

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 55

SEPTEMBER-OCTOBER

Nos. 9 and 10

DYPINGITE, A NEW HYDROUS BASIC CARBONATE OF MAGNESIUM, FROM NORWAY

GUNNAR RAADE, *Mineralogisk-Geologisk Museum,
Universitetet i Oslo, Norway.*

ABSTRACT

The new mineral dypingite was found in the Dypingdal serpentine-magnesite deposit, Snarum, South Norway, where it occurs as a thin cover on serpentine. It is of late secondary origin, deposited from cold, leaching solutions. Chemical analysis of 100 mg of handpicked material yielded the formula $5\text{MgO} \cdot 4\text{CO}_2 \cdot 6\text{H}_2\text{O}$ or $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. By heating at 150°C , dypingite is converted to hydromagnesite, $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$ or $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$.

Dypingite forms white globular aggregates, averaging 0.3 mm, with radiating structure. It has a pearly lustre and is both fluorescent (light blue) and phosphorescent (yellow-green). Refractive indices are $\alpha = 1.508$, $\beta = 1.510$, $\gamma = 1.516$ and the calculated specific gravity (Gladstone and Dale formula) is 2.15. The strongest reflections on X-ray powder diagrams are (in Å): 10.6 (100), 5.86 (90), 6.34 (60), 2.53 (50), 2.17 (50). Infrared absorption spectrum and DTA curve are very similar to those of hydromagnesite.

X-ray powder data are also given for giorgiosite, an imperfectly known basic magnesium carbonate from Santorin. Strongest reflections (Å): 3.40 (100), 3.29 (70), 2.92 (60), 4.44 (40), 3.97 (40), 2.46 (40).

INTRODUCTION

Serpentine specimens covered with a white surface alteration product, in appearance very much resembling hydromagnesite, were collected by the author in 1961 from the serpentine-magnesite deposit at Dypingdal, Snarum, South Norway. Optical spectrography showed large amounts of Mg, only very minor amounts of Fe, Ca, Al, Si (probably due to admixture of serpentine), and traces of Mn, Ti, B. Microchemical tests showed the presence of Mg and CO_2 .

The X-ray powder pattern was not identical with hydromagnesite or any other known magnesium carbonate mineral. A detailed examination showed the substance to be a new mineral, closely related to hydromagnesite. The name dypingite (pronounced 'dip-ing-ite') is for the locality. The mineral and name were approved in advance of publication by the Commission on New Minerals and Mineral Names, I.M.A. Type material is preserved at the Mineralogical-Geological Museum, University of Oslo, Norway.

OCCURRENCE

Small serpentine-magnesite bodies occur in the Precambrian rocks of Snarum west of the Oslo Region. These form steeply dipping, elongated lenses up to about 100 m long and 15 m wide. The wall rocks are anthophyllite-bearing quartzite, amphibolite, and breccia.

The Dypingdal deposit was formerly worked for magnesite and serpentine, today the rock is used for ornamental purposes. Several interesting minerals are found here, *e.g.* serpentine pseudomorphs after forsterite, hydrotalcite/manasseite, szaibelyite, hematite crystals, etc. (Jösang, 1960 and 1966).

PHYSICAL PROPERTIES

Dypingite forms white globular aggregates often showing radiating structure, occurring as a thin cover on serpentine or more rarely on hydrotalcite. Larger aggregates have a pearly luster. It is easily dissolved in cold dilute hydrochloric acid with effervescence.

The mineral shows a light blue fluorescence in ultraviolet light, both long-wave and short-wave, and a yellow-green phosphorescence, giving best response to middle-wave radiation.

Exact optical measurements were not possible due to the fine-grained nature of the mineral (average thickness of fibers $\frac{1}{2}\mu\text{m}$). It is colourless in transmitted light, locally pigmented. Radiating aggregates consist of fibers with \pm elongation. The fibers seem to be elongated parallel to the *Y* axis. $\alpha = 1.508$, $\beta = 1.510$, $\gamma = 1.516$.

It was not possible to determine hardness or specific gravity. From the rule of Gladstone and Dale the specific gravity is calculated to 2.15 (*k* values from Larsen and Berman, 1934).

X-RAY POWDER DATA

The powder data are given in Table 1. The mineral is finely crystalline and always gives somewhat diffuse reflections. The pattern slightly resembles that of hydromagnesite with regard to the inner lines, but is clearly different (compare Fig. 1). Attempts at indexing the pattern were not successful. The material is unfortunately not suited for single crystal work. Dypingite may be monoclinic (as is hydromagnesite).

