

THE CHEMICAL COMPOSITION OF HYDROTALCITE AND THE HYDROTALCITE GROUP OF MINERALS.

By WILLIAM F. FOSHAG,

Of the Department of Geology, United States National Museum.

The hydrotalcite group as here considered comprises the minerals hydrotalcite, pyroaurite, stichtite, and brugnatellite. Of these hydrotalcite and pyroaurite have been long known but their true chemical nature remained hidden. They have been considered hydrated oxides, a considerable and rather constant carbon dioxide content having been entirely disregarded. New analyses of hydrotalcite and stichtite are here presented. Further analyses are necessary before the chemical composition of this group can be definitely established. Before any definite conclusions can be drawn from any analysis, however, the homogeneity of the material, as determined under the petrographical microscope, must be established.

HYDROTALCITE.

HOCHSTETTER, *Journ. Prakt. Chem.*, vol. 27, p. 378, 1842.

HERMANN, *Journ. Prakt. Chem.*, vol. 40, p. 11, 1847.

HERMANN, *Journ. Prakt. Chem.*, vol. 46, p. 257, 1849.

SHEPARD, *Amer. Journ. Sci.*, vol. 12, p. 209, 1851.

JOHNSON, *Amer. Journ. Sci.*, vol. 12, p. 361, 1851.

Hydrotalcite was first described by Hochstetter from the Shishimsk District in the Urals, where it occurred implanted on schist. It was later described from Snarum, Norway, under the name volknerite. Hydrotalcite from Kongsberg, Norway (U. S. Nat. Mus., No. 13191), was selected for analysis. The material consisted of curved lamellar masses of a white color and pearly luster. Under the microscope the material is made up of basal cleavages with refractive index about 1.510. Sections normal to the basal cleavage showed a birefringence of low order. The material was very pure, only a few grains of foreign material appearing. The results of an analysis on this material and another partial analysis, together with the calculated ratios, are given in the following table:

Analyses and ratios of hydrotalcite.

Constituents.	Per cent.		Ratios.	
SiO ₂	0.44			
Al ₂ O ₃	15.32	} 17.60	1.00	1×1.00
Fe ₂ O ₃	1.89			
CaO	None.			
MgO	39.72	} 40.40	6.1	6×1.00
FeO28			
CO ₂	7.60	7.60	1.07	1×1.07
H ₂ O	35.46	35.75	12.4	12×1.03
	100.71			

This leads to the formula $6\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$ or $\text{MgCO}_3 \cdot 5\text{Mg}(\text{OH})_2 \cdot 2\text{Al}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$.

Pyrognostics.—Before the blowpipe the mineral glows with intense light, but does not fuse, and becomes silvery white. Heated in a closed tube it decrepitates, gives abundant water, and turns silvery white. It is easily soluble in acids, leaving a slight residue.

The mineral houghite described by C. U. Shepard from St. Lawrence County, New York, is probably hydrotalcite, as pointed out by J. D. Dana. In appearance it is very similar to the hydrotalcite from Norway. Under the microscope it shows a weak birefringence and an index of refraction of about 1.510. The material is considerably intermixed with spinel and other minerals, so that a chemical analysis would lead to no definite results. The analyses by Johnson, therefore, can mean but little. The mineral is derived from spinel.

STICHTITE.

PETTERD, Cat. of the Minerals of Tasmania, p. 167, 1910.

WARD, Cat. of the Minerals of Tasmania, p. 169, 1910.

HEZNER, Centralbl. f. Min., etc., p. 18, 1912.

HIMMELBAUER, Tsch. Min. u. Pet. Mitth., vol. 31, p. 32, 1912.

Tasmanian Dept. of Mines, Geol. Surv. Record No. 2, 1914.

This mineral was described by Petterd first as kammererite and later as a new mineral. It occurs in irregular masses, veins, and blebs in a yellowish green serpentine, near the Adelaide Mine at Dundas, Tasmania. The color is lilac weathering to brown. It is foliated in character and has an oily luster. Under the microscope the mineral shows a fibrous structure radially disposed about nuclei of chromite. The two analyses of the mineral are widely divergent and lead to quite different ratios. In neither case is there any mention of the homogeneity of the material analyzed as determined under the petrographical microscope. These analyses are given below.

