Some observations on the properties of dypingite, $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$, and related minerals

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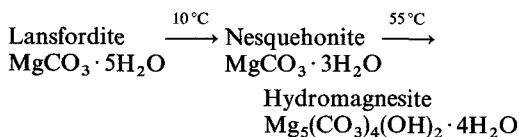CSIRO, Division of Mineral Chemistry, PO Box 124, Port Melbourne, Vic, 3207, Australia

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ABSTRACT. Dypingite, $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$, was found in materials obtained during the production of high purity magnesia from crude magnesite by the calcination/CO_2-leaching process. The snow-white, finely crystalline dypingite contained 41.0% MgO; the theoretical value is 41.5%. The X-ray powder data revealed a long period structure with a strong peak at 31.0 Å. The five strongest reflections (Å) and their estimated intensities (I/I_0) were 10.4 (100), 31.0 (40), 15.62 (40), 5.86 (30), and 6.34 (20). The DTA curve showed ten endothermic reactions with maxima at 43, 50, 77, 86, 105, 127, 180, 260, 420, and 514 °C and an exothermic reaction at 495 °C.

As part of a detailed examination of the production of high purity magnesia from crude magnesite by the calcination/CO_2-leaching process (Canterford et al., 1981, 1983), the phases that precipitate when the clarified magnesium bicarbonate solution is heated and/or aerated are being studied. The chemical composition of the precipitate that forms is affected markedly by the temperature of the solution. For a carbon dioxide partial pressure of 1 atmosphere, the approximate transformation temperatures are reported as follows (Langmuir, 1965).

$$\underset{\substack{\text{Lansfordite}\\MgCO_3 \cdot 5H_2O}}{}\xrightarrow{10\,°C}\underset{\substack{\text{Nesquehonite}\\MgCO_3 \cdot 3H_2O}}{}\xrightarrow{55\,°C}$$

$$\underset{\substack{\text{Hydromagnesite}\\Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O}}{}$$

The data on these phases are now well established (Davies and Bubela, 1973; Hill et al., 1982).

In a number of precipitation tests carried out by Causmag International at 50–60 °C, particularly those carried out on a pilot-plant scale in which accurate temperature control was difficult to achieve, the X-ray patterns of the products showed the presence of variable amounts of nesquehonite and hydromagnesite, with lesser amounts of giorgiosite and dypingite, $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$ (Raade, 1970). It is to be noted that the phases identified in this work are not true minerals—that is, they are synthetic, but they correspond to phases found in nature.

The X-ray pattern of one of the samples received for study from Causmag International indicated that it was essentially pure dypingite, with only trace amounts of nesquehonite. The sample weighed approximately 2 g; it was kept at 22 °C for more than six months without any structural changes being observed.

During the course of the present study, the results were compared with other hydrated magnesium carbonate minerals such as dypingite (Raade, 1970), giorgiosite (Friedel, 1975), hydromagnesite (Sawada et al., 1978; Davies and Bubela, 1973), lansfordite (Hill et al., 1982), and an unnamed mineral from Japan (Suzuki and Ito, 1973), and with the synthetic compound 'protomagnesite' (Davies and Bubela, 1973).

The mineral giorgiosite (Friedel, 1975) is given the same formula as dypingite—viz., $Mg_5(CO_3)_4$ $(OH)_2 \cdot 5H_2O$. However, this agrees less well with the published analysis for giorgiosite (39.99% MgO, 35.26% CO_2, and 24.42% H_2O) than does the formula $Mg_5(CO_3)_4(OH)_2 \cdot 6H_2O$. The compound 'protomagnesite' (Davies and Bubela, 1973) was not given a formula. However, the published analysis yields a composition near $Mg_5(CO_3)_4$ $(OH)_2 \cdot 11H_2O$.

Optical microscopy. The hydrated magnesium carbonate compounds obtained by the calcination/CO_2-leaching process form large chalk-like aggregates of a white, pale-grey, or light-pink colour.

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Coloured samples (particularly pink) were shown by chemical analysis to be contaminated with Fe_2O_3. The dypingite sample itself was white, forming globular aggregates up to 0.1 mm in diameter. Under ultraviolet light (short wave and long wave), it was neither fluorescent nor phosphorescent.

