

The vibrational spectra of BaMg(CO₃)₂ (norsethite)

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Abstract

The FTIR spectra of synthetic BaMg(CO₃)₂ (norsethite) are measured at ambient temperature and atmospheric pressure, and the influence of formation conditions on the FTIR spectra is investigated. The results are compared with those for natural norsethite from Långban (Sweden) and Rosh Pinah (Namibia). The Raman spectrum of synthetic norsethite is reported, too. A number of first-order internal modes of the carbonate ion group (ν_1 , ν_2 , ν_3 , ν_4) are found to be infrared and Raman active. Additionally, the ($\nu_1+\nu_3$) and ($\nu_1+\nu_4$) combination modes and the ($2*\nu_2$) overtone are observed in the FTIR and Raman spectrum, respectively. The carbon isotopic-shift coefficient for ν_2 due to the substitution of ¹²C by ¹³C ($\nu_2(^{13}\text{CO}_3^{2-})/\nu_2(^{12}\text{CO}_3^{2-}) = 0.971 \pm 0.002$), observed by FTIR spectroscopy, agrees with the theoretical value of 0.969.

KEYWORDS: norsethite, BaMg(CO₃)₂, synthesis, formation conditions, phase diagram, carbon isotopes, Fourier transform infrared spectroscopy, Raman spectroscopy.

Introduction

THE mineral norsethite (BaMg(CO₃)₂) an ordered rhombohedral double carbonate was originally described from the sedimentary Green River formation, Wyoming (Mrose *et al.*, 1961). Later on it was also found in hydrothermal and metamorphic environments (Åberg and Charalampides, 1988; Steyn and Watson, 1967; Sundius and Blix; 1965)

and even in carbonatites (Platt and Woolley, 1990). In agreement with its apparently wide range of natural formation conditions, successful synthesis of BaMg(CO₃)₂ has been described between 20° and 90°C from aqueous solutions (Lippmann, 1967, 1968, 1973; Hood *et al.*, 1974; Morrow and Ricketts, 1986; Böttcher, 1994), by grinding (Longo and Voight, 1989), and at 500°C and 15 kbars by solid-state reaction (Chang, 1964). Norsethite is of some interest because of its analogy to the mineral dolomite (CaMg(CO₃)₂) whose widespread occurrence is still not fully understood (Lippmann, 1967, 1973; Morrow and Ricketts, 1986; Böttcher, 1994),

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Mineralogical Magazine, April 1997, Vol. 61, pp. 249-256

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and its indication of low-sulphate depositional environments (Finlow-Bates, 1987).

According to single crystal X-ray diffraction measurements, norsethite belongs to space group $R\bar{3}m$ (Effenberger and Zemmann, 1985) with an ordering of the two cations on alternating layers. The structure of $BaMg(CO_3)_2$ was also investigated by infrared and Raman spectroscopy in a fundamental study by Scheetz and White (1977). The Raman spectrum reported in this paper, however, was broad and the frequency shifts were weak, ill defined and some internal modes were even not observed. The authors attributed these difficulties to their procedure for the synthesis of $BaMg(CO_3)_2$ from highly supersaturated aqueous solutions at low temperatures and they supposed that the structure of the synthesized carbonate possibly had not equilibrated into a well-ordered form.

In the present study, the influence of formation conditions on the FTIR spectra of synthetic $BaMg(CO_3)_2$ is investigated, and the results are compared with those for natural norsethite. The Raman spectrum of synthetic norsethite is reported, too.

Materials and experimental methods

Natural samples. The natural norsethite samples 830005 and M847 are from Långban, Sweden (Åberg and Charalampides, 1988; Sundius and Blix; 1965) and from Rosh Pinah, Namibia (Steyn and Watson, 1967), respectively. Besides norsethite, sample 830005 also contained dolomite, braunite, and minor ericssonite and barytocalcite. In the 106–210 μm grain size fraction, norsethite was separated from the other minerals by heavy-liquids and handpicking until no foreign XRD peaks with intensities above 1% were detected. The chemical composition of norsethite 830005 was measured by X-ray fluorescence spectroscopy (Philips PW 2400 X-ray fluorescence spectrometer) using the glass pellet technique. The results are presented in Table 1.

