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

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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/CO₂-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).

$$\begin{array}{c} Lansfordite & \xrightarrow{10\,^{\circ}\mathrm{C}} & Nesquehonite & \xrightarrow{55\,^{\circ}\mathrm{C}} \\ Mg\mathrm{CO}_3\cdot 5\mathrm{H}_2\mathrm{O} & & Mg\mathrm{CO}_3\cdot 3\mathrm{H}_2\mathrm{O} \\ & & & Hydromagnesite \\ & & Mg_5(\mathrm{CO}_3)_4(\mathrm{OH})_2\cdot 4\mathrm{H}_2\mathrm{O} \end{array}$$

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

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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, Mg₅(CO₃)₄(OH)₂·5H₂O (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)₂·5H₂O. However, this agrees less well with the published analysis for giorgiosite (39.99% MgO, 35.26% CO₂, and 24.42% H₂O) than does the formula $Mg_5(CO_3)_4(OH)_2$ ·6H₂O. 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)₂·11H₂O.

Optical microscopy. The hydrated magnesium carbonate compounds obtained by the calcination/CO₂-leaching process form large chalk-like aggregates of a white, pale-grey, or light-pink colour.

Coloured samples (particularly pink) were shown by chemical analysis to be contaminated with Fe₂O₃. 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).

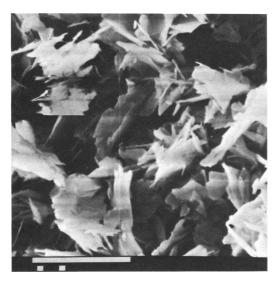


Fig. 1. Secondary electron photomicrographs of dypingite. Bar = $10 \mu m$.

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±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% CO₂, and 18.83% H₂O is 9MgO·7CO₂·12H₂O or Mg₉(CO₃)₇(OH)₄·10H₂O (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 Al₂O₃ 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 CO2. 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 CO₂, 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

Friedel (1975) Raade (1970) This study Suzuki & Ito (1970) d(\$A\$) obs.		carbonate l	hydrate mine	eral.				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Giorgiosite		Dypingite				Unnamed mineral	
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11.80	d(Å) obs.	I/I _o est.	d(Å) obs.	I/I _o est.	d(Å) obs.	I/I _o est.	d(Å) obs.	I/I _o est.
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-								33
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Table I. X-ray powder data for giorgiosite, dypingite, and an unnamed magnesium carbonate hydrate mineral.

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.

$$\begin{array}{c} 5\{\text{MgCO}_3 \cdot 3\text{H}_2\text{O}\} \rightarrow \\ \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot X\text{H}_2\text{O} \\ + \text{CO}_2 \uparrow + \{15 - (X+1)\}\text{H}_2\text{O} \uparrow. \end{array}$$

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-CO₂-H₂O. 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-CO₂-H₂O system is well established. The stability of the members of this group decreases with increasing H₂O content.

The second group has as its basis Mg₂(CO₃)-

^{*} Chrysotile interference

[†] Nesquehonite interference.

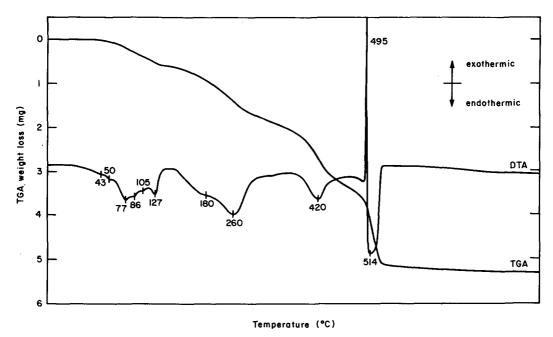


Fig. 2. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves for dypingite, heated at $10\,^{\circ}\text{C/min}$ in static air.

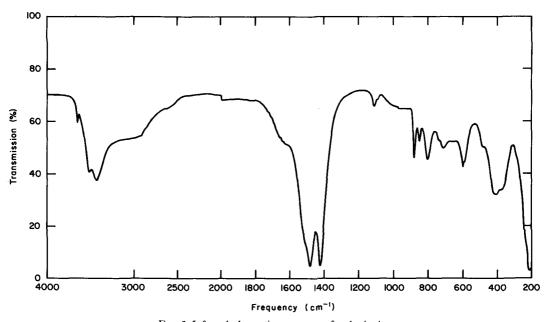


Fig. 3. Infrared absorption spectrum for dypingite.

(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, Mg₃(CO₃)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.

Freque	ncy cm ⁻¹		
A	В		
3650	3650	(OH) ⁻¹	Stretching vibration.
3510	3510		
3450	3440	H ₂ O	Stretching vibration.
	2920		
P	1660	н ₂ о	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-CO₂-H₂O system, these minerals and compounds fall on a line which connects protomagnesite with hydromagnesite. The line, if projected, joins the main MgCO₃-H₂O line at a point with the composition MgCO₃·18H₂O. However, minerals in that part of the MgO-CO₂-H₂O system are unstable. It is not unreasonable to conclude that a theoretical phase of the composition MgCO₃·18H₂O will decompose to lansfordite, MgCO₃·5H₂O, 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	мg0:CO ₂ :H ₂ O				
MgO	Periclase	MgO				
MgCO ₃	Magnesite	MgO.CO2				
Mg(OH) ₂	Brucite	мg0.H ₂ 0				
MgCO ₃ .2H ₂ O	Barringtonite	MgO.CO ₂ .2H ₂ O				
MgCO3.3H2O	Nesquehonite	Mg0.CO2.3H2O				
MgCO ₃ .5H ₂ O	Lansfordite	мg0.CO ₂ .5H ₂ O				
м ₈₂ со ₃ (он) ₂ .3н ₂ о	Artinite	2Mg0.C0 ₂ .4H ₂ 0				
Mg5(CO3)4(OH)2.4H2O	Hydromagnesite	5Mg0.4C0 ₂ .5H ₂ 0				
Mg5(CO3)4(OH)2.5H2O	Dypingite	5Mg0.4C0 ₂ .6H ₂ O				
Mg5(CO3)4(OH)2.6H2O	Giorgiosite*	5Mg0.4CO ₂ .7H ₂ O				
Mg5(CO3)4(OH)2.8H2O	Unnamed**	5Mg0.4CO ₂ .9H ₂ O				
Mg ₅ (CO ₃) ₄ (OH) ₂ .11H ₂ O	Protomagnesite***	5Mg0.4C0 ₂ .12H ₂ 0				

Recalculated from Friedel (1975) based on 40% MgO content.

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.

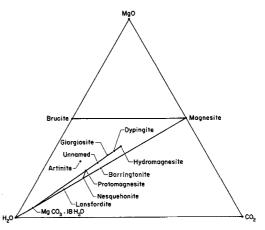


Fig. 4. The hydrated magnesium carbonate minerals in the MgO-CO₂-H₂O system.

^{**} Suzuki and Ito (1973).

 $^{^{\}star\star\star\star}$ Theoretical formula calculated from Davies and Bubela (1973)

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