A thin section was prepared by setting a dispersed sample in a resin on a microscope slide and sealing with a coverslip. Under the microscope in transmitted light, the dypingite was colourless and fine-grained with fibrous appearance; its refractive index and birefringence were low. Most of the elongated crystals appeared curved. No impurities were observed.

Scanning electron microscopy. A sample, prepared by spreading dypingite on a carbon block, was gold coated. Under low magnification (less than × 1000), only globular or almost globular aggregates were visible. However, high magnifications revealed plates (with a shape resembling monoclinic symmetry) which slowly changed in shape. The edges appeared to decompose to form asymmetrical, angular flakes (fig. 1).
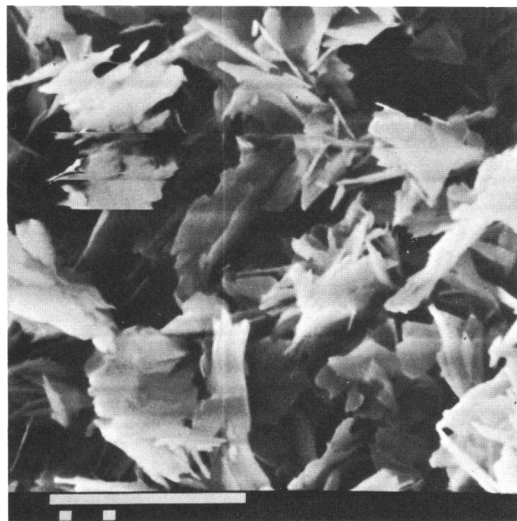

FIG. 1. Secondary electron photomicrographs of dypingite. Bar = 10 μm.

Chemical analysis. The MgO content was determined by a titrimetric method using EDTA with Eriochrom black T as an indicator. The EDTA was standardized against magnesium metal. The MgO content found was $41.0 \pm 0.2\%$; loss on ignition at 600 °C (30 min.) was 56.23% and at 1000 °C (30 min.) was 58.32%. The theoretical values for

dypingite are 41.5% MgO and 58.5% loss on ignition.

The calculated formula for this compound on the basis of 41.0% MgO, 34.09% CO_2, and 18.83% H_2O is $9MgO \cdot 7CO_2 \cdot 12H_2O$ or $Mg_9(CO_3)_7(OH)_4 \cdot 10H_2O$ (theoretical MgO content 40.9%). This calculated formulae approaches that of dypingite.

X-ray data. The sample was identified as dypingite on the basis of its X-ray diffraction pattern. X-ray powder data were obtained using Ni-filtered Cu-$K\alpha$ radiation, a scanning speed of 0.5°/min., time constant 1 s, and a 0.25° slit. The X-ray diffraction pattern, taken at about 22 °C, is given in Table I.

The pattern agrees closely with the data given by Raade (1970). The only major difference is that our dypingite shows a peak at 31.0 Å. This has not been reported previously, probably because of high background at such low diffraction angles.

After the loss on ignition at 600 °C was determined, the calcine was X-rayed. The X-ray diffraction pattern showed that conversion to cubic MgO (periclase) was almost complete. The broadness of the peaks indicated the poor crystallinity of the sample at this temperature.

Thermal analysis data. Simultaneously recorded DTA/TGA curves are shown in fig. 2. A 10.13 mg sample was heated in static air from room temperature (20 °C) to 1000 °C at a heating rate of 10 °C/min. with Al_2O_3 as a reference material. The DTA curve shows a series of endothermic peaks with maxima at 43, 50, 77, 86, 105, 127, 180, 260, 420, and 514 °C, representing the loss of hygroscopic moisture, water of crystallization, hydroxyl water, and CO_2. The exothermic reaction which takes place at 495 °C is caused by the crystallization of MgO (Sawada *et al.*, 1978, 1979). The DTA pattern is different from that published by Raade (1970), but shows some agreement with the pattern of the unnamed mineral described by Suzuki and Ito (1973).

The weight losses were measured at two different points and the results are as follows: up to 200 °C, 18.83%, above 200 °C, 34.09%. The last loss was mainly due to CO_2, the total loss is 52.92%.