In agreement with the description of the occurrence of norsethite at Rosh Pinah (Steyn and Watson, 1967), sample M847 was a mixture of norsethite and low-magnesian calcite. According to the relations between infrared absorption band positions and chemical composition in the system $CaCO_3$ – $MgCO_3$, established by Böttcher and Gehlken (1995, 1996), the magnesian calcite contains about 2.5 mol.% $MgCO_3$ in solid-solution. Very small amounts of magnesite were also indicated by the XRD patterns. Norsethite was separated from the other carbonates by heavy-liquid.

Synthetic carbonates. Six different types of experiments were carried out for the synthesis of norsethite.

TABLE 1. Chemical composition of natural norsethite from Långban (sample 830005). CO_2 was assumed to balance the cations

| Sample 830005 | |
|-------------------|------|
| BaO (wt.%) | 52.3 |
| MgO (wt.%) | 13.2 |
| MnO (wt.%) | 2.3 |
| PbO (wt.%) | 0.73 |
| CaO (wt.%) | 0.57 |
| FeO (wt.%) | 0.11 |
| Zn^{2+} (mg/kg) | 135 |
| Sr^{2+} (mg/kg) | 80 |
| Ni^{2+} (mg/kg) | 25 |
| CO_2 (wt.%) | 31.1 |

N-41 was synthesized following the procedure of Hood *et al.* (1974) with slight modifications: a $BaMg(CO_3)_2$ gel was precipitated at 20°C by the mixing of equal volumes of a 0.5 M Na_2CO_3 solution with a solution 0.06 M in $BaCl_2$ and 0.10 M in $MgCl_2$. Following rigorous stirring by a magnetic stirrer for a few minutes, the gel was altered in the unstirred mother solution at 20°C (thermoconstant room) for 744 h in a sealed polyethylene bottle ($V = 500 cm^3$). The same experimental set-up was used for the synthesis of N-51. However, the metal-bearing solution was 0.08 M in $BaCl_2$, 0.08 M in $MgCl_2$ and 0.017 M in $CaCl_2$. This procedure is similar to the one reported by Hood and Steidl (1973), for benstonite synthesis, which had been used by Scheetz and White (1977) for the synthesis of norsethite.

N-9 was synthesized by the reaction of 500 mg synthetic $BaCO_3$ with 412 mg artificial nesquehonite ($MgCO_3 \cdot 3H_2O$) in a glass bottle ($V = 1100 cm^3$) completely filled with a 0.02 M $NaHCO_3$ solution. Run duration at 20°C (thermoconstant room) was 1690 h. For preparation of N-2, the amount of nesquehonite and the concentration of the $NaHCO_3$ solution were increased to 500 mg and 0.175 M, respectively, and the reaction lasted for 1731 h. N-18 was synthesized by the reaction of 50 mg synthetic $BaCO_3$ with 41 mg artificial nesquehonite in a sealed 316 ss vessel ($V = 40 cm^3$) filled with 0.02 M $NaHCO_3$ solution. Run duration at 90°C (Heräus oven) with continuous rotation of the reaction vessels at 38 rds/min was 124 h.

Sample LON-1 has been synthesized by Longo and Voight (1989) by grinding a mixture of Na_2CO_3 , and the chloridic salts of barium and magnesium in a Step 8000 ball mill.

Synthetic nesquehonite ($MgCO_3 \cdot 3H_2O$) was prepared at 20°C by the slow degassing of CO_2

from an aqueous solution 1 M in $\text{Mg}(\text{NO}_3)_2$ and 0.5 M in NaHCO_3 . The first precipitate occurred after about 12 h as radial-fibrous spherules at the bottom of the vessel. After 140 h the solid was washed and dried for 48 h at room temperature, and, prior to experimental use, was carefully ground in an agate mortar. Synthetic magnesite (MgCO_3) has previously been prepared at 250°C (Böttcher *et al.*, 1992), and synthetic witherite (BaCO_3) is a reagent grade chemical (Merck). All chemicals were of reagent grade quality.

Methods

All solids were characterized by X-ray powder diffraction (Philips or Siemens X-ray goniometer with Ni-filtered $\text{Cu-K}\alpha$ radiation).

For the determination of their ^{13}C contents, the synthetic and natural norsethite samples (except for M847, LON-1 and MgCO_3 ; see below) were prepared for isotope analysis by the reaction with 100% phosphoric acid, to which a small surplus of P_2O_5 had been added (McCrea, 1950). The measurements were carried out on a Finnigan MAT 251 triple collector mass spectrometer at the Geochemical Institute of Göttingen University. The data were corrected for the usual isobaric interferences following the procedure of Craig (1957).