INFRARED ABSORPTION ANALYSIS

The infrared spectra of dypingite and hydromagnesite are shown in Figure 2. The hydromagnesite curve is virtually identical with that published by Mumpton *et al.* (1965). The two spectra are remarkably similar, suggesting a close structural relationship between these minerals.

TABLE 1. X-RAY POWDER DATA FOR DYPINGITE

I/I_0 est.	d (Å) obs.	I/I_0 est.	d (Å) obs.	I/I_0 est.	d (Å) obs.
30	15.2	40	3.16	50	2.17
100	10.6	40	3.07	5	2.11
10	7.89	5	2.96	5	2.09
10	7.37	40	2.93	20	2.02
60	6.34	30	2.84	10	1.99
90	5.86	20	2.81	10	1.96
5	5.52	20	2.78	5	1.92
20	4.45	50	2.53	5	1.90
30	4.20	5	2.50	5	1.73
10	4.10	10	2.41	5	1.68
10	3.90	5	2.36	5	1.66
10	3.68	5	2.34	5	1.64
10	3.49	20	2.25	5	1.61
10	3.33	20	2.21	5	1.52

Guinier quadruple focusing camera, effective diameter 22.9 cm, Fe radiation, Mn filter
Internal standard: lead nitrate.

Absorption bands resulting from OH^- groups (3650 cm^{-1}) and water of crystallization (3510 and 3450 cm^{-1}) are identical for both, as are CO_3^{2-} stretching bands (1480 , 1420 , 1120 cm^{-1}) and CO_3^{2-} bending bands (880 , 850 , 800 cm^{-1}). Two small absorption bands at 1020 and 940 cm^{-1} seem to be characteristic for dypingite.

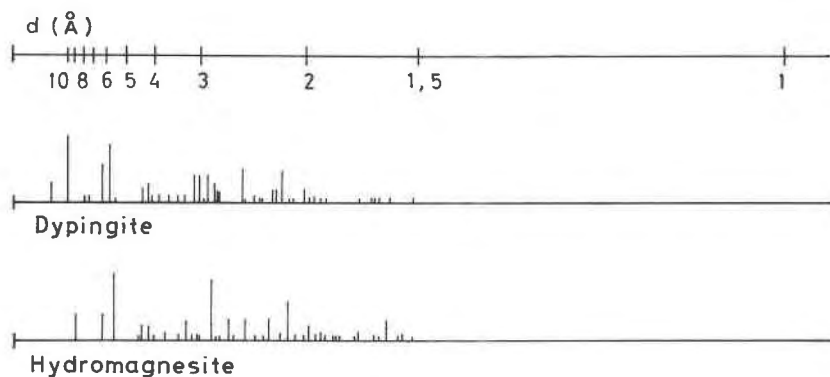


FIG. 1. Diagrammatic representation of dypingite and hydromagnesite powder patterns, constructed for 9 cm Debye-Scherrer films and Fe radiation. Powder data for hydromagnesite from Murdoch (1954). Vertical scale indicates the relative intensities of the reflections.

