

# A basic magnesium carbonate, a possible dimorph of artinite, from Unst, Shetland

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## Abstract

Efflorescent outgrowths and compact vein-like material from brucite-rich specimens is a basic magnesium carbonate and possibly a dimorph of artinite. X-ray, infrared, chemical and thermal data reveal the material to be different from known natural basic magnesium carbonates.

## Introduction

A SUITE of brucite specimens from Swinna Ness, Unst, Shetland, registered between 1871 and 1894, possesses efflorescent outgrowths which have developed during museum storage. The efflorescence occurs as free-standing, individual outgrowths, mealy regions, or as a coating. It is possible, however, that in one specimen (RMS G 1871.3.1) the same material, which forms coherent vein-like areas several millimetres thick may represent an original phase in the sheared sample. Furthermore, the coherent variant is intimately associated with traces of brucite whereas superficial material tends to be brucite-free. The coherent areas are physically unlike efflorescences developed directly from pyrite for they are too compact, vein-like and seem to lack a primary source.

Scanning electron microscopy reveals both types have ragged, scaly surfaces totally devoid of crystal faces or edges. The general appearance is akin to a series of thin layers deposited consecutively over a 'badland' topography, then solution modified.

## Physical and optical properties

Apart from the generalities noted above, detailed physical and optical properties proved difficult to ascertain. The material is soft, porous, and snow white on fresh surfaces. Suspension in diluted bromoform yielded a density of  $1.67 \text{ gm/cm}^3$  which is considerably at variance with the calculated value of  $1.94 \text{ gm/cm}^3$  derived from the ideal formula. Optically it appears similar to exceptionally fine-grained 'cloudy-chalk'; consequently, only a mean R.I. of 1.495 was obtainable by immersion. This value is somewhat lower than the  $\beta$  index,

1.534, of artinite (see later) reported by Palache *et al.* (1951) although using the theoretical artinite composition and calculated density, the mean calculated R.I. is 1.492 using the Gladstone-Dale constants of Mandarino (1981). All specimens tested were readily soluble in dilute HCl acid with strong effervescence.

## X-ray powder data

The powder data could not be matched with that of known natural basic magnesium carbonates. A slight resemblance to the yoshikawaite pattern (Suzuki and Ito, 1973; Hey, 1980) was noted in respect of a high  $d$  spacing line being present at  $11.6 \text{ \AA}$  in the Unst phase. However, unlike yoshikawaite, lines higher than  $d$   $11.6 \text{ \AA}$  have not been recorded by powder photography. A continuous gradation exists from the sharpest pattern (Table 1) to the poorest, broad-line pattern (Table 2) produced by material derived from a single specimen (RMS G 1871.3.1). Very slight grinding virtually destroys the structure; consequently, most powder photographs were taken using unground samples. The coherent type invariably contains traces of brucite which are readily detectable on the X-ray films by the presence of streaky spots. It must be emphasised, at this stage, this is physically admixed brucite as opposed to brucite generated during thermal studies (see chemical interpretation).

The best patterns obtained resemble that of the synthetic compound  $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (PDF 7-410). Powder data in Table 1 are tentatively indexed by analogy with that from the above using  $a = 11.45$ ,  $b = 24.17$ ,  $c = 7.54 \text{ \AA}$  and  $\beta$   $105.21^\circ$ ; cell volume =  $2016 \text{ \AA}^3$ . Both infrared and electron probe microanalysis show that the  $\text{SO}_4^{2-}$  anion

TABLE 1. X-ray powder diffraction data for a basic magnesium carbonate from Unst, Scotland.

d meas.	I est.	hkl	d calc.
11.60	100	020	12.00
7.30	20	001	7.28
6.40	90	130	6.51
5.89	20	121	6.04
4.92	30	121	4.97
4.81	30	050	4.83
4.64	20	041	4.65
4.21	10	231	4.30
3.97	80	151	3.97
3.81	10	{211	{3.88
		{160	{3.78
		{002	{3.64
		{310	{3.64
3.64	10	{250	{3.64
3.51	20	231	3.53
3.40	10	132	3.41
3.34	10	{330	{3.35
		{222	{3.35
3.22	10	{260	{3.25
		{161	{3.24
		{102	{3.21
		{171	{3.09
3.06	5	{251	{3.05
		{311	{2.96
2.95	60	{351	{2.94
		{360	{2.719
2.718	30	{212	{2.712
		{152	{2.678
2.672	20	{341	{2.677
		{281	{2.599
2.598	30	{271	{2.595
		{412	{2.532
2.528	40	{371	{2.525
2.471	20		
2.406	20		
2.350	5		
2.290	5		
2.235	10		
2.180	5		
2.111	10		
2.068	10		
2.029	5		
1.969	10		
1.854	10		
1.707	10		
1.633	5		
1.524	10		
1.362	5		

