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# CONSTITUTION AND POLYMORPHISM OF THE PYROAURITE AND SJÖGRENITE GROUPS

## CLIFFORD FRONDEL,

Harvard University, Cambridge, Massachusetts.\*

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#### ABSTRACT

The carbonate-hydroxides pyroaurite, stichtite and hydrotalcite are shown by x-ray study to be isostructural. The dimorphism suggested by Aminoff and Broomé in 1930 for pyroaurite is definitely proven, and is shown to extend to stichtite and hydrotalcite. Rhombohedral and hexagonal groups are recognized both of which conform to the formula  $Mg_{6}R_{2}(OH)_{16}CO_{3} \cdot 4H_{2}O$ , where  $R^{3}$ =Fe,Cr or Al. Data for the six species involved (three being here described as new) follow:

	Cell Contents (Hexagonal unit)	<i>a</i> <sub>0</sub>	Co	ω	e	Proven Localities	
Pyroaurite	3(Mg <sub>6</sub> Fe <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> ·4H <sub>2</sub> O)	6.19	46.54	1.564	1.543	8	
Stichtite	$3(Mg_6Cr_2(OH)_{16}CO_3 \cdot 4H_2O)$	6.18	46.38	1.545	1.518	3	
Hydrotalcite	$3(Mg_6Al_2(OH)_{16}CO_5 \cdot 4H_2O)$	6.13	46.15	1.511	1.495	4	

RHOMBOHEDRAL OR PYROAURITE GROUP

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 240.

Sjögrenite	Mg6Fe2(OH)16CO2 · 4H2O	6.20	15.57	1.573	1.550	1
Barbertonite	Mg6Cr2(OH)16CO3 4H2O	6.17	15.52	1.557	1.529	3
Manasseite	$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$	6.12	15.34	1.524	1.510	3

HEXAGONAL OR SJÖGRENITE GROUP (New)

The observed structural cells derived from single-crystal and powder x-ray pictures have one-half  $a_0$  and  $c_0$  for the rhombohedral series and one-half  $a_0$  for the hexagonal series as compared with the values cited. The dimensions here given are required for rational cell contents. Dimensionally,  $c_{0(\text{rh},)}:c_{0(\text{hex},)}=3:1$  and the halved value of  $a_0$  (ca. 3.1) for both series is nearly identical with  $a_0=3.12$  of brucite.

The hexagonal and rhombohedral polymorphs very commonly occur intimately admixed, and in part are mutually oriented with rhombohedral  $\{0001\}$   $[10\overline{1}0]$  parallel hexagonal  $\{0001\}$   $[10\overline{1}0]$ . The minerals are lamellar on  $\{0001\}$ , often with partially or completely random stacking of microcrystals about [0001].

Brugnatellite,  $Mg_6Fe(OH)_{13}CO_3 \cdot 4H_2O$ , is distinct from the minerals at hand, and the identity of houghite with hydrotalcite is confirmed. New localities for pyroaurite include Val Malenco and Val Ramazzo, Italy, and the first occurrence in the United States, at Blue Mont, Maryland.

#### INTRODUCTION

The constitution and inter-relations of pyroaurite, stichtite, hydrotalcite and brugnatellite have long been matters of much confusion and uncertainty. The principal factors contributing to this have been the lack of adequate crystallographical data, and the complex and somewhat unusual composition of the several species coupled with the generally unsatisfactory nature of the available chemical analyses. A further complicating factor has been the lack of correlation between the many published contributions to the subject. In particular, the x-ray study of pyroaurite by Aminoff and Broomé in 1930, with its indication of polymorphism, has been overlooked. The work of Manasse in 1915 which established the constitutional role of  $CO_2$  in hydrotalcite and pyroaurite also has gone unnoticed.

In the present study it was found by x-ray and optical methods that almost all specimens of hydrotalcite, stichtite and pyroaurite, regardless of locality, are not homogeneous, but are intimate mixtures of hexagonal and rhombohedral substances of very similar physical and identical chemical properties. The earlier work will be reviewed in detail before the descriptive part of the study is presented.

## ACKNOWLEDGMENTS

The writer wishes to express his thanks to Dr. H. V. Ellsworth of the Geological Survey of Canada, for a gift of pyroaurite from Rutherglen, Ontario, recently analyzed by him, and to Dr. E. Poitevin also of the Geological Survey of Canada, for a gift of stichtite from Black Lake, Quebec. Grateful acknowledgment likewise is made to Dr. W. F. Foshag, U. S. National Museum, for a loan of a specimen of hydrotalcite from Kongsberg, Sweden, analyzed by him in 1920, and for other specimens of hydrotalcite and brugnatellite. Other study material included stichtite from Barberton, Transvaal, presented to the Harvard collection by A. L. Hall and presumably part of the material analyzed by him in 1922, and a large suite of specimens of pyroaurite from Långban, Sweden, mostly from the collection of G. Flink. Additional study material is described on the following pages. The writer also wishes to express his appreciation to Professor Harry Berman, Harvard University, for his interest and aid in the investigation.

# RHOMBOHEDRAL OR PYROAURITE GROUP

# Pyroaurite

Historical. Pyroaurite was originally described and analyzed from Långban, Sweden, by Igelström (1865). Additional analyses were later contributed by Mauzelius (in Flink, 1910), Johansson (in Aminoff and Broomé, 1930) and Manasse (1915). Subsequently a pyroaurite-like mineral was found at Haaf-Grunay, Scotland, by Heddle (1878), who proposed the new name igelstromite, and the mineral was later said (Heddle, 1910) to occur at Hagdale and Nikka Vord, Unst. The analyses of the Haaf-Grunay material are relatively low in CO<sub>2</sub>, and Foshag (1920) has suggested that the material was probably a mixture of brucite, hydromagnesite and limonite. This interpretation seems improbable, since Heddle states that the ignited mineral is strongly magnetic; ignited pyroaurite is highly magnetic due to the conversion of the Fe<sup>3</sup> to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite).<sup>1</sup> In 1894 a new occurrence of pyroaurite was discovered at Nordmark, Sweden, by Sjögren and was analyzed by Mauzelius. This material is notable for the large content of MnO (4.5 per cent) and for the apparent absence of CO<sub>2</sub>. The CO<sub>2</sub> was not sought in the analysis and may have been included in the H<sub>2</sub>O as determined by loss on ignition. More recently, analyses have been reported by Kurnakov and Černych (1928) of material from Bashenowo in the Urals, and by Ellsworth (1939) of exceptionally pure material from Rutherglen, Ontario. The Bashenowo material contains a notable amount of Al, apparently in substitution for Fe, but possibly due to admixture. Pyroaurite also has been reported from Kraubat, Styria, and from two localities in southern Serbia by Meixner (1937, 1938) but chemical analyses are lacking.

