite is readily recognized by its higher index of refraction and higher specific gravity, as shown in TABLE II, in which the physical properties of the group are given.

The second occurrence of schallerite, analysis 9 of TABLE I, is somewhat less rich in  $As_2O_5$ . The formula assigned, in accordance with the schallerite and friedelite formulae above given, is:  $Mn_8[(SiO_3)_6 \cdot (OH)_2(As_2O_5)^{1/2}] + 3H_2O$ , in which less of the hydroxyl is replaced by the pyroarsenious acid radical. The index of refraction and the specific gravity of this material are somewhat lower than that of the original schallerite, as is to be expected from its lower arsenic content.

## PYROSMALITE

The isomorphism of pyrosmalite with friedelite has been well established by others. The formula, written in the manner of friedelite is:  $R_8[(SiO_3)_6(OH,Cl)_4] + 3H_2O$ , where  $R = Fe^{++}, Mn^{++}$ . The introduction of iron in the structure of pyrosmalite raises the index of refraction somewhat, as is seen in the values for the physical constants in TABLE II.

## MOLYBDOPHYLLITE

Aminoff<sup>5</sup> has placed this mineral in the friedelite group as a result of an X-rays study despite the fact that it seems to differ markedly in its chemical constitution. The formula here suggested to show its relation to the other members of the group is:  $R_8[(SiO_3)_4(OH)_8] + H_2O$ , where  $R = Mg:Pb = 1:1$ . This formula departs from the others given above in that magnesium and lead replace the manganese, and there is less of the metasilicate present in proportion to the hydroxyl. The general structure of the formula, however, remains the same. The composition calculated from the formula together with the analysis by Flink<sup>8</sup> is given below.

	1.	2.
SiO <sub>2</sub>	18.15	17.35
MgO	11.71	11.68
PbO	61.09	64.47
Na <sub>2</sub> O	0.82	
K <sub>2</sub> O	0.69	
Al <sub>2</sub> O <sub>3</sub>	0.46	
H <sub>2</sub> O	6.32	6.50
	<hr/>	<hr/>
	99.24	100.00

1. Molybdophyllite—Långbån, G. Flink analyst.
2. Calculated composition for formula in text.

## MINERALS SHOWING LESS CERTAIN RELATION TO THE FRIEDELITE GROUP

## BEMENTITE

Bementite has been shown by Pardee, Larsen, and Steiger<sup>9</sup> to be the same as karyopilite. The probable relationship of karyopilite to friedelite has been pointed out by Groth<sup>10</sup> and Clarke.<sup>11</sup> Adopting the average of three analyses, by Steiger

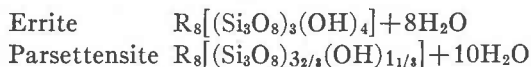
and König, the following formula may be written for bementite:  $Mn_3[(SiO_3)_7(OH)_2] + 4H_2O$ . Bementite is said to be orthorhombic with three pinacoidal cleavages. The optical properties, however, are such that it may without difficulty be considered as similar to the members of the friedelite group. In bementite  $\alpha = c$  as in friedelite. It is sensibly uniaxial and is negative. The likeness of the physical properties of these two minerals comes out clearly in TABLE II. Genetically it is more difficult to trace relationship between them and further study is needed before any definite conclusion can be reached.

Dixenite<sup>12</sup> and mcgovernite<sup>7</sup> are somewhat similar in composition and may well be related to the friedelite group. Flink assigns to dixenite the formula  $R SiO_3 \cdot 2R_2(OH)(AsO_3)$ . Mcgovernite may be written  $R_2SiO_4 \cdot R_2[(OH)(AsO_3 \cdot AsO_4)] \cdot 3R(OH)_2$ . Optically the two minerals differ somewhat for dixenite is optically negative, mcgovernite positive and with a lower birefringence. What has just been said refers to dixenite, type I. Dixenite, type II, also from Långban, which has not yet been analyzed approaches mcgovernite more nearly in optical properties and they have the same appearance, with highly micaceous structure, pearly luster and a bronze-red color. It seems not unlikely that this form of dixenite will prove to have a composition very similar to that of mcgovernite.

Hematolite,<sup>13</sup> a poorly defined species from Nordmark, Sweden, is so much like members of the friedelite group in its physical properties that a close chemical relationship probably exists. The analyses as yet are obviously unsatisfactory but they indicate that hematolite differs from schallerite chiefly in the absence of silica which is replaced by the hydroxyl and the arsenate radical. The arsenic was found to be present in two states of oxidation by the senior author. Sufficient material for a quantitative analysis was not available.

Parsettensite and errite,<sup>14</sup> two recently described minerals from Switzerland have been suggested as members of this group. The authors believe that there is not a sufficiently close relationship chemically, although they have the same pearly cleavage on the base and are essentially hydrous silicates. There is a considerable excess of silica in any formula analogous to that of friedelite which can be assigned to them. It is, however, possible to consider them related if one assumes that the trisilicate radical may replace the

metasilicate. The formulae may be written to conform with that of friedelite in the following manner:



#### CONCLUSION

This study suggests the necessity of further work on some of the minerals discussed. The work of Aminoff\* on X-ray crystal data of friedelite, pyrosmalite and molybdophyllite should be extended to include bementite, schallerite, dixenite, mcgovernite, and hematolite. A clue to the complex structural relations between minerals in which different acid radicals replace each other may be gained by such an x-ray study.

Further analyses of hematolite and dixenite of the second type are needed.

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