Cu K $\alpha$ , Ni filter, 114.6mm camera. Above indexed with :  
a 11.45, b 24.17, c 7.54 $\text{\AA}$  and  $\beta$  105.21 $^\circ$ . Cell volume = 2016 $\text{\AA}^3$

and sulphur, respectively, are virtually absent. Additionally, the data do not fit those for the compound  $4\text{MgO} \cdot 3\text{CO}_2 \cdot 3\text{H}_2\text{O}$  reported by Walter-Lévy (1937).

### Infrared studies

The spectrum obtained from the Unst sample (Fig. 1) indicates a hydrated and/or basic carbonate although unlike that of hydromagnesite. Yoshikawaite and dypingite are higher hydrates of hydromagnesite and all three yield virtually indistinguishable spectra. Nesquehonite and artinite generate spectra that can be distinguished from each other and both are dissimilar from that of hydromagnesite (White, 1971). The Unst material

TABLE 2. Powder pattern of poorly crystallised, broad-line material.

d meas, approx	I est. (very approx)
13.5	100
6.6	60
4.9	50
4.0	60
3.5	20
3.0	40
2.74	20
2.62	30
2.29	10
2.11	10
2.00	10
1.90	20
1.81	10
1.74	10
1.38	5

bears a close family resemblance to that of artinite, with absorptions at 1590, 1530, 1440, 1025, 835, 660 and  $440\text{ cm}^{-1}$ .

### Chemical and thermal studies

Preparation of grain mounts for EPMA proved extremely difficult and of the few grains analysed Mg, Ca and Fe are the only significant elements detected, apart from 0.1% S. MgO values range from 33.8 to 37.1%, FeO from 0.1 to 12.8% and CaO from 0.1 to 4.7%. The most satisfactory analysis yielded MgO 34.8%, CaO 4.7% and FeO 0.7%.

In view of the above difficulties approximately 10 mg was hand picked, brucite flakes removed as far as possible, and 5 mg then used for X-ray fluorescence analysis (EDS), 1.8 and 1.0 mg utilised for EGA and TGA respectively. X-ray fluorescence results are in general agreement with EPMA work and are as follows: MgO 31.9%, SiO $_2$  2.6%, CaO 2.0%, FeO 0.9% (total iron) and SO $_3$  0.7% (TGA loss 64.6%) total 102.7%.

The TGA and EGA curves (Figs. 2 and 3) demonstrate that up to about 260  $^\circ\text{C}$  water of crystallisation is lost in two stages, the bulk being

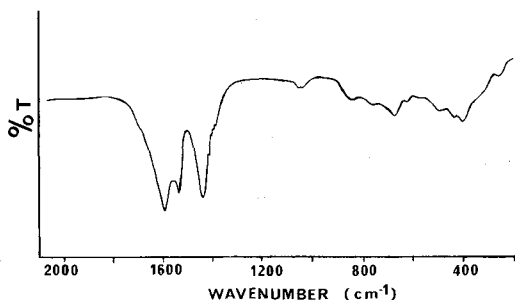


FIG. 1. Infrared absorption spectrum for basic magnesium carbonate (KBr disc).

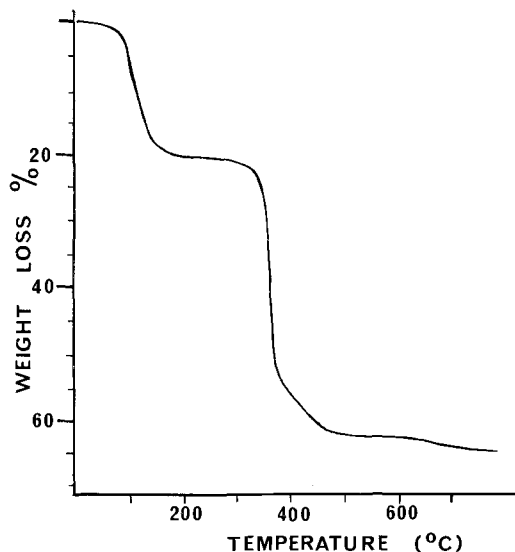


FIG. 2. Thermogravimetric analysis curve for basic magnesium carbonate heated at 15 °C/min in N<sub>2</sub> (25 cm<sup>3</sup>/min).