The new analysis was made upon material in the type collection of the United States National Museum (No. 87454, gift of Robert Sticht). It was crushed and examined under the microscope for homogeneity. The only foreign material detected was the chromite. The mineral was easily soluble in hydrochloric acid with effervescence, and left, beside a residue of chromite, a small amount of flocculent silica. The solution was evaporated to dryness and the separated silica filtered off. The iron, aluminum, and chromium were separated from the magnesia by a double precipitation with ammonium hydroxide. The filtered hydroxides were fused with sodium carbonate, the fusion leached with hot water, the residue dissolved, and the iron precipitated twice. The aluminum was precipitated from the solution after the oxidization of the chromium by evaporation of the filtrate with nitric acid and potassium chlorate. The chromium was reduced by evaporation with hydrochloric acid and alcohol and precipitated twice with ammonium hydroxide. The carbon dioxide was determined by absorption in a potash bulb and the water by Penfield's method.

Analyses and ratios of stichtite.

Constituents.	Petterd.	Ratios.		
SiO ₂				
Fe ₂ O ₃	9.0	0.050	} 0.76	1×.76
Cr ₂ O ₃	11.5	.075		
FeO.....				
MgO.....	36.0	.900	5.5	5×1.1
CO ₂	7.2	.164	1.00	1×1.00
H ₂ O.....	36.1	2.00	12.2	12×1.01
	99.8			

Constituents.	Hezner.	Recalc. per cent.	Ratios.		
SiO ₂	3.87				
Fe ₂ O ₃					
Cr ₂ O ₃	20.44	21.28	0.140	} 1.00	1×1.00
FeO.....	1.1	1.14	.016		
MgO.....	37.12	38.67	.967	} 7.02	7×1.03
CO ₂	10.45	10.88	.248		
H ₂ O.....	27.26	28.39	1.56	11.14	11×1.01
	100.24				.

Analyses and ratios of stichtite—Continued.

Constituents.	Original per cent.	Recalc. per cent.	Ratios.		
SiO ₂	2.09
Fe ₂ O ₃	4.04	4.14	0.025	} 1.00	1×1.00
Al ₂ O ₃	2.24	2.28	.022		
Cr ₂ O ₃	14.08	14.36	.095		
CaO.....	Trace.
MgO.....	36.59	37.33	.937	6.00	6×1.00
FeO.....	.28
CO ₂	6.94	7.08	.160	1.13	1×1.13
H ₂ O.....	33.01	33.78	1.87	13.2	12×1.10
	99.27

This leads to the formula, 6MgO. R₂O₃. CO₂. 12H₂O. The above analyses show some differences, but the results are sufficiently close to 6MgO. R₂O₃. CO₂. 12H₂O to be satisfactory. Below are repeated the analyses as compared with the composition required by the formula. In the case of Petterd's and the new analyses the differences are not great.

Analyses and calculated composition of stichtite.

Constituents.	Theory (per cent).	Hezner (per cent).	Petterd (per cent).	Foshag (per cent).
SiO ₂	3.87	2.09
Cr ₂ O ₃	23.39	20.44	11.5	14.08
Fe ₂ O ₃	9.0	4.04
Al ₂ O ₃	2.24
FeO.....	1.1028
MgO.....	38.51	37.12	36.0	36.59
CO ₂	6.75	10.45	7.2	6.94
H ₂ O.....	34.57	27.26	36.1	33.01

Pyrognostics.—Before the blowpipe stichtite glows with intense light, turns light gray, and becomes magnetic, but does not fuse. Heated in a closed tube the mineral turns gray and then brown, gives abundant water, and becomes magnetic.

PYROAURITE.

IGELSTRÖM, *Ofv. Ak. Stockh.*, vol. 22, p. 608, 1865.

SJÖGREN, *Geol. Inst. Univ. Upsala*, vol. 2, p. 59, 1894.

FLINK, *Geol. Inst. Univ. Upsala*, vol. 5, p. 87, 1900.