Carbon isotope compositions of samples M847, LON-1 and MgCO_3 were determined by combustion isotope-ratio-monitoring mass spectrometry (C-irmMS). About 0.7 mg per sample were combusted in an elemental analyser (Carlo Erba EA 1108) connected to a Finnigan MAT 252 mass spectrometer through a split interface (Finnigan MAT Conflo II). Pure Sn cups (99.9%; Lüdi) were used as sample containers which had been carefully cleaned in CH_2Cl_2 , acetone and deionised H_2O and dried at 110°C. The isotope measurements were carried out on the liberated CO_2 in a continuous stream of He (grade 5.0) versus an in-house CO_2 gas standard. Data evaluation has been carried out with the Finnigan MAT Isodat[®] 5.2 software taking into account the interferences by ^{17}O (Santrock *et al.*, 1985), and blanc correction for the carbon content of the Sn cups. Synthetic carbonates which had previously been measured following conventional preparation by the reaction with phosphoric acid were used as external standards. Isotope ratios are given in the δ -notation with respect to the PDB standard. The precision of the isotope measurements including sample preparation is better than ± 0.2 ‰.

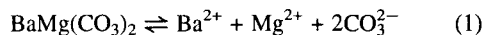
The FTIR spectra were measured at ambient temperature and atmospheric pressure with a Mattson 3000 type FTIR spectrometer between 4000 and 400 cm^{-1} using specimens with grain

sizes less than 2 μm , embedded in KBr. 2.5, 5 and 10 mg samples were mixed in an agate mortar with 1 g KBr. Pellets were obtained under vacuum at a pressure of 7.5 tons/ cm^2 . The precision of the measured wave-numbers is ± 1 cm^{-1} for ν_1 , ν_2 , ν_4 , $(\nu_1+\nu_3)$ and $(\nu_1+\nu_4)$, and about ± 3 cm^{-1} for ν_3 . To control the stability of norsethite under the high-pressure conditions during pellet preparation and to rule out a partial reaction between KBr and the carbonate, the FTIR spectrum of sample 830005 was additionally measured from nujol mull. No difference was observed between the norsethite infrared absorption band positions using the two different techniques.

Raman spectra were measured at ambient temperature and atmospheric pressure with a Ramanor U-1000 multichannel micro-Raman spectrometer (Jobin Yvon Instruments SA) as described by Reutel (1991). The sample was excited using a 514.5 nm laser line from a Coherent Innova-90 5 W Ar^+ ion laser, with an energy of 1 W.

Results and discussion

The experimental formation of $\text{BaMg}(\text{CO}_3)_2$. Figure 1 shows a Lippmann phase diagram (Lippmann, 1980) for the system BaCO_3 – MgCO_3 – H_2O at 25°C and 1 bar total pressure. Unfortunately, the solubility product of $\text{BaMg}(\text{CO}_3)_2$ has not hitherto been determined. Therefore, a tentative value for the solubility product constant at 25°C is calculated from the Gibbs free energies of formation (ΔG_f°) of the aqueous ions (Wagman *et al.*, 1982) and a hypothetical value for the solid which is estimated according to the method described by La Iglesia and Félix (1994). The thermodynamic properties of the basic polyhedral units (BaO , MgO , CO_2) were taken from La Iglesia and Félix (1994), using for barium the oxygen coordination number 9. This approach yields for $\Delta G_f^\circ(\text{BaMg}(\text{CO}_3)_2)$ a value of -2166.6 kJ/mol. For the solubility product according to



a pK value of 16.81 is obtained for 25°C and 1 bar total pressure.

In the Lippmann phase diagram, the solutus curve for norsethite is positioned below the solutus for witherite for aqueous solutions with $X_{\text{Mg,aq}}$ values above 0.68 in agreement with evidence from synthesis experiments (see above and Lippmann, 1973). An excess of dissolved magnesium above barium, derived from the dissolution of nesquehonite and witherite in the closed system, seems to be essential for the norsethite reaction running until completion. If magnesite formation is taken into account, norsethite is only stable between $X_{\text{Mg,aq}}$ values of 0.68 and 0.83.