<sup>1</sup> The nature and orientation of the ignition products of pyroaurite will be described jointly with H. V. Ellsworth in a forthcoming paper.

The formula  $3Mg(OH)_2 \cdot Fe(OH)_3 \cdot 3H_2O$  originally derived by Igelström was accepted by Sjögren (1894) and by Aminoff and Broomé (1930), and the considerable and rather even tenor of  $CO_2$  in the analyses was ascribed to alteration. The analyses by Heddle (1878) of the pyroaurite-like mineral from Haaf-Grunay are close to the formula given above. Manasse, in 1915, re-examined the composition of the mineral in the light of a dehydration study and three new analyses, and concluded that the  $CO_2$  was constitutional. The formula derived by Manasse is

# $Mg_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O \cdot$

Later, Foshag (1920) independently reached the conclusion that the formula given above represented the composition of the species. Ellsworth (1939) on the basis of new analyses and a dehydration study of unquestionably fresh material from Ontario, also concludes that this formula is correct, but indicates that the content of water of crystallization probably is closer to  $5H_2O$  than  $4H_2O$ . The analyses of Ellsworth (1939), Johansson (in Aminoff and Broomé, 1930) and Manasse (1915) are cited in columns 1, 2 and 3, in Table 1.

	1	2	3	4	5	6	7	8	
MgO	35.84	35.44	35.60	37.72	39.72	39.84	36.76	39.38	
FeO		0.10			0.28				
MnO	0.01	0.28							
Fe <sub>2</sub> O <sub>5</sub>	23.37	23.19	23.73	4.18	1.89	0.90	0.20	0.21	
Cr <sub>2</sub> O <sub>3</sub>				14.51					
Al <sub>2</sub> O <sub>8</sub>		0.11		2.30	15.32	15.16	19.65	16.59	
$CO_2$	7.30	7.01	6.49	7.15	7.60	7.26	6.98	7.48	
H <sub>2</sub> O	33.66	33.62	33.12	34.14	35.46	36.83	36.13	36.34	
Rem.		0.41	0.67		0.44	0.14	0.35		
Total	100.18	100.16	99.61	100.00	100.71	100.13	100.07	100.00	
	Cei	l Conten	NTS OF TH	ie Rhomi	BOHEDRAI	Polymo	RPHS		Theory
Mø	17.8	17 6	17 7	18_3	17.9	18.0			18
Fe	5.8	5.8	5.9	)	11.12				
Cr	0.0	0.0	0.17	5.6					6
Al				0.0	5.9	5.7			- (
C	3 3	3 2	3.0	3.2	3.1	3.0			3
Ĥ	73.2	74.6	73.6	74.0	71.6	74.2			72
0	69.7	70.0	69.2	70.0	68.9	69.5			69

TABLE 1. CHEMICAL ANALYSES AND CELL CONTENTS OF MEMBERS OF THE Pyroaurite and Sjögrenite Groups

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#### PYROAURITE AND SJÖGRENITE GROUPS

	CE	ll Con	TENTS OF	THE HEX	AGONAL I	OLYMORI	PHS		Theory
Mg		5.8	5.9	6.1	6.1	6.1	5.7	6.0	6
Fe		1.9	2.0						
Cr				1.9					2
Al					2.0	1.9	2.4	2.0	)
С		1.1	1.0	1.1	1.1	1.0	1.0	1.1	1
н		24.7	24.4	24.7	24.3	25.2	24.8	24.9	24
0		23.2	23.0	23.4	23.4	23.6	23.6	23.6	23

1. Pyroaurite. Rutherglen, Ontario. Pure sample. Semi-micro analysis. Ellsworth (1939).

 "Pyroaurite." Långban, Sweden. Known to be a mixture of pyroaurite and sjögrenite. Rem. is SiO<sub>2</sub>. Johansson anal, in Aminoff and Broomé (1930).

 "Pyroaurite." Långban, Sweden. Presumed to be a mixture of pyroaurite and sjögrenite. Rem. is insol. 0.39 and Mn<sub>2</sub>O<sub>3</sub> 0.28. Manasse (1915).

4. "Stichtite." Dundas, Tasmania. Presumed to be a mixture of stichtite and barbertonite. Recalculated to 100% after the deduction of  $SiO_2$  2.09, and FeO 0.28 as chromite. Foshag (1920).

5. "Hydrotalcite." Kongsberg, Norway. Known to be a mixture of hydrotalcite and manasseite. Rem. is SiO<sub>2</sub>. Foshag (1920).

6. "Hydrotalcite." Snarum, Sweden. Presumed to be a mixture of hydrotalcite and manasseite. Rem. is insol. Manasse (1915).

 Manasseite. Snarum, Sweden. Pure sample, but contains gibbsite. Rem. is SiO<sub>2</sub>. F. A. Gonyer anal., October, 1940.

8. Manasseite. Analysis 7 recalculated to 100% after deduction of SiO<sub>2</sub> 0.35, and gibbsite 6.38 (on basis of 6 Mg atoms per cell).