The mineral pyroaurite was first discovered at Långban by Igelstrom who gave its composition as Fe₂O₃. 6MgO. 15H₂O. Sjögren first described the crystallography of this mineral from material from the Moss mine in Nordmarken. Analysis of material from Långban gave Igelström the following results:

Analyses and ratios of pyroaurite from Långban.

Constituents.	Per cent.	Ratios.		
Fe ₂ O ₃	23.92	0.149	1	1 x 1.00
MgO.....	34.04	.805	5.4	5 x 1.08
CO ₂	7.24	.165	1.11	1 x 1.11
H ₂ O.....	34.54	2.14	14	14 x 1.00
	99.74			

Since FeO was not determined in the original analysis some of the mineral from Långban in the United States National Museum (No. 93013) was analyzed for ferrous iron, with the result, FeO, 0.74 per cent. The pyroaurite from Långban, however, is described as opaque even under the microscope, indicating that some alteration had taken place. The above-mentioned specimen in the United States National Museum consisted of large hexagonal platy crystals, which, under the microscope, showed an index of refraction of approximately 1.55 and weak birefringence. The sections of the crystals do not show uniform extinction, but extinguish as a mass of randomly oriented plates, suggesting perhaps that they are pseudomorphic.

The pyroaurite from Moss mine gave Sjögren on a 0.0205 g. portion the results tabulated below:

Analyses and ratios of pyroaurite from Mossgrufo.

Constituents.	Per cent.	Ratios.		
Insol.....	0.5			
Fe ₂ O ₃	22.0	0.14	} 6.5	1.0 6 x 1.09 14 x 1.01
MnO.....	4.5	.06		
MgO.....	34.8	.86		
H ₂ O.....	36.1	2.01		
	97.9			

The H₂O was determined by ignition loss and no doubt includes some of the CO₂. FeO was not determined. Both of the above analyses are very unsatisfactory, but indicate that the formula of pyroaurite is very probably 6MgO. R₂O₃. CO₂. 12H₂O.¹

The considerable content of MnO in Sjögren's analysis is worthy of note and indicates that a manganese member of the series may exist.

Hedde described a mineral as pyroaurite from the Island of Haaf Grunay. It occurred as thin seams in yellow serpentine. The anal-

¹ An analysis of pyroaurite by Mauzelius (Arkiv for Kemi. Min. ock Geol., vol. 3, No. 3, 1910), has been overlooked. Fe₂O₃, 23.20, MnO 0.21, MgO 35.08, CaO 0.54, H₂O 33.69, SiO₂ 0.29, CO₂ 6.91. Sum 99.97. This analysis leads to the formula for pyroaurite given.

yses, while agreeing well with the theoretical values required by the formula $6\text{MgO} \cdot \text{R}_2\text{O}_3 \cdot 15\text{H}_2\text{O}$. were made upon impure material. If the determination of the carbon dioxide content is correct the mineral can not be pyroaurite. It is probably a mixture of hydromagnesite, brucite, and limonite.

Sjögren points out the crystallographic similarity between pyroaurite and chalcophanite. The value for c for pyroaurite is given as 3.6072, calculated from the angle $10\bar{1}0:10\bar{1}1=76^\circ 30'$ while c for chalcophanite is given as 3.5267 from $10\bar{1}0:10\bar{1}1=76^\circ 12'$. Chalcophanite is a mineral very likely to occur at Långban, at least the manganese member, and it is possible that pyroaurite is derived from it. Since chalcophanite is derived from franklinite or jacobsite we have the interesting genetic relations—hydrotalcite from spinel, stichtite from chromite, pyroaurite from jacobsite through chalcophanite.

Pyrognostics.—Before the blowpipe the mineral turns golden brown, becomes magnetic, but does not fuse. In a closed tube it turns brown, then golden brown, gives abundant water, and becomes magnetic.

BRUGNATELLITE.

ARTINI, *Real. Acc. Linc.*, vol. 18, p. 3, 1909.

PELOUX, *Museo Civico di Storia Naturale, Genova*, vol. 46, p. 34, 1913.

Brugnatellite was described in 1909 as a new mineral by Artini. It occurs at an old asbestos mine in the Val Malenco. Artini's analysis is the only one available and the material was carefully examined under the microscope and found to be homogeneous and free from artinite, hydromagnesite, brucite, etc., and with but a trace of serpentine. Artini's analysis is given below:

Analyses and ratios of brugnatellite.