expelled between 30 and 145 °C, and thus representing 3H<sub>2</sub>O. This loss represented 19.7% of the sample weight. In artinite the corresponding loss occurs between 250 and 300 °C (Muchi and Matsumoto, 1979). A large loss (35.4%) between 260 and 360 °C for the Unst basic magnesium carbonate is due to simultaneous evolution of CO<sub>2</sub> and OH. A marked contrast in the thermal behaviour of artinite is apparent for, in the latter, CO<sub>2</sub> evolution occurs during the interval 450 to 550 °C (Muchi

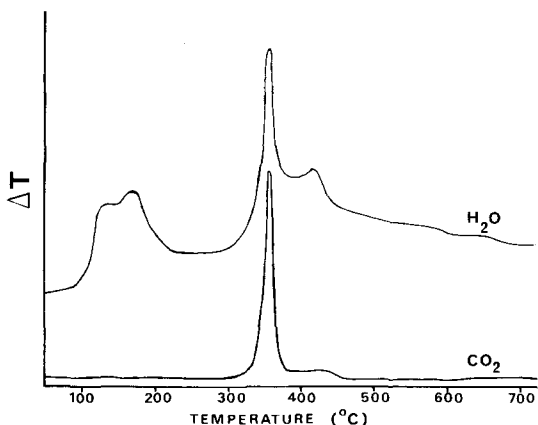


FIG. 3. Evolved gas analysis curves from basic magnesium carbonate heated at 15 °C/min in N<sub>2</sub> (300 cm<sup>3</sup>/min).

and Matsumoto, op. cit.). From EGA CO<sub>2</sub> was ascertained at 21% in the Unst material. Beyond 360 °C, and up to approximately 450 °C, a further 7.5% loss is attributed to 24 wt. % brucite and a final 2% loss due to serpentine impurity. Static heating of a very small sample, followed by an X-ray photograph of the product, revealed that at 350 °C for 3 minutes, periclase and brucite (smooth lines on powder pattern) were produced. Expulsion of the water of crystallisation does not appear to destroy the structure, unlike artinite, although with simultaneous CO<sub>2</sub> and OH evolution the structure transforms to periclase (from the magnesium carbonate component) and brucite. Muchi and Matsumoto (op. cit.) reported that artinite broke down to an amorphous magnesium carbonate and brucite. The 24 wt. % brucite determined from TGA is generated from the thermal decomposition of the Unst material and not attributed to physically admixed brucite impurity.

### Interpretation

On a 1 mg sample, and assuming errors of ± 10%, 19% CO<sub>2</sub>, 14.4% OH<sub>2</sub> and 21.7% H<sub>2</sub>O yield molecular ratios of 1:1.86:2.79 respectively, thus requiring Mg<sub>2</sub> for charge balance. Of the natural basic magnesium carbonates only artinite and pokrovskite (Ivanov *et al.*, 1984) possess CO<sub>3</sub>:OH in a 1:2 ratio, and both X-ray powder patterns are quite distinct from that in Table 1. As sulphur is demonstrably very low, and assuming 2(OH) ⇌ (SO<sub>4</sub>) in the compound Mg<sub>4</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O, it could, conceivably, explain why the Unst material is 'isostructural'. Additionally, with the above substitution 'Mg<sub>4</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>·6H<sub>2</sub>O' equals artinite which theoretically contains 41.0% MgO, 22.38% CO<sub>3</sub>, 9.16% OH as water and 27.46% H<sub>2</sub>O. From the results the best chemical balance suggests the 10 mg analysed material contained approximately 90% basic magnesium carbonate, 5% brucite and 6% serpentine.

In conclusion, the Unst basic magnesium carbonate is possibly a dimorph of artinite and isostructural with the synthetic compound Mg<sub>4</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O. It possesses a different XRD pattern, thermal behaviour and IR spectrum to most natural basic magnesium carbonates. Suzuki and Ito (1973) suggest that yoshikawaite resulted from evaporation of groundwaters percolating through serpentinite, and not brucite or serpentine weathering. A similar origin for the Unst phase seems highly probable with the 'drying out' occurring during storage. The coherent material may well represent a phase formed in the field due to a copious supply acting as a cement in small shear zones.

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