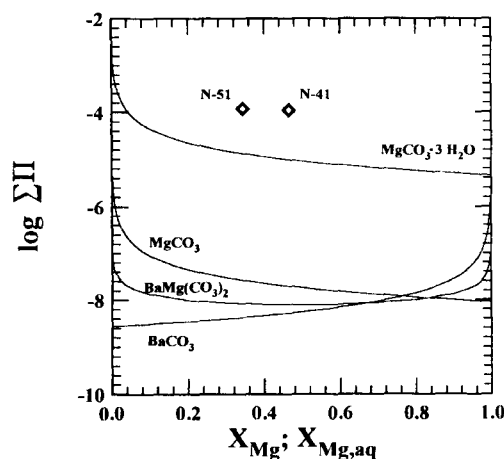


FIG. 1. Lippmann phase diagram for the system at 25°C and 1 bar total pressure. The soluti were calculated taking the respective pK values of witherite, magnesite, nesquehonite and $\text{BaMg}(\text{CO}_3)_2$ to be 8.56 (Busenberg and Plummer, 1986), 8.05, 5.25 (Kharaka *et al.*, 1988) and 16.81 (this study). X_{Mg} and $X_{\text{Mg,aq}}$ are the solids mole fraction and the aqueous activity fraction, respectively, and $\Sigma\Pi$ is the total activity product. Saturation calculations on the initial run solutions were carried out for 20°C with Solmineq.88 PC/Shell (Kharaka *et al.*, 1988; Wiwchar *et al.*, 1988) based on an ion association model and using the mixing option. The phase diagrams at 20°C and 90°C are expected to show the same general relations.

The synthesis procedures from aqueous solutions were designed to prepare norsethite with different precipitation rates.

The initial solutions of experiments N-41 and N-51 were highly supersaturated with respect to witherite, norsethite, hydromagnesite, magnesite and nesquehonite (Fig. 1), and run N-51 also with respect to calcite, aragonite, dolomite and huntite. The initial SI values ($\text{SI} = \log \text{IAP/K}$) with respect to witherite and norsethite, for instance, were 4.4 and 8.3 for run N-41, and high precipitation rates of the carbonates were observed. The initial carbonate gel was allowed to alter in contact with the mother solution. Short-time experiments of type N-41 demonstrated, that the first norsethite crystals, detectable by XRD and FTIR spectroscopy, were formed within a few hours. Upon alteration the crystallinity of the precipitate increased, and the final solids of runs N-41 and N-51 consisted of $\text{BaMg}(\text{CO}_3)_2$ accompanied by minor BaCO_3 and traces of hydrated (hydroxy) magnesium carbonate. The amount of coexisting foreign phases was higher in run N-51 compared with N-41.

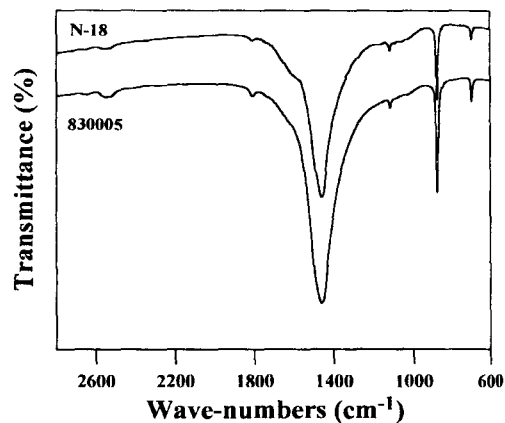
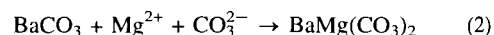


FIG. 2. FTIR spectra of synthetic $\text{BaMg}(\text{CO}_3)_2$ (N-18) and natural norsethite (830005) (2.5 mg of sample per 1000 mg KBr).

For the BaCO_3 transformation experiments at 20°C it was found that synthetic nesquehonite is initially completely dissolved, and the rate of the following formation of norsethite is limited by the subsequent slow dissolution of BaCO_3 according to the overall reaction (Lippmann, 1973)



Therefore, in experiments N-2, N-9 and N-18 the solutus curve of witherite (Fig.1) should not have been exceeded, and formation of synthetic norsethite should have proceeded from an only slightly supersaturated solution.