Crystallography. The crystallography of pyroaurite was first described by Sjögren (1894), who regarded the crystals from Nordmark as hexagonal with pyramidal hemihedry and calculated the ratio of a:c=1:3.6072from  $\{0001\} \land \{1011\} = 76^{\circ}30'$ . The pyramidal hemihedry is based on the occurrence of a third order prism, probably  $\{21\overline{30}\}$ , obliquely truncating the edges of  $\{10\overline{1}0\}$ . Observed forms are:  $\{0001\}$ ,  $\{10\overline{1}0\}$ ,  $\{1011\}$ , {2130} (?). In 1900 Flink described a new find of pyroaurite at Långban, and distinguished what he termed two habits for the species. One type consisted of broad thin hexagonal plates flattened on {0001} and bounded laterally by  $\{40\overline{4}1\}$ . The crystals of the second type were smaller, with {0001}, {0221} and {1011}, and had a decided rhombohedral development. Both habits were referred to the same axes, with a:c=1:1.6557from  $\{0001\} \land \{40\overline{4}1\} = 82^{\circ}33'$ .<sup>2</sup> The apparent hexagonal pyramid on the crystals earlier described by Sjögren from Nordmark was interpreted by Flink as equally developed positive and negative rhombohedra, which closely approximate in position {0221} and {2021} in his unit for the

<sup>2</sup> Flink gives  $81^{\circ}33'$  which his other measured angles, on crystals of the second type, indicate to be a misprint for  $82^{\circ}33'$ . Aminoff and Broomé (1930) remeasured several crystals and obtained  $81^{\circ}25'$  and  $81^{\circ}22'$ . They accepted Flink's value and calculated a:c=1:1.4574.

Långban crystals. Morphological data are lacking for the other known occurrences of pyroaurite.

An x-ray study of the Långban pyroaurite was made by Aminoff and Broomé in 1930. They found that the material included both a rhombohedral and a hexagonal substance, and that these substances corresponded with the rhombohedral and hexagonal habits recognized by Flink. The two substances occur intimately intergrown, and almost all of the apparently homogeneous single crystals of pyroaurite afforded Laue and powder photographs with both hexagonal and rhombohedral diffraction effects. They found it impossible to establish the composition of either of the two substances, since there was no certainty that any of the existing analyses referred solely to one or the other of the two substances, and it was not feasible to examine by x-ray means sufficient material for a new analysis. They then assumed that the two substances were polymorphous, and an effort was made to determine the cell contents and analyze the structure. The following x-ray data were obtained (hexagonal coordinates):

	$a_0$	$c_0$	$a_0 \cdot c_0$
"Hexagonal pyroaurite"	3.097	15.56	1:5.024
"Rhombohedral pyroaurite"	3.089	23.23	1:7.520

In the calculation of the cell contents the  $CO_2$  reported in the analyses was regarded as secondary, and the formula taken as  $3Mg(OH)_2$ . Fe- $(OH)_3.3H_2O$ . It was then found that the number of formula-units in the unit cells were 0.49 and 0.75 for the hexagonal and rhombohedral substances, respectively,—results which in themselves are out of the question. Efforts to detect greater axial periods were unsuccessful, and the suggestion was made that special properties of the structure factor suppressed all of the reflections corresponding to the real identity period in one or several directions. The assumption was then made that  $a_0$  for the two substances should be doubled, giving  $Z_{rh.} = 1$  in the rhombohedral unit and  $Z_{hex.} = 2$ , and an ingenious attempt based on so-called structural isomery was made to analyze the structures.

An x-ray Laue study of pyroaurite from Långban has also been reported by Comucci (1930), who says that the mineral is monoclinic, pseudo-hexagonal, with a:b:c=0.84:1:2.60 and  $\beta=90^{\circ}41'$ . Cell dimensions are not given. These results may be due to a maladjustment of the crystal or to use of a deformed crystal.

*Optical Data*. The older optical data on pyroaurite are tabulated below. Hitherto it has not been known to which of the modifications of pyroaurite this data is pertinent, but the present study proves that the

#### PYROAURITE AND SJÖGRENITE GROUPS

Locality	ω	6	Observed
Rutherglen, Ontario	$1.560 \pm 0.003$	$1.543 \pm 0.003$	Ellsworth (1939)
Långban, Sweden	$1.565 \pm 0.003$		Larsen (1921)
	1.562	1.529	Manasse (1915)
Southern Serbia	1.563	$1.543 \pm 0.002$	Meixner (1937)
Kraubat, Styria	1.567 (Na)		Meixner (1938)

data for the Rutherglen mineral certainly, and for the other material presumably, relate to the rhombohedral modification.

Pleochroic, with  $\omega$  yellow to brown,  $\epsilon$  nearly colorless. Sometimes biaxial, with small 2V and variable.

New Data. Rhombohedral Pyroaurite. Type specimens of the transparent green pyroaurite from Rutherglen, Ontario, were examined through the kindness of Dr. H. V. Ellsworth. The morphology, optical properties and x-ray powder pattern (see Fig. 1) of this mineral proved to be identical with the characters of the so-called rhombohedral pyroaurite from Långban, as given by Flink, and by Aminoff and Broomé, and independently determined by the writer on specimens from the Flink collection. The Rutherglen mineral is entirely homogeneous and fresh, and the analysis by Ellsworth (column 1, Table 1) thus indicates the true composition of the rhombohedral species.

		Atomic Contents of Cell					
Analysis (Rutherglen)	Atomic Quotient	Observed cell $a_0 = 3.095$ $c_0 = 23.27$	c <sub>0</sub> doubled	$a_0$ doubled	$c_0$ times eight, or $a_0$ and $c_0$ doubled	Theory	
Fe <sub>2</sub> O <sub>3</sub> 23.37	Fe 0.293	Fe=0.73	1.5	2.9	5.85	6	
MgO 35.84	Mg 0.889	Mg = 2.2	4.4	8.9	17.7	18	
$H_2O$ 32.97	Н 3.663	H=9.2	18.3	36.6	73.2	72	
CO <sub>2</sub> 7.30	C 0.166	C=0.41	0.83	1.66	3.3	3	
MnO 0.01	0 3.492	O=8.71	17.4	34.8	69.6	69	

TABLE 2. ATOMIC CONTENTS OF SOME	MULTIPLE	PYROAURITE	UNIT	CELLS
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An x-ray Weissenberg study was made of a single-crystal of the Rutherglen material. The lattice-type is rhombohedral and the cell dimensions are:  $a_0=3.095$ ,  $c_0=23.27$ , in hexagonal coordinates. These data confirm the findings of Aminoff and Broomé. The cell contents calculated from the observed dimensions on the basis of Ellsworth's analysis prove to be irrational. Accepting the validity of the analysis and the specific gravity (=2.14), then the observed cell dimensions must be sub-multiples of the true cell. The cell contents calculated on the basis of simple multiples of the observed cell are listed in Table 2. Rational cell contents which satisfy the essential condition that the number of atoms of a given kind must be three or a multiple of three for the unit cell in hexagonal coordinates, are afforded by the following alternatives:

The observed  $a_0$  and  $c_0$  are half of the true values. The observed  $c_0$  is one-eighth of the true value.