The data from this study are in good agreement with the unnamed mineral (Suzuki and Ito, 1973) as far as peaks above 250 °C are concerned. Below 300 °C, this work is compatible with both the unnamed mineral (Suzuki and Ito, 1973) and dypingite (Raade, 1970).

Infrared spectrum. The infrared absorption spectrum of dypingite is shown in fig. 3 and Table II. The disk was prepared using 200 mg KBr for 1 mg of sample. There are many similarities between the spectrum of the present sample and the dypingite of Raade (1970). A significant difference, however, is

Table I. X-ray powder data for giorgiosite, dypingite, and an unnamed magnesium carbonate hydrate mineral.
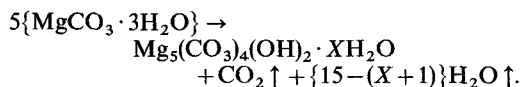
Giorgiosite		Dypingite				Unnamed mineral	
Friedel (1975)		Raade (1970)		This study		Suzuki & Ito (1973)	
d(Å) obs.	I/I$_0$ est.	d(Å) obs.	I/I$_0$ est.	d(Å) obs.	I/I$_0$ est.	d(Å) obs.	I/I$_0$ est.
-	-	-	-	31.00	40	33.20	62
11.80	100	15.20	30	15.62	40	16.36	33
9.95	25	10.60	100	10.40	100	10.82	55
-	-	7.89	10	7.89	15	8.14	12
-	-	7.37	10	-	-	7.35*	29
6.89	17b	6.34	60	6.34	20	6.454†	55
5.85	35	5.86	90	5.86	30	5.887	100
5.38	25	5.52	5	5.51	5	5.602	10
5.19	11	-	-	5.24	5	-	-
-	-	-	-	-	-	4.587	10
4.44	55	4.45	20	4.44	10	4.448	29
4.20	20	4.20	30	4.19	13	4.206	38
-	-	4.10	10	4.10	3	4.123	10
3.97	12b	3.90	10	3.91	5	3.919	7
3.69	17	3.68	10	3.68	2	3.66*	12
3.51	25	3.49	10	3.484	6	3.523	17
3.38	70	3.33	10	3.33	5	3.35	7
3.28	70	3.16	40	3.16	10	3.20	29
3.02	20	3.07	40	3.076	15	3.12	26
-	-	-	-	-	-	3.033†	7
-	-	2.96	5	2.952	15	2.997	7
2.919	55	2.93	40	2.928	17	2.933	57
-	-	-	-	2.87	12	2.864	19
2.827	30	2.84	30	2.847	18	-	-
-	-	2.81	20	2.81	10	-	-
2.722	20	2.78	20	2.78	10	2.77	7
2.687	17	-	-	2.661	10	2.663	24
2.615	35	2.53	50	2.53	11	2.543	14
2.562	30	2.50	5	2.50	5	2.512*	17
2.495	35	-	-	2.421	6	2.454*	14
2.456	25	2.41	10	2.41	8	-	-
-	-	2.36	5	2.36	5	-	-
2.339	25	2.34	5	2.34	5	2.345	14
2.295	9	2.25	20	2.25	11	-	-
2.252	25	-	-	2.233	10	-	-
2.194	15	2.21	20	2.21	10	2.226	17
2.138	17	-	-	2.174	12	2.183	33
2.107	20	2.17	50	2.17	15	-	-
1.997	25	2.11	5	2.11	6	2.1127	21
1.842	20	2.09	5	2.09	5	-	-
1.439	70	-	-	2.03	5	-	-
1.226	15	2.02	20	2.02	6	2.0294	17
1.015	17	-	-	2.00	6	-	-
1.013	9	1.99	10	1.99	6	1.9889	24
0.507	45	1.96	10	1.96	6	-	-
-	-	1.92	5	1.92	4	1.9232	14
-	-	1.90	5	1.90	4	1.8994	7
-	-	-	-	-	-	1.848	14
-	-	1.73	5	1.732	5	1.731	14
-	-	-	-	1.726	5	-	-
-	-	1.64	5	1.64	5	1.6447	12
-	-	1.61	5	1.605	7	1.6078	12
-	-	1.52	5	-	-	-	-

* Chrysotile interference
† Nesquehonite interference.

the absence of the two small absorption bands at 1020 and 940 cm^{-1}, which Raade believed to be characteristic of dypingite.