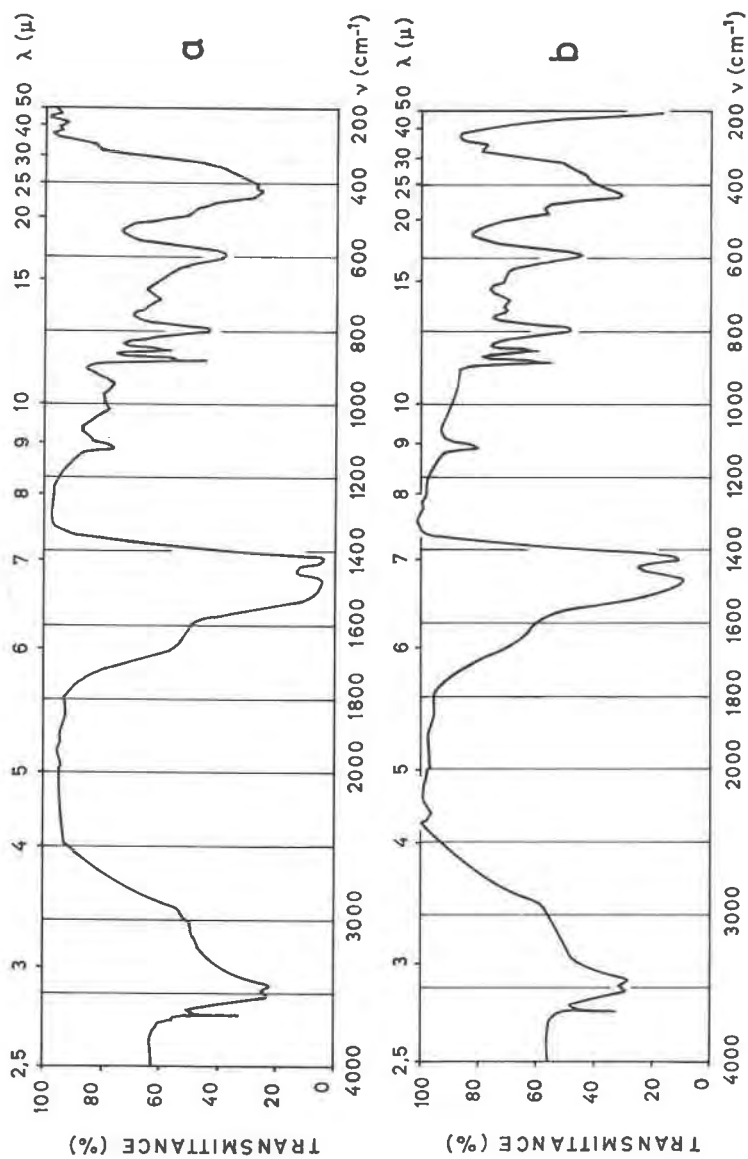


Fig. 2. Infrared absorption spectra of dypingite (a) and hydromagnesite (b). Disk technique, 1.2 mg dypingite per 300 mg CsI, 1.2 mg hydromagnesite per 300 mg KI.

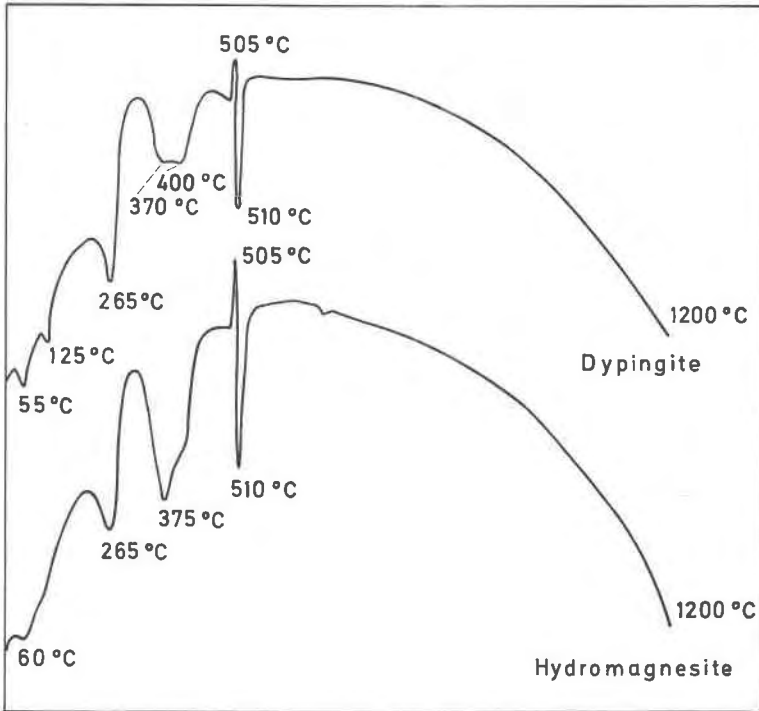


FIG. 3. DTA curves of dypingite and hydromagnesite. Rate of heating 10 deg/min; thermocouple Pt/Pt+13% Rh; reference junction 0°C; reference material Al_2O_3 .

DIFFERENTIAL THERMAL ANALYSIS

Samples of dypingite (5.6 mg) and hydromagnesite (6.3 mg) were heated in air at one atmosphere from room temperature to 1200°C (Fig. 3). Hydromagnesite shows four endothermic peaks: a very small one at 60°C (hygroscopic water) and three major ones at 265, 375, 510°C (water of crystallization, OH groups, CO_2). An exothermic peak at 505°C is prominent (crystallization of cubic MgO). It should be noted that this DTA curve, which was obtained with a very sensitive apparatus (Du Pont 900 thermal analyzer), is rather different from those published previously (Beck, 1950. Hsiu-Chang and Hsieh-Yen, 1965).