The latter alternative must be excluded, since a [0001] period of 186 Å is extremely improbable, and the doubled cell, with  $a_0 = 6.19$  and  $c_0 = 46.54$ , is indicated as the true cell.<sup>8</sup> However, no evidence was found on strongly over-exposed Weissenberg, rotation or powder photographs of a multiple cell, nor did Aminoff and Broomé find evidence of a multiple cell. The space group of the pseudo-cell as found by the Weissenberg method is R3m, R3m or R32. The cell contents on the basis of the doubled cell in hexagonal coordinates are Mg<sub>18</sub>Fe<sub>6</sub>(OH)<sub>48</sub>(CO<sub>3</sub>)<sub>3</sub>·12H<sub>2</sub>O, and the simplest formula for the mineral is

## $Mg_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O \cdot$

This formula is identical with that earlier derived by Manasse (1915) and Foshag (1920).<sup>4</sup> It may be noted that all of the creditable analyses of "pyroaurite" are very close to the above formula, in spite of the fact that all of the analyses presumably, and analyses 2 and 3 in Table 1 certainly, represent mixtures. This is due to the fact that the admixed materials, as shown beyond, are polymorphous modifications.

The physical and other properties of rhombohedral pyroaurite need not be treated here. The forms  $\{02\overline{2}1\}$  and  $\{10\overline{1}1\}$  observed by Flink on crystals from Långban become  $\{01\overline{1}5\}$  and  $\{20\overline{2}5\}$ , respectively, in the doubled structural unit. Transformation

#### Flink to Frondel 0100/1000/0010/0005.

The name to be given to this mineral presents a problem, since the true symmetry of the original pyroaurite described by Igelström from Långban is unknown. The name pyroaurite is here arbitrarily restricted to the rhombohedral modification. Localities known definitely to afford (rhom-

<sup>3</sup> It may be remarked that Aminoff and Broomé obtained rational cell contents with Z=3 for their formula for a cell of one-half the volume here required. This is due to the circumstance that, by mere chance, their formula had a molecular weight almost exactly one-half that of the formula here accepted.

<sup>4</sup> An alternative but much less probable interpretation of the composition of pyroaurite which does not require multiplication of the observed cell edges may be mentioned. The mineral may be represented as having a defect structure in point of CO<sub>3</sub> content with a compensating amount of Fe<sup>3</sup> substituting for Mg. The formula may be written as (Mg, Fe<sub>x</sub>)<sub>3</sub>(OH)<sub>6</sub>(CO<sub>3</sub>)<sub>x/2</sub> · 1<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O, where x=ca. 0.75 and Mg:Fe=3:1.

bohedral) pyroaurite include Långban, Sweden; Rutherglen, Ontario; Kraubat, Styria, Germany; Medenikamen and Belikamen, Serbia; Val Malenco and Val Ramazzo, Italy; and Blue Mont, Maryland. At Blue Mont, the first locality in the United States, the mineral occurs as a flaky coating on a joint plane in serpentine.

The hexagonal mineral commonly admixed with pyroaurite is described on a following page under the name sjögrenite.

## Hydrotalcite

Historical. Hydrotalcite occurs only as foliated and contorted platy to fibrous masses, The mineral was originally described from Snarum, Norway, by Hostetter in 1842, who regarded the considerable amount of CO<sub>2</sub> in his analysis as due to alteration and considered the mineral an aluminate. J. D. Dana (1850) and Hermann (1847) rightly placed the mineral near brucite. Four analyses of the Snarum mineral by Rammelsberg (1859) also recorded large and rather constant amounts of  $CO_2$ , which were ascribed to admixed basic magnesium carbonate. A similar mineral was described by Hermann (1847) from Slatoust, in the Urals and regarded as a distinct species under the name voelknerite. Later, Hermann (1849) and also Rammelsberg (1856) urged the identity of this mineral with the Snarum material. The CO<sub>2</sub> reported in one of the analyses of the voelknerite was again ascribed to admixture. A probable third occurrence of hydrotalcite was recognized by J. D. Dana (1851), who pointed out that the supposed species houghite, described by Shepard (1851) from Somerville, New York, was a mixture of the so-called voelknerite and spinel. Analyses of this material by Johnson (1851) and by Root (1868) are of little value. An analysis of material from a new occurrence at Nordmark, Norway, was given by Foshag in 1920.

The validity of the species hydrotalcite itself was questioned by Kenngott (1866), who considered the material from both Snarum and Slatoust as a mixture of gibbsite, magnesite and brucite. Later writers, including Tschermak (1905), Zirkel (1898) and Bauer (1904) also held that the material was a mixture, probably of gibbsite and brucite, and this view was taken as highly probable by Hintze (1910). The species rank of the mineral was established by Manasse, in 1915, who contributed four new analyses together with dehydration and optical data and derived the formula:

## $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O \cdot$

Manasse proved that the  $CO_2$  was constitutional, and showed that hydrotalcite was the aluminum analogue of pyroaurite. It may be remarked, however, that J. D. Dana (1868) earlier considered that pyroaurite was the ferrian analogue of hydrotalcite, and that Igelström (1865) and Groth (1889) believed that the two species were isomorphous. Also, Himmelbauer (1913) had stated his belief that hydrotalcite was the aluminum analogue of the chromium mineral stichtite, and, earlier, Petterd (1910) considered stichtite to be the chromium analogue of pyroaurite. Both of these writers, and also Hezner (1912), admitted the constitutional role of the CO<sub>2</sub>. Foshag, in 1920, similarly concluded that the CO<sub>2</sub> was constitutional and that stichtite, hydrotalcite and pyroaurite all had the same general formula,  $Mg_6R_2(OH)_{16}CO_3 \cdot 4H_2O$ , where R=Cr, Al or Fe. Recently, analyses of hydrotalcite of undemonstrated homogeneity from Snarum, and from a new locality at Bashenowo in the Urals, have been reported by Kurnakov and Černych (1928). They state the formula of hydrotalcite as  $Mg_9Al_4(OH)_{24}(CO_3)_3 \cdot 8H_2O$  and give an analogous formula for pyroaurite. The analyses and dehydration data of these workers are out of line with the results of others.