Constituents.	Per cent.	Ratios.		
Insol.....	1.03			
Fe_2O_3	13.20	0.080	0.45	$\frac{1}{2} \times .90$
MnO	1.80	.025	} 6.2	6 x 1.03
MgO	42.79	1.07		
CO_2	7.78	.177	1.00	1 x 1.00
H_2O	33.77	1.87	10.6	10 x 1.06
	100.37			

These ratios give the formula $6\text{MgO} \cdot \frac{1}{2}\text{R}_2\text{O}_3 \cdot \text{CO}_2 \cdot 10\frac{1}{2}\text{HO}_2$. which may be written $\text{MgCO}_3 \cdot 5\text{Mg}(\text{OH})_2 \cdot \text{Fe}(\text{OH})_3 \cdot 4\text{R}_2\text{O}$. This corresponds to pyroaurite, less one molecule of $\text{Fe}(\text{OH})_3$.

However, if we consider one molecule of $\text{Fe}(\text{OH})_3$ replaced by its equivalent of magnesia—that is, $1\frac{1}{2}\text{Mg}(\text{OH})_2$ —we get a formula requiring a composition given below:

Comparison of analyses of brugnatellite with values to suit formulas.

Constituents.	Artini's.	MgCO ₃ .5Mg (OH) ₂ Fe (OH) ₃ .4 H ₂ O.	MgCO ₃ .5Mg (OH) ₂ 1½ Mg(OH) ₂ Fe(OH) ₃ . 4H ₂ O.
Fe ₂ O ₃	13.39	14.41	12.40
MgO.....	44.45	43.62	46.87
CO ₂	7.89	7.93	6.87
H ₂ O.....	34.27	34.04	33.75

Which of these formulas is the correct one, or whether brugnatellite is identical with pyroaurite can only be determined by additional analyses.

Pyrognostics.—Before the blowpipe the mineral turns golden yellow, but does not fuse and becomes magnetic. In the closed tube it turns black, then golden yellow; yields considerable water, and becomes magnetic.

Pelloux describes a mineral from Mount Ramazzo as brugnatellite, but gives no analysis. Specimens from this locality in the United States National Museum (No. 93008) show a light brown, pearly mineral with an index of refraction of about 1.536, and very low birefringence, not pleochroic. This material is too scanty and impure for an analysis.

A comparison of the properties of these minerals further brings out the isomorphous relationship:

Comparison of properties of minerals of the hydrotalcite group.

Hydrotalcite.	Pyroaurite.	Stichtite.	Brugnatellite.
White.....	Light brown.....	Lavender purple..	Rose, light brown.
Translucent.....	Translucent.....	Translucent.....	Translucent.
Uniaxial.....	Uniaxial.....	Uniaxial.....	Uniaxial.
Cleavage basal.....	Cleavage basal.....	Cleavage basal.....	Cleavage basal.
Sp. gr. 2.04–2.09.....	Sp. gr. 2.07.....	Sp. gr. 2.12.....	Sp. gr.
<i>n.</i> 1.510.....	<i>n.</i> 1.55 (approx.).....	<i>n.</i> 1.542.....	<i>n.</i> 1.533.
Biref weak.....	Biref weak.....	Biref. 10.026.....	
Pleochroism, none...	Pleochroism, none..	Very slightly pleochroic.	Pleochroic.

SUMMARY.

The formula for the hydrotalcite group of minerals is shown to be MgCO₃. 5Mg(OH)₂. 2R(OH)₃. 4H₂O, and the present members are hydrotalcite, MgCO₃. 5Mg(OH)₂. 2Al(OH)₃. 4H₂O; stichtite, MgCO₃. 5Mg(OH)₂. 2Cr(OH)₃. 4H₂O; pyroaurite, MgCO₃. 5Mg(OH)₂. 2Fe(OH)₃. 4H₂O.

The chemical composition of brugnatellite and its relation to the other minerals of this group remains in doubt.

The three members have apparently the same mode of genesis and result from the alteration of the corresponding members of the spinel group.