Discussion. Intermediate hydrate phases may form during the decomposition of nesquehonite to hydromagnesite by a reaction of the following type.

$$5\{MgCO_3 \cdot 3H_2O\} \rightarrow$$
$$Mg_5(CO_3)_4(OH)_2 \cdot XH_2O$$
$$+ CO_2 \uparrow + \{15 - (X+1)\}H_2O \uparrow.$$

The known values for X are: $X = 4, 5, 6, 8, 11$. Protomagnesite, (Davies and Bubela, 1973), dypingite (Raade, 1970), the unnamed mineral studied by Suzuki and Ito (1973) and giorgiosite (Friedel, 1975) are accepted intermediate hydrates.

Information on anhydrous and hydrated magnesium carbonate minerals and compounds is presented in Table III. Fig. 4 presents the positions of the various minerals and synthetic compounds in the system $MgO-CO_2-H_2O$. The hydrated magnesium carbonate minerals and compounds may be separated into three groups.

The first group has as its basis, magnesite with variable numbers of water molecules. The known minerals in this group are barringtonite, nesquehonite, and lansfordite. Their position in the $MgO-CO_2-H_2O$ system is well established. The stability of the members of this group decreases with increasing H_2O content.

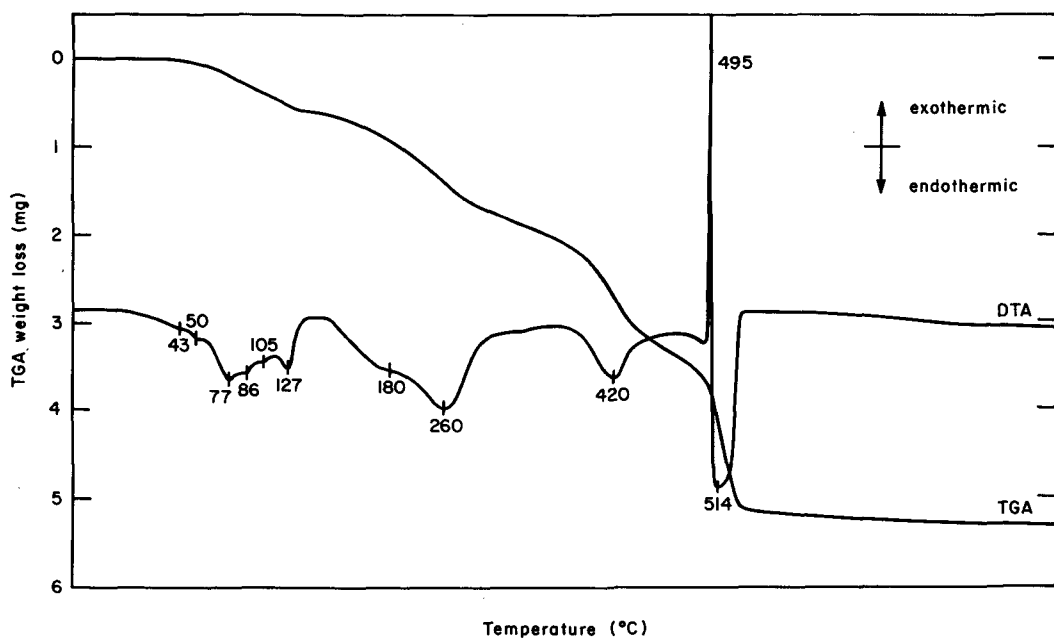The second group has as its basis $Mg_2(CO_3)$-