*Optical Data*. The older optical data for hydrotalcite are summarized below. The data apparently refer to the rhombohedral polymorph of hydrotalcite described beyond.

Locality	ω	e	Observer
Snarum, Norway	$1.516 \pm 0.003$	$1.504 \pm 0.003$	Larsen (1921)
	1.511	1.494	Manasse (1915)
	Birefringence	= 0.0152	Kurnakov and Černych (1928)
Bashenowo, Urals	Birefringence	=0.0148	Kurnakov and Černych (1928)
Kongsberg, Norway	$1.510 \pm 0.003$	$1.495 \pm 0.003$	Larsen (1921)
	1.510		Foshag (1920)
St. Lawrence Co., New York	$1.511 \pm 0.003$	$1.496 \pm 0.003$	Larsen (1921)

The material from Bashenowo and Slatoust is said by Kurnakov and Černych (1928) to be optically positive; this may refer to the sign of elongation and not to the optical character, which in an OH-layer-lattice of the present type should be negative. Michel-Lévy and Lacroix (1888) give the average index (for Na) as 1.47, birefringence=0.014, for the material from Snarum.

New Data. Rhombohedral Hydrotalcite. An x-ray powder and optical study was made of hydrotalcite from Somerville and Amity, New York, of the specimen from Kongsberg analyzed by Foshag (1920), and of five specimens from Snarum, Norway. The x-ray study showed that all of the specimens with the exception of the material from Somerville were intimate mixtures of a hexagonal substance with a rhombohedral material identical in pattern with rhombohedral pyroaurite (Figs. 1, 2). The mineral from Somerville gave a purely rhombohedral pattern. The dePYROAURITE AND SJÖGRENITE GROUPS



FIG. 1. X-ray powder photographs of members of the pyroaurite and sjögrenite groups.



FIG. 2. X-ray powder photographs of admixed and pure members.

gree of admixture varies in different specimens from the same locality and in different parts of the same specimen, but the rhombohedral substance usually predominates greatly. Correlated optical and x-ray study gave the following optical data: The rhombohedral substance has  $\omega = 1.510$  to 1.518 and  $\epsilon = 1.495$  to 1.502, in part biaxial due to strain with small 2V, varying to 0° in the same flake. These values are very

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close to those cited in the literature for "hydrotalcite." The hexagonal substance had  $\omega = 1.524$  and  $\epsilon = 1.510$ , in part biaxial with small 2V and variable. Optical evidence of admixture is difficult to establish, apparently because the hexagonal and rhombohedral substances occur together as submicroscopic flakes interlaminated on  $\{0001\}$ , but was definitely proven in several specimens.

The x-ray powder pattern of the rhombohedral substance is identical with that of rhombohedral pyroaurite, aside from a slight difference in cell dimensions (Figs. 1, 2). The dimensions calculated from the powder pattern are:  $a_0 = 3.065$ ,  $c_0 = 23.07$ , in hexagonal coordinates. The composition of the mineral can not be fixed directly, since none of the analyses of hydrotalcite are definitely known to have been made on a homogeneous rhombohedral sample. The following evidence, however, establishes with reasonable certainty the formula

## $Mg_6Al_2(OH)_{16}CO_3 \cdot H_2O$

#### for the mineral, analogous to the formula of pyroaurite:

1. The x-ray data indicates that the mineral is isostructural with pyroaurite. The slightly smaller cell dimensions correspond to the substitution of Al for Fe.

2. Analyses of samples known or presumed to be mixtures, specifically including the Kongsberg material analyzed by Foshag, which is found by x-ray study to be a mixture in almost equal proportions of the two substances, yield a formula with the identical ratio of pyroaurite. This also is presumptive evidence of the polymorphic relation of the hexagonal and rhombohedral substances. The cell contents calculated for two of the creditable analyses are given in columns 5 and 6, Table 1, and are in close accord with the formula given above. The doubled cell, with  $a_0=6.13$ ,  $c_0=46.15$ , is again required.

The symmetry of the original hydrotalcite of Hostetter (1842) from Snarum is unknown, and the name hydrotalcite is here arbitrarily restricted to the rhombohedral modification. The hexagonal substance commonly admixed with hydrotalcite is described on a following page under the name manasseite.

#### STICHTITE

*Historical.* Stichtite occurs only massive, as aggregates of fibers or plates, often matted or contorted, and as cross-fiber veinlets. The mineral was originally described from Dundas, Tasmania, by Petterd in 1910, and was analyzed by Wesley (in Petterd, 1910) and later by Hezner (1912) and Foshag (1920). Hezner, unaware of the work of Petterd, described her material as a new species, chrombrugnatellite. Himmelbauer (1913) later showed the identity of Hezner's mineral with stichtite. A

second occurrence of the mineral, near Barberton in the Transvaal, was described by A. L. Hall (1922) with an analysis by McCrae and Weall. Recently a third occurrence, at Cunningsburgh, Shetland Islands, Scotland, was described and analyzed by Read and Dixon (1933). Stichtite also has been found at the Megantic mine, Black Lake, Quebec, by Poitevin and Graham (1918), but analyses are lacking.