At temperatures above 125°C dypingite gives a DTA curve nearly identical with that of hydromagnesite. The exothermic peak and the major endothermic peaks are the same (except that the 375°C peak is more flattened). At lower temperatures, however, dypingite shows two pronounced endothermic peaks at 55 and 125°C.

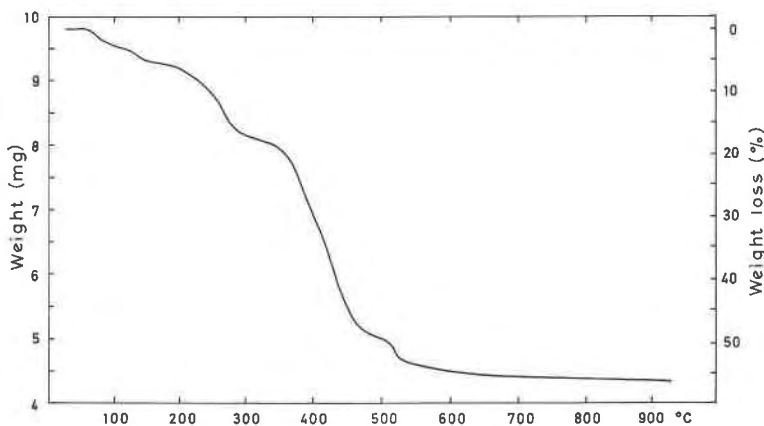


FIG. 4. Thermogravimetric curve of dypingite. Rate of heating 10 deg/min.

THERMOGRAVIMETRIC ANALYSIS

Heating of dypingite in air at one atmosphere produces the thermogravimetric curve shown in Figure 4. The total weight loss is 55.7 percent; 3.5 percent is lost below 125°C (small amounts of serpentine were present in the sample). The end product is MgO (periclase), as shown by X-ray examination.

TABLE 2. CHEMICAL ANALYSIS OF DYPINGITE

Analyst: John Marinenko

	(1)	(2)	(3)	(4)
MgO	38.3	39.4	4.60 5	41.5
CaO	<0.2			
Total iron as Fe ₂ O ₃	0.2			
CO ₂	36.3	37.3	4.00 4	36.2
Total H ₂ O	22.7	23.3	6.12 6	22.3
Acid insoluble	2.0			
	99.5	100.0		100.0
Loss on ignition	58.8			

- (1) Figures in weight percent. Magnesium was determined volumetrically with EDTA; calcium by atomic absorption; total iron by *o*-phenantroline spectrophotometric procedure; CO₂ and total H₂O gravimetrically in a semimicro train. Acid insoluble means insoluble in hot dilute HCl.
- (2) Recalculation to 100 percent, omitting minor constituents.
- (3) Mole proportions.
- (4) Theoretical composition for 5MgO·4CO₂·6H₂O.

CHEMICAL COMPOSITION

100 mg were carefully handpicked and purified for chemical analysis under the binocular microscope. Small amounts of serpentine and possibly hydrotalcite and magnesite were present as impurities in the final product. The result of the analysis is given in Table 2. The mole proportions are rather close to $5\text{MgO}\cdot 4\text{CO}_2\cdot 6\text{H}_2\text{O}$. Hydromagnesite has the composition $5\text{MgO}\cdot 4\text{CO}_2\cdot 5\text{H}_2\text{O}$. (Some authors still quote the formula as $4\text{MgO}\cdot 3\text{CO}_2\cdot 4\text{H}_2\text{O}$, although the evidence of Fenoglio (1936) in support of the 5:4:5 ratio was fairly conclusive).

According to this analysis, dypingite is a mineral very near to hydromagnesite in chemical composition, containing just one extra molecule of water. This is supported by all the data presented: 1) the DTA curves are nearly identical, but show that dypingite contains some loosely bound water which is lost at comparatively low temperatures; 2) thermogravimetric analysis indicates a weight loss of 3.5 percent below 125°C ; the theoretical value for loss of one mole of water from $5\text{MgO}\cdot 4\text{CO}_2\cdot 6\text{H}_2\text{O}$ is 3.7 percent; 3) the infrared spectra are nearly identical; 4) although the X-ray powder patterns are clearly different, they do show some similarities. The final proof is rendered by the fact that when dypingite is heated at 150°C for several hours, it is completely converted into hydromagnesite, as shown by X-ray analyses. The X-ray diagram of the heated dypingite is in every detail identical with hydromagnesite.