FIG. 2. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves for dypingite, heated at 10 °C/min in static air.
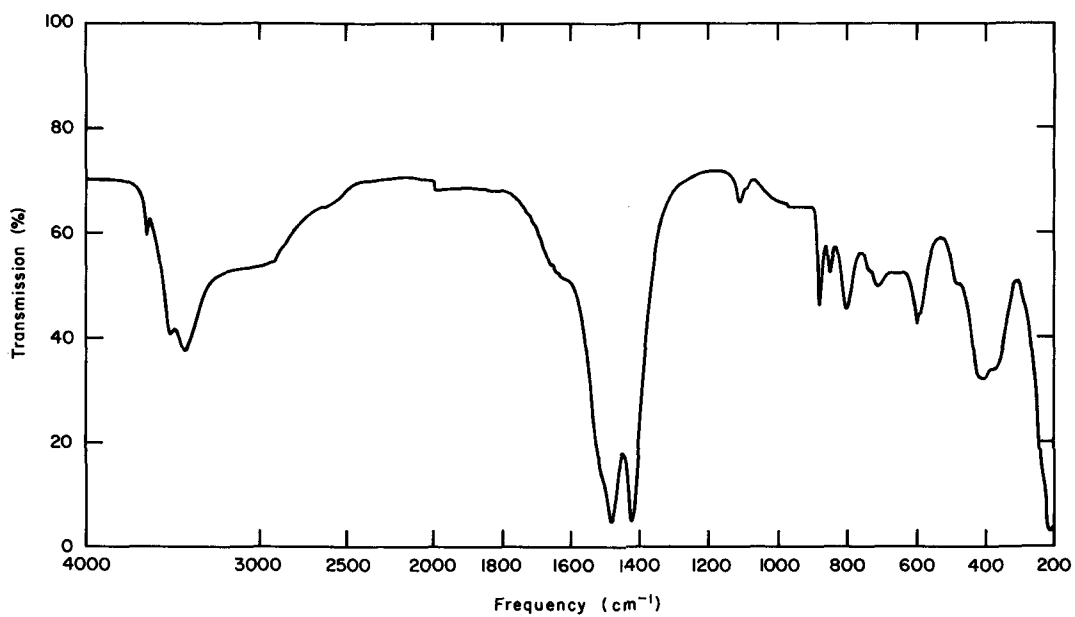

FIG. 3. Infrared absorption spectrum for dypingite.

(OH)$_2$ and contains water of hydration. Only one mineral, artinite, is known in this group.

The third group is of considerable interest. It has five known members; four occur as natural minerals and one is known only as a synthetic compound. All have a similar basic composition, $Mg_3(CO_3)_4$ (OH)$_2$, and as with the first group, variable amounts of water of hydration ranging from 4 to 11 molecules.

Table II. Infrared absorption spectra of dypingite. A, Raade (1970); B, this work.

Frequency cm^{-1}			
A	B		
3650	3650	(OH)$^{-1}$	Stretching vibration.
3510	3510		
3450	3440	H$_2$O	Stretching vibration.
	2920		
P	1660	H$_2$O	Bending vibration.
	1645		
1480	1480		
1420	1422	CO$_3^{-2}$	Asymmetrical stretching vibration.
1120	1112		Symmetrical stretching vibration.
1020	--		
940	--		
880	881		
850	850	CO$_3^{-2}$	Bending vibration bands.
800	800		(881 and 800 equally strong)
P	740		
P	715		
P	665		
P	600		
P	475		
P	410		
	375		

P - Present in the spectrum published by Raade (1970) but not assigned.

In the MgO-CO$_2$-H$_2$O system, these minerals and compounds fall on a line which connects protomagnesite with hydromagnesite. The line, if projected, joins the main MgCO$_3$-H$_2$O line at a point with the composition MgCO$_3 \cdot 18$H$_2$O. However, minerals in that part of the MgO-CO$_2$-H$_2$O system are unstable. It is not unreasonable to conclude that a theoretical phase of the composition MgCO$_3 \cdot 18$H$_2$O will decompose to lansfordite, MgCO$_3 \cdot 5$H$_2$O, which itself is unstable and decomposes to nesquehonite at temperatures > 10°. According to various authors (Dell and Weller, 1959; Kazakov et al., 1959; Davies and

Table III. Updated information on various hydrated magnesium carbonate minerals.