Stichtite occurs intimately admixed with chromite and serpentine and unquestionably homogenous material has not yet been analyzed. Petterd derived the formula 5Mg(OH)<sub>2</sub>·MgCO<sub>3</sub>·2(Cr,Fe)(OH)<sub>3</sub>·5H<sub>2</sub>O, but the MgO:(Cr,Fe)<sub>2</sub>O<sub>3</sub> ratio of his analysis is closer to 7:1 than 6:1. Hezner obtained the formula  $5Mg(OH)_2 \cdot 2MgCO_3 \cdot 2Cr(OH)_3 \cdot 4H_2O$  after the deduction of 16.49 per cent impurity. Foshag, working on material stated to be homogeneous except for admixed chromite (although the analysis contains 2.09 per cent SiO<sub>2</sub>, suggesting the presence of serpentine), obtained the formula 5Mg(OH)2 · MgCO3 · 2Fe(OH)3 · 4H2O, analogous to the formula derived by him for pyroaurite and hydrotalcite. Hall (1922) doubted that the mineral had a definite composition. Read and Dixon recalculated their analysis and the earlier analyses after deducting SiO<sub>2</sub> as serpentine and FeO as chromite, FeCr<sub>2</sub>O<sub>4</sub>. On this basis all of the analyses agree fairly well with the formula  $5Mg(OH)_2 \cdot MgCO_3 \cdot$ Mg[CO<sub>3</sub>(OH)<sub>2</sub>] · 2(Cr,Fe)(OH)<sub>3</sub> · 4H<sub>2</sub>O. However, no great confidence can be placed in this or in the other formulae proposed in view of the uncertainity as to the composition and amount of the impurities present. This is particularly true of the admixed chromite, which while assigned the formula FeCr<sub>2</sub>O<sub>4</sub>, for the purposes of the calculation, actually in nature is usually both highly magnesian and ferrian. A considerable error in this respect may be introduced in the analysis of the Cunningsburgh mineral, which as recalculated by Read and Dixon contains 27.89 per cent chromite as FeCr<sub>2</sub>O<sub>4</sub> and but 45.97 per cent stichtite. Hezner deducted from her analysis 11.23 per cent serpentine as H<sub>4</sub>Mg<sub>3</sub>Si<sub>2</sub>O<sub>9</sub>, although her separate analysis of the serpentinous rock forming the matrix of the specimen contains FeO above any interpretation of the Cr2O3 as chromite," and otherwise differs considerably from the formulae given. A similar objection can be raised against the deduction of serpentine as H4Mg3-Si<sub>2</sub>O<sub>9</sub> in the recalculation by Read and Dixon of the stichtite from Barberton, as a separate analysis of the serpentinous matrix of the stichtite shows it to be highly ferruginous.

*Optical Data*. The older optical data for stichtite are tabulated below. It is shown beyond that the data for the Dundas mineral refer to rhombohedral stichtite, and that the data for the Cunningsburgh material probably refer to the hexagonal polymorph, barbertonite.

Locality	ω	ie -	Observer		
Dundas, Tasmania	1.542	1.516	Himmelbauer (1913)		
Cunningsburgh, Scotland	1.559 (Na)	1.543 (Na)	Read and Dixon (1933)		

Faintly pleochroic in violet, with absorption  $\omega > \epsilon$ . Elongation positive. In part biaxial with small 2V and variable.

New Data. Rhombohedral Stichtite. Stichtite from Dundas, Tasmania, from Black Lake, Quebec, and from the Barberton district, Transvaal, was examined by optical and x-ray methods. The x-ray study showed that the Dundas and Barberton materials were intimate mixtures of a hexagonal substance with a rhombohedral substance identical in pattern with (rhombohedral) pyroaurite and hydrotalcite (Fig. 1). The material from Black Lake was composed solely of the rhombohedral substance. The material from Dundas was composed very largely of the rhombohedral substance, and optically some samples were homogeneous with  $\omega = 1.545$ ,  $\epsilon = 1.518$ , in part biaxial due to strain with small and variable 2V. These indices are very close to those given by Himmelbauer for the material from Dundas analyzed by Hezner. The Barberton material was largely composed of the hexagonal substance. Optically it consists mostly of a mineral with  $\omega = 1.557$ ,  $\epsilon = 1.529$ , with a portion of the material having  $\omega$  about 1.547. The latter value evidently represents the admixed rhombohedral substance. The material with the higher indices apparently corresponds to the so-called stichtite from Cunningsburgh, Scotland, described by Read and Dixon (1933). Material from this locality was not available for study.

The cell dimensions of the rhombohedral substance as obtained from a powder photograph are:  $a_0 = 3.09$ ,  $c_0 = 23.19$  in hexagonal coordinates. The composition of the mineral can not be established directly, since none of the analyses of so-called stichtite are known to refer solely to the rhombohedral modification. The isostructural relation to hydrotalcite and pyroaurite indicated by the x-ray data, however, makes it reasonably certain that rhombohedral stichtite is the chromium member of the group with the formula:

# $Mg_6Cr_2(OH)_{16}CO_3 \cdot 4H_2O.$

The cell contents calculated on the basis of the doubled cell  $(a_0 = 6.18, c_0 = 46.38)$  for the analysis of the Dundas material by Foshag are given in Table 1, column 4, and are fairly close to the requirements of the formula indicated above.

The original stichtite of Petterd (1910) came from Dundas, Tasmania, and the name stichtite is conveniently retained to refer to the rhombohedral modification, which predominates at this locality. The hexagonal substance commonly admixed with stichtite is described on a later page under the name barbertonite.

# Hexagonal or Sjögrenite Group Sjögrenite

Broad plates of so-called pyroaurite from Långban with the hexagonal habit, recognized by Flink (1900) and by Aminoff and Broomé (1930), were examined by the Laue method and found to be hexagonal. The interior portion of large flakes had  $\omega = 1.573 \pm 0.003$ ,  $\epsilon = 1.550 \pm 0.005$ , but the indices varied somewhat, especially toward the margins of the plates. The indices are notably higher than those of rhombohedral pyroaurite. The *x*-ray powder photograph of a homogeneous sample was indexed in terms of a hexagonal cell with the dimensions:  $a_0 = 3.10$ ,  $c_0 = 15.57$ . These dimensions are identical with those for the hexagonal substance recognized by Aminoff and Broomé. Optical or other evidence which definitely associates any of the reported analyses of so-called pyroaurite with the hexagonal substance is lacking. The following evidence, however, indicates that the hexagonal substance has the formula:

## $Mg_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$

and hence is polymorphous with pyroaurite:

1. The mineral is found by x-ray study to be isostructural with the hexagonal minerals manasseite and barbertonite, described beyond, which occur associated with hydrotalcite and stichtite, respectively. A new analysis of manasseite and indirect evidence for both manasseite and barbertonite indicate that they have the general formula  $Mg_6R_2(OH)_{16}CO_3 \cdot 4H_2O$  and are polymorphous with hydrotalcite and stichtite. The isostructural relation to these minerals indicates that the hexagonal substance here described has the same general formula.