DISCUSSION

The compounds $5\text{MgO}\cdot 4\text{CO}_2\cdot 5\text{H}_2\text{O}$ and $5\text{MgO}\cdot 4\text{CO}_2\cdot 6\text{H}_2\text{O}$ were synthesized by Menzel and Brückner (1930). They report that the X-ray

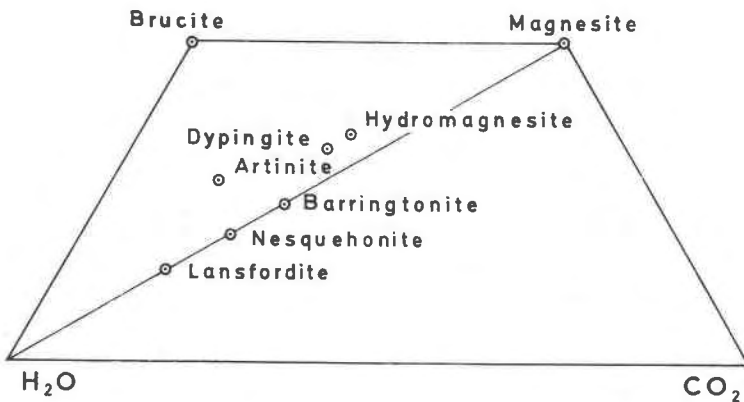


FIG. 5. Part of the system $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$. Mineral formulas are plotted in mole percent. Barringtonite, $\text{MgCO}_3\cdot 2\text{H}_2\text{O}$, was described by Nashar (1965).

TABLE 3. X-RAY POWDER DATA FOR GIORGIOSITE

I/I_0 est.	d (Å) obs.	I/I_0 est.	d (Å) obs.	I/I_0 est.	d (Å) obs.
10	7.81	100	3.40	20	2.26
10	6.82	70	3.29	20	2.19
30	5.80	60	2.92	20	2.11
30	5.35	10	2.70	20	1.98
40	4.44	30	2.62	10	1.94
30	4.14	30	2.56	10	1.88
40	3.97	10	2.49	20	1.84
10	3.72	40	2.46	10	1.81
20	3.51	10	2.29		

9 cm Debye-Scherrer camera, Fe radiation, Mn filter.

spectra of the two substances are identical. However, their pictures only show a few, broad lines. In fact, it is possible to tell them apart by considering spacing differences.

Dypingite is of recent formation in the Dypingdal deposit, since it occurs as a weathering product on material in the dumps. It is probably deposited from cold, leaching solutions during wintertime. (For a discussion of the stability of carbonates in the system $MgO - CO_2 - H_2O$, see Langmuir, 1965).

CONCLUSION

The following basic magnesium carbonates are now known in nature: artinite, $Mg_2[(OH)_2|CO_3] \cdot 3H_2O$; hydromagnesite, $Mg_5[OH](CO_3)_2 \cdot 4H_2O$; and dypingite, $Mg_5[OH](CO_3)_2 \cdot 5H_2O$ (Fig. 5).

Giorgiosite is a very poorly described basic magnesium carbonate from the Santorin islands (Lacroix, 1905). Caillère (1943) reported that the X-ray spectrum and DTA curve are not identical with hydromagnesite. This is supported by my own investigations on material from the original locality. Since the X-ray powder data were never published, they are given here in Table 3.

A number of basic magnesium carbonates are described in the chemical literature. As X-ray data are almost invariably lacking, most of these are extremely suspect. Giorgiosite is not identical with the compound $4MgO \cdot 3CO_2 \cdot 3H_2O$, described by Walter-Lévy (1937), and for which proper X-ray data are given.

ACKNOWLEDGEMENTS

I would like to thank people at the following institutions for valuable assistance: Mineralogisk-Geologisk Museum, Universitetet i Oslo (X-ray work, optical determinations); Institutt for Geologi, Universitetet i Oslo (optical spectrography, DTA); Kjemisk

Institut, Universitetet i Oslo (infrared absorption analysis); Mineralogisches Institut, Universität Kiel (thermogravimetric analysis). Special thanks are extended to J. Marinenko of U. S. Geological Survey, Washington, D. C., for the chemical analysis. A sample of giorgiosite was received from S. Caillère of Muséum National d'Histoire Naturelle, Paris. Professors K. S. Heier and H. Neumann kindly read the manuscript. The English text was corrected by B. Jensen.

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Manuscript received, March 3, 1970; accepted for publication, June 2, 1970.