Formula	Mineral	MgO:CO$_2$:H$_2$O
MgO	Periclase	MgO
MgCO$_3$	Magnesite	MgO.CO$_2$
Mg(OH)$_2$	Brucite	MgO.H$_2$O
MgCO$_3$.2H$_2$O	Barringtonite	MgO.CO$_2$.2H$_2$O
MgCO$_3$.3H$_2$O	Nesquehonite	MgO.CO$_2$.3H$_2$O
MgCO$_3$.5H$_2$O	Lansfordite	MgO.CO$_2$.5H$_2$O
Mg$_2$CO$_3$(OH)$_2$.3H$_2$O	Artinite	2MgO.CO$_2$.4H$_2$O
Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O	Hydromagnesite	5MgO.4CO$_2$.5H$_2$O
Mg$_5$(CO$_3$)$_4$(OH)$_2$.5H$_2$O	Dypingite	5MgO.4CO$_2$.6H$_2$O
Mg$_5$(CO$_3$)$_4$(OH)$_2$.6H$_2$O	Giorgiosite[*]	5MgO.4CO$_2$.7H$_2$O
Mg$_5$(CO$_3$)$_4$(OH)$_2$.8H$_2$O	Unnamed[**]	5MgO.4CO$_2$.9H$_2$O
Mg$_5$(CO$_3$)$_4$(OH)$_2$.11H$_2$O	Protomagnesite[***]	5MgO.4CO$_2$.12H$_2$O

[*] Recalculated from Friedel (1975) based on 40% MgO content.
[**] Suzuki and Ito (1973).
[***]Theoretical formula calculated from Davies and Bubela (1973)

Bubela, 1973) nesquehonite is the precursor of hydromagnesite, but there is evidence that decomposition proceeds via several intermediate phases. It is not clear whether each decomposition reaction will proceed via the formation of each of the intermediate phases. In other words, several decomposition mechanisms seem possible. On the other hand, it is quite clear that hydromagnesite is the final decomposition product.
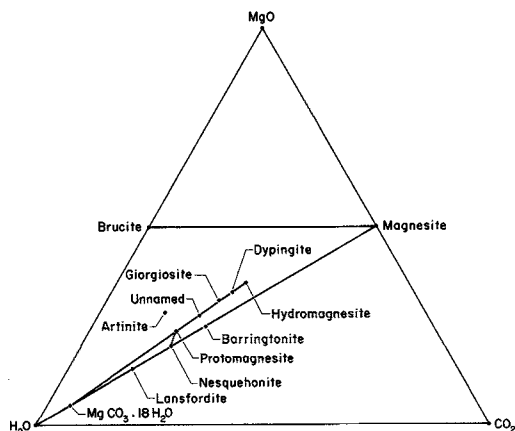

Fig. 4. The hydrated magnesium carbonate minerals in the MgO-CO$_2$-H$_2$O system.

REFERENCES

Canterford, J. H., Everson, P. T., and Moyle, F. J. (1981) *Proc. Australs. Inst. Mining Met.* no. 277, 45–52.
———— and Moorrees, C. O. (1983) Ibid. 288, 29–36.
Davies, P. J., and Bubela, B. (1973) *Chem. Geol.* **12**, 289–300.
Dell, R. M., and Weller, S. W. (1959) *Trans. Faraday Soc.* **55**, 2203–20.

Friedel, B. (1975) *Neues Jahrb. Mineral Monatsh.* 196.
Hill, R. J., Canterford, J. H., and Moyle, F. J. (1982) *Mineral Mag.* **46**, 453–7.
Kazakov, A. V., Tikhomirova, M. M., and Plotnikova, V. I. (1959) *Int. Geol. Rev.* **1** (10), 1–39.
Langmuir, D. (1965) *J. Geol.* **73**, 730–54.
Raade, G. (1970) *Am. Mineral.* **55**, 1457–65.
Sawada, Y., Uematsu, K., Mizutani, N., and Kato, M. (1978) *Thermochimica Acta,* **27**, 45–59.
———— Yamaguchi, J., Sakurai, O., Uematsu, K., Mizutani, N., and Kato, M. (1979) Ibid. **33**, 127–40.
Suzuki, I., and Ito, M. (1973) *J. Japan Assoc. Miner. Petr. Econ. Geol.* **68**, 353–61.