2. Unit cell contents expressing the formula given above are afforded by Johansson's analysis of a sample from Långban known to be a mixture of the hexagonal substance and pyroaurite, by Manasse's and other creditable analyses of the Långban material (which can be presumed to represent mixtures) and by the analysis of Ellsworth on the pure Rutherglen pyroaurite (see columns 2 and 3, Table 1). This is presumptive evidence both of the correctness of the formula and of the polymorphic relation of the hexagonal substance to pyroaurite. Rational cell contents, however, are afforded only when the observed  $a_0$  is doubled (=6.20).

The name sjögrenite is proposed for the mineral here described in honor of Hjalmar Sjögren (1856–1922), Swedish mineralogist and formerly Professor of Mineralogy at the University of Stockholm, who described the occurrence of so-called pyroaurite at Nordmark, Sweden. The properties of sjögrenite are as follows: Hexagonal; structure cell  $a_0 = 6.20$ ,  $c_0 = 15.57$ . Crystals are broad basal plates bounded laterally by

striated and indistinct pyramids or a prism. Hardness =  $2\frac{1}{2}$ . Specific gravity = 2.11 (observed), 2.11 (calculated). Uniaxial negative, with  $\omega = 1.573$ ,  $\epsilon = 1.550$ . Color creamy white, yellowish, nearly colorless; luster on cleavages pearly. Known only from Långban, Sweden, where it occurs mostly in parallel growths with pyroaurite.

## MANASSEITE

The hexagonal substance recognized in the x-ray powder photographs of hydrotalcite from Snarum and Kongsberg, Norway, and Amity, New York, has a pattern identical with those of sjögrenite and the chromium mineral barbertonite, described beyond. The observed cell dimensions are:  $a_0 = 3.06$ ,  $c_0 = 15.34$ . One of the specimens from Snarum was almost entirely free from admixture with hydrotalcite and was analyzed by Mr. F. A. Gonyer (column 7, Table 1). Under the microscope this material was found to contain minute embedded grains of a mineral identified with some certainty as gibbsite, and rare grains of diaspore and an unidentified mineral. The cell contents calculated for this analysis are in satisfactory agreement with the formula:

## $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O \cdot$

It is necessary, however, to double the observed value of  $a_0$ , as with sjögrenite. The agreement with the formula becomes very close if the analysis is recalculated after the deduction of 6.38 per cent gibbsite (column 8, Table 1). The analysis by Foshag (1920) of the so-called hydrotalcite from Kongsberg, which is found on x-ray study of the analyzed specimen to represent a mixture in almost equal proportions of hydrotalcite and the hexagonal substance here described (see Fig. 2), also affords cell contents (column 5, Table 1) in satisfactory agreement with the formula cited above. These facts indicate with reasonable certainity that the mineral is identical in composition with hydrotalcite.

The name manasseite is proposed for this mineral in honor of Ernesto Manasse (1875–1922), Italian chemist, mineralogist and petrographer, formerly Professor of Mineralogy at the University of Florence, who made important contributions to our knowledge of hydrotalcite and pyroaurite. The properties of manasseite are as follows: Hexagonal; structure cell:  $a_0 = 6.12$ ,  $c_0 = 15.34$ . Occurs as contorted lamellar-fibrous masses. Perfect cleavage {0001}. Hardness 2. Specific gravity  $2.05 \pm 0.05$  (observed), 2.00 (calculated). Color white to bluish white, with a pearly luster on the cleavages. Uniaxial negative, with  $\omega = 1.524$ ,  $\epsilon = 1.510$ , and in part biaxial due to strain with small 2V varying to 0° in the same flake.

#### BARBERTONITE

The hexagonal substance recognized in the x-ray powder patterns of stichtite from Dundas, Tasmania, and Barberton, Transvaal, is identical in pattern with sjögrenite and manasseite (Fig. 1). The cell dimensions are:  $a_0 = 3.085$ ,  $c_0 = 15.52$ . Analyses known to refer only to the hexagonal substance are lacking, but the isostructural relation to sjögrenite and manasseite indicates that the mineral is the chromium member of the hexagonal group with the formula:

# $Mg_6Cr_2(OH)_{16}CO_3 \cdot 4H_2O$

and is polymorphous with stichtite. The indices of the mineral ( $\omega = 1.557$ ,  $\epsilon = 1.529$ ) are very close to those of the so-called stichtite from Cunningsburgh, Scotland, and the analysis by Read and Dixon (1933) of this material may represent the hexagonal substance. While neither this analysis nor the analysis cited by Hall (1922) for the Barberton material is satisfactory, due to gross admixture with serpentine and chromite as previously discussed, the ratios derived from them are fairly close to those of the formula given above. The cell contents (column 4, Table 1) calculated on the basis of the analysis by Foshag (1920) of the (admixed) material from Dundas, also are close to the formula given. The observed  $a_0$  must again be doubled to give rational contents, as in the case of sjögrenite and manasseite.

The name barbertonite is proposed for the mineral after the occurrence in the Barberton district, Transvaal. The properties of barbertonite are as follows: hexagonal; structure cell:  $a_0 = 6.17$ ,  $c_0 = 15.52$ . Occurs as contorted lamellar-fibrous masses and as cross-fiber veinlets. Hardness =  $1\frac{1}{2}$ -2. Specific gravity =  $2.10 \pm 0.05$  (observed), 2.11 (calculated). Perfect cleavage {0001}. Color rose-pink to violet. Uniaxial negative, with  $\omega = 1.557$ ,  $\epsilon = 1.529$ , and in part biaxial due to strain with small and variable 2V.

# Mode of Intergrowth of the Polymorphs

Sjögrenite occurs at Långban as oriented growths upon pyroaurite, with sjögrenite  $\{0001\}$  [1010] parallel pyroaurite  $\{0001\}$  [1010]. An x-ray study of the growths is given by Aminoff and Broomé (1930). Pyroaurite occurs analogously oriented upon brucite at Kraubat, Styria (Meixner, 1938). The  $a_0$  values of pyroaurite (=6.19), sjögrenite (=6.20) and brucite ( $3.12 \times 2 = 6.24$ ) are nearly alike, and the mutual orientation doubtlessly is conditioned by a near identity in arrangement and spacing of the OH ions in the  $\{0001\}$  layers.