The following sequence of experiments with increasing precipitation rate is estimated: $\text{N-9} < \text{N-2} < \text{N-18} \ll \text{N-41} < \text{N-51}$.

The vibrational spectra. The FTIR spectra of synthetic $\text{BaMg}(\text{CO}_3)_2$ (N-18) and natural norsethite (830005), and selected parts of the Raman spectrum of sample N-18 are presented in Figs. 2 and 3 respectively. The wave-numbers of infrared absorption bands and Raman shifts are compiled in Tables 2 and 3. The assignment of infrared and Raman modes follows Bischoff *et al.* (1985), Hexter (1958), Sterzel and Chorinsky (1968), Sterzel and Schnee (1970) and White (1974).

The fundamental ν_1 , ν_2 , ν_3 and ν_4 modes are found to be active in the FTIR spectrum of $\text{BaMg}(\text{CO}_3)_2$ (Table 2). They arise from the symmetric stretching, the out-of-plane bending, the asymmetric stretching and the in-plane bending mode of the carbonate ion group, respectively (White, 1974; McMillan and Hofmeister, 1988). Respective average wave-numbers of 1117, 880, 1467 and

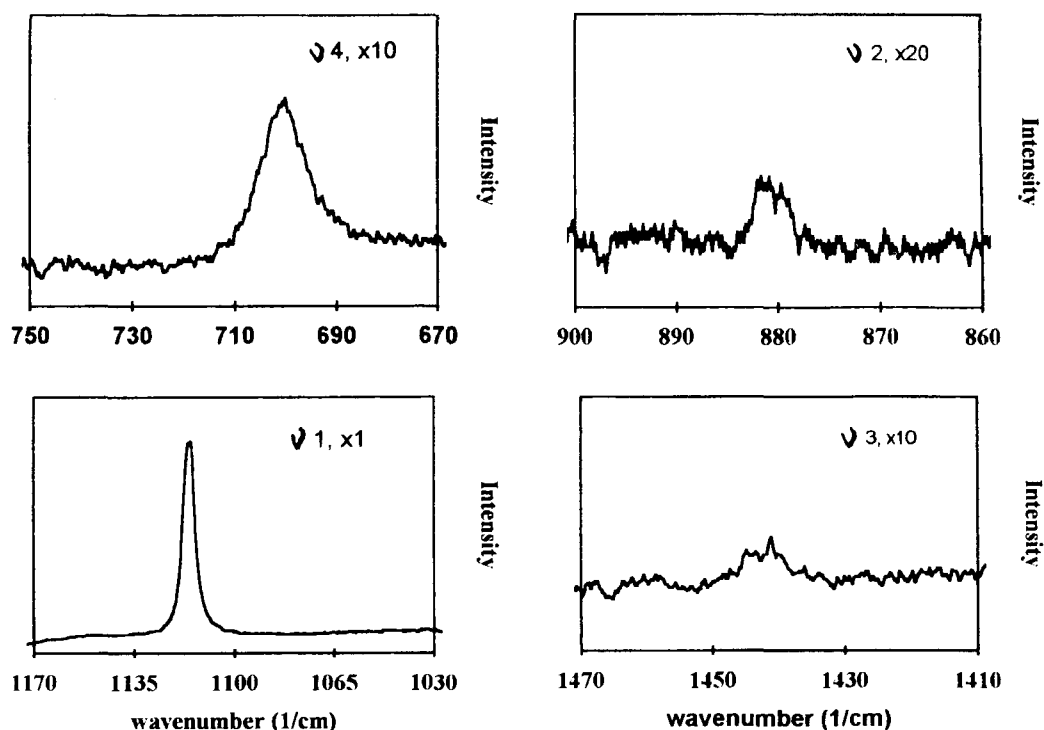


Fig. 3. Selected parts of the Raman spectrum of synthetic norsethite, $\text{BaMg}(\text{CO}_3)_2$ (N-18). Scaling factors are given relative to the ν_1 mode.

702 cm^{-1} are observed. Additionally, the $(\nu_1+\nu_3)$ and $(\nu_1+\nu_4)$ combination modes occur at 2554 and 1809 cm^{-1} . Very weak and broad bands are observed

near 2533 and 2652 cm^{-1} which have probably to be attributed to complex combinations of internal mode frequencies with a lattice mode. No lattice modes are

TABLE 2. FTIR spectroscopic data and isotopic compositions of natural and synthetic norsethites ($\text{BaMg}(\text{CO}_3)_2$)

| Mode | N-18 | N-9 | N-2 | N-41 | N-51 | LON-1 | M847 | 830005 | BaCO_3 " | MgCO_3 * |
|------------------------|------------|-------|-------|------------------|------------------|-------|-------|--------|-------------------|-------------------|
| $(\nu_1+\nu_3)$ | 2558 (w) | 2556 | 2556 | 2556 | 2547 | 2556 | 2552 | 2552 | 2452, 2474 | 2537 |
| $(\nu_1+\nu_4)$ | 1811 (vw) | 1811 | 1811 | 1809 | 1803 | 1809 | 1806 | 1809 | 1751 | 1831 |
| ν_3 | 1461 (s,b) | 1466 | 1479 | 1473 | 1461 | 1479 | 1453 | 1461 | 1447 | 1448 |
| ν_1 | 1118 (m) | 1117 | 1116 | 1117 | 1115 | 1117 | 1116 | 1116 | 1060 | 1108 |
| $\nu_2(^{12}\text{C})$ | 879.9 (s) | 880.0 | 879.8 | 879.6 | 879.4 | 880.7 | 879.6 | 879.4 | 857.0 | 885.6 |
| $\nu_2(^{13}\text{C})$ | 854.0 (w) | 852.6 | 852.6 | 854.9 | n.d. | 858.4 | 853.0 | 853.0 | 841.2 | 855.0 |
| ν_4 | 701.9 (m) | 702.0 | 702.1 | 702.0 | 702.1 | 701.4 | 702.1 | 701.4 | 693.5 | 748.1 |
| lattice | n.d. | n.d. | n.d. | 360 [#] | 360 [#] | n.d. | n.d. | n.d. | n.d. | n.d. |
| $\delta^{13}\text{C}$ | -4.4 | -5.1 | -5.4 | -4.2 | n.d. | -7.0 | -8.4 | +0.4 | -7.6 | -17.4 |

s: strong, m: medium, w: weak, sh: shoulder, b: broad, v: very

Units of infrared-frequencies and δ -values are (cm^{-1}) and (‰), respectively, n.d.: not determined

[#] Measured with a conventional grating instrument (Perkin Elmer 683)

* Böttcher and Gehlken (1996)

" Böttcher *et al.* (1996a).

TABLE 3. Raman frequency shifts of synthetic norsethite ($\text{BaMg}(\text{CO}_3)_2$) N-18, witherite (BaCO_3 ; Merck p.a. chemical) and magnesite (MgCO_3)

| | N-18 | BaCO_3 | MgCO_3^* |
|------------------------------------|-------------|-----------------|-------------------|
| $2 \cdot \nu_2 (\text{CO}_3^{2-})$ | 1757 (w) | 1769 | 1762 |
| $\nu_3 (\text{CO}_3^{2-})$ | 1443 (w, b) | 1421 | 1444 |
| $\nu_1 (\text{CO}_3^{2-})$ | 1118 (s) | 1060 | 1093 |
| $\nu_2 (\text{CO}_3^{2-})$ | 882 (vw) | 844 | n.d. |
| $\nu_4 (\text{CO}_3^{2-})$ | 701 (w) | 690 | 738 |
| L (CO_3^{2-}) | 294 (w, b) | n.d. | 329 |

s: strong, m: medium, w: weak, b: broad, v: very
Units of Raman frequency shifts are (cm^{-1})

* Bischoff *et al.* (1985).

observed in the investigated mid-infrared frequency range ($4000\text{--}400 \text{ cm}^{-1}$). According to measurements with a conventional grating instrument, a lattice mode was found near 360 cm^{-1} for synthetic norsethite (Table 2). The FTIR spectra of the synthetic and natural samples are very similar. The increase in precipitation rate of the synthetic carbonates does not cause significant changes of the absorption band positions of the internal modes, except for ν_3 . Additionally, slightly smaller wave-numbers of the ($\nu_1 + \nu_4$) and one ($\nu_1 + \nu_3$) mode are observed for precipitates from highly supersaturated aqueous solutions (N-41, N-51) and the carbonate prepared by grinding (LON-1) compared with the products from slow transformation runs. The relatively high variability of the ν_3 mode in the different spectra is possibly caused by differences in the crystallinity or imperfections of the synthetic norsethites. Additional incorporation of small amounts of foreign elements into the carbonate lattice (Table 1) may have led to small wave-number shifts for the natural norsethites (Table 2). No additional absorption bands attributable to $\text{BaMg}(\text{CO}_3)_2$ were observed due to the different synthesis procedures. Extra bands in the spectra of the N-41 and N-51 run products were essentially due to the presence of minor BaCO_3 which was confirmed by XRD.