Manasseite and barbertonite commonly occur admixed with their rhombohedral analogues, and the existence of a mutual orientation simi-

lar to that between sjögrenite and pyroaurite was sought by an x-ray Laue examination of cleavage flakes of the intergrowths. A very unusual mode of association was found. The hexagonal and rhombohedral analogues appear to consist of microscopic or submicroscopic plates interlaminated on  $\{0001\}$  with a partially or completely random stacking of the plates about [0001]. This arrangement is deduced from Laue photographs such as are shown in Fig. 3. in which the complete circles are found to be loci of reflection of single planes (spots) on normal single-crystal Laue photographs taken along [0001]. Figure 3, right, shows a partially random stacking in a mixture composed largely of barbertonite. A com-



FIG. 3. Laue photographs taken along [0001] of cleavage flakes of manasseite (left) and of a barbertonite-stichtite intergrowth (right). Fe radiation.

pletely random stacking about [0001] was found in a cleavage flake composed entirely of manasseite. The pyroaurite from Rutherglen gives a perfect single-crystal photograph, without asterism or circles.

The origin of the random character of the intergrowths is difficult of explanation. The occurrence of the minerals as more or less contorted masses in serpentine suggests that mechanical deformation has been effective. It is also obscure why the polymorphs should so commonly occur together in the first place. The extended laminar character of the intergrowths and the relatively large development of surface between the two phases makes it seem improbable that the association represents an incomplete polymorphic inversion. Possibly the association is primary, and the appearance of one or the other modification over brief periods of time

## PYROAURITE AND SJÖGRENITE GROUPS

during crystallization may be a chance phenomenon involving a choice between closely related structures of essentially equal thermodynamic stability. The polymorphism presumably arises in differences in the manner or period of stacking of hydroxide layers (i.e., OH-cation-OH layers) along [0001]. A brucite-like arrangement almost certainly constitutes one of the layer motifs. The mutual association possibly unites the structure of the two phases in such a manner that identical layers adjoin, defining a virtual third phase in the contact region. This may be a brucite block of structure in the present instance. The virtual contact phase possibly insulates, and maintains a zero interfacial energy between, the two polymorphs proper and prevents transformation.

## Brugnatellite

Brugnatellite was originally described and analyzed by Artini (1909) from the Val Malenco, Lombardy, Italy. Later, the mineral was reported by Pelloux (1913) and analyzed by Artini (1922) from Monte Ramazzo, Liguria, Italy. A third occurrence of the mineral, at Viu, Val di Lanzo, Piedmont, Italy, was analyzed by Fenoglio (1927), and an analysis of an additional occurrence, at Cogne, Val d'Aosta, Italy was reported by Fenoglio (1938). Brugnatellite is said by Larsen and Goranson (1932) to occur at Iron Hill, Colorado, but no description is given.

Both Artini and Fenoglio recognized the constitutional role of the  $CO_2$ , and deduced the formula:

# $Mg_6Fe(OH)_{13} \cdot CO_3 \cdot 4H_2O.$

This formula differs from that of pyroaurite and sjögrenite in containing one-half as much Fe<sup>3</sup>. In 1938 Fenoglio described an x-ray Laue and powder study of brugnatellite. He obtained a hexagonal (trigonal) cell with  $a_0=5.47$  and  $c_0=15.97$ , and with  $Z=0.97\sim1$  on the basis of the formula given above. The optical data for brugnatellite are tabulated below.

Locality	ω	e	Observer
Val Malenco, Italy Monte Ramazzo, Italy	1.533 (Na) 1.535 1.540±0.003	1.510±0.005	Artini (1909) Larsen (1921) Larsen (1921) Foshag (1920) Artini (1922) Fenoglio (1927)
Val di Lanzo, Italy	1.536 1.536 1.537±0.001 (Na)		

Pleochroic, with  $\omega$  yellowish red and  $\epsilon$  colorless.

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New Data. Type brugnatellite was not available for study. A specimen labeled brugnatellite from the original locality in the Val Malenco proved to be an intimate mixture of a pale yellow uniaxial negative mineral with  $\omega = 1.535$  to 1.540 (brugnatellite ?) with artinite, chrysotile, hydromagnesite, brucite and abundant pyroaurite. The x-ray powder pattern was largely that of pyroaurite, with additional lines due to admixture. Three specimens labelled brugnatellite from Monte Ramazzo were also examined and proved on x-ray and optical study to be mixtures largely of pyroaurite and brucite.

The possibility suggested itself that the pyroaurite in the specimens actually is brugnatellite, and that this species is isostructural with pyroaurite with a defect lattice in point of Fe<sup>3</sup> content. The fact that pyroaurite has not been previously reported from these localities encourages this view-granting the authenticity of the specimens. However, the Laue data given for brugnatellite by Fenoglio (1938), who appears to have used analyzed type material, show that the lattice mode is primitive hexagonal, and in this differs from the centered (rhombohedral) lattice of pyroaurite, while the point-symmetry is trigonal, and in this differs from the hexagonal mineral sjögrenite. The cell dimensions and powder patterns also are unlike, as are the indices of refraction. Further, the four analyses of brugnatellite, from four different localities, uniformly show a Fe<sup>3</sup> content one-half that of pyroaurite and sjögrenite. This fact, however, is not rigorous evidence against a defect lattice, although it is true that uniformly simple and numerically small ratios between occupied and vacant positions are generally lacking in defect structures as commonly defined. The conclusions seem forced that brugnatellite is a distinct species from pyroaurite and sjögrenite, and that pyroaurite occurs associated with brugnatellite at Val Malenco and Val Ramazzo.

Two additional carbonate-hydroxides of Mg and Fe were recognized in the course of the present study as new and different from the minerals at hand, and the mineralogy of the magnesium carbonate-hydroxides appears to be complex. The ill-defined pyroaurite-like materials described by Heddle (1878) from Haaf-Grunay and by Sjögren (1894) from Nordmark, and the so-called hydrotalcite from Slatoust and Bashenowo also may represent distinct species.

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