The synthetic and natural norsethite samples contain ^{13}C in its natural abundance (about 1 atom% ^{13}C ; Table 2). A small satellite band which is shifted to lower wave-numbers with respect to the main ν_2 band has been assigned to the out-of-plane bending mode of $^{13}\text{CO}_3^{2-}$ (Böttcher *et al.*, 1997; Sterzel and Chorinsky, 1968). From the data in Table 2 an average frequency shift of 26 cm^{-1} due to the substitution of ^{12}C by ^{13}C is calculated. This is slightly smaller than the value for pure

magnesite (31 cm^{-1} ; Table 2) but differs significantly from the result for witherite (16 cm^{-1} ; Table 2). The carbon isotopic-shift coefficient for $\text{BaMg}(\text{CO}_3)_2$ ($\nu_2(^{13}\text{CO}_3^{2-})/\nu_2(^{12}\text{CO}_3^{2-}) = 0.971 \pm 0.002$) agrees with the theoretical value for rhombohedral and orthorhombic carbonates (0.969; Golyshev *et al.*, 1981). The respective coefficients for synthetic magnesite and witherite are 0.968 and 0.982.

The Raman spectrum of $\text{BaMg}(\text{CO}_3)_2$ shows the fundamental ν_1 , ν_3 and ν_4 modes at 1118, 1443, and 701 cm^{-1} (Fig. 3), and a broad lattice mode at about 294 cm^{-1} (Table 3). Additionally, a weak band is observed at 882 cm^{-1} which is assigned to the fundamental ν_2 mode. This is supported by the agreement with the FTIR measurements where ν_2 is positioned at 880 cm^{-1} (Table 2). Accordingly, the overtone of the out-of-plane bending mode ($2 \cdot \nu_2$) is observed at 1757 cm^{-1} (Table 3). The same set of Raman-active modes has previously been found for $\text{PbMg}(\text{CO}_3)_2$ (Böttcher *et al.*, 1996).

Vibrational spectra of synthetic norsethite have, as yet, only been measured in the study of Scheetz and White (1977). The results for the few reported Raman-active modes are similar to the present measurements, although generally shifted to lower wave-numbers. The infrared spectrum presented by Scheetz and White (1977), however, differs significantly from the FTIR spectra obtained in the present study for synthetic and natural pure norsethite samples. Besides the unsplit infrared-active ν_2 , ν_3 and ν_4 modes of $^{12}\text{CO}_3^{2-}$ (Table 2), Scheetz and White (1977) observed intense bands near

ν_2 , ν_4 , and near 445 cm^{-1} , and ν_1 was not found. An infrared spectrum similar to the one presented by Scheetz and White (1977) was obtained by the alteration of carbonate gel from a run N-51-type experiment for 744 h at 60°C , where BaCO_3 and

probably some other unspecific carbonate phases were additionally present. Therefore, the differences between the results of the present study and the previous measurements are assumed to be mainly due to the synthesis procedure used by Scheetz and White (1977). These authors previously assumed that their procedure for the synthesis of $\text{BaMg}(\text{CO}_3)_2$ from highly supersaturated aqueous solutions may have led to a structure that had not equilibrated into a well-ordered form. However, the differences have actually to be explained by the coprecipitation of additional carbonates besides $\text{BaMg}(\text{CO}_3)_2$.

Acknowledgements

The authors wish to thank Prof. Dr D.K. Hallbauer and Dr J.M. Longo for the supply of samples M847 and LON-1, respectively. Synthesis experiments were carried out while the first author was at the Geochemical Institute of Göttingen University. M.E.B. is indebted to Prof. Dr F. Lippmann for bringing a publication to his attention, and to F. Schoster for carrying out the XRF measurement. The authors also wish to thank an anonymous journal reviewer for his constructive suggestions.

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[Manuscript received 3 June 1996:

revised 31 July 1996]