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^{13}C MAS NMR spectroscopy of inorganic and biogenic carbonates

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ABSTRACT

This paper presents the results of a ^{13}C MAS NMR (magic-angle-spinning nuclear magnetic resonance) spectroscopic study of a variety of reagent, synthetic, and naturally occurring inorganic and biogenic carbonate phases. The range of ^{13}C chemical shifts for different carbonates is small, varying from 166.3 ppm for a synthetic magnesian calcite (~41 mol% $MgCO_3$) to 169.9 ppm for aragonite. This small range of chemical shifts is consistent with very small differences in the C–O bonding in different carbonates and can be qualitatively understood if related to small changes in the paramagnetic deshielding terms of traditional NMR chemical-shift theory. ^{13}C NMR methods allow quantitative determination of calcite/aragonite ratios in physical mixtures. For calcites, the ^{13}C peak width increases with increasing Mg content.

INTRODUCTION

^{13}C NMR spectroscopy has been a routine tool of organic chemistry for many years, but there has been little investigation of the ^{13}C NMR behavior of inorganic phases. This paper presents the first reported systematic ^{13}C MAS NMR study of carbonates. Phases investigated include reagent alkali (Li, Na, Cs) carbonates, synthetic calcium carbonates, natural calcites and aragonites of biogenic and nonbiogenic origin, and natural magnesite and cerussite. ^{13}C NMR spectroscopy is particularly attractive because ^{13}C has nuclear spin (I) = ½ and, thus, does not suffer from quadrupolar effects. Its natural abundance, however, is only 1.1%, making spectrum acquisition slow.

Previous ^{13}C NMR studies of carbonates include a T_1 study of calcite (Lauterbur, 1958) and reported ^{13}C chemical shifts of 167.5 ppm for calcite, 169.1 ppm for magnesite, 169.9 ppm for aragonite, and 167.7 ppm for dolomite (Sherriff et al., 1987). These values are in excellent agreement with ours.

The major objectives of this study were to determine the ^{13}C NMR chemical shifts of the phases, to investigate the effects of structure and composition on these chemical shifts, and to determine if (Ca,Mg) order-disorder of magnesian calcite (>4 mol% $MgCO_3$), calcite (<4 mol% $MgCO_3$), and dolomite can be investigated via ^{13}C NMR.

An additional objective was to determine whether NMR spectroscopy might provide a viable alternative to powder X-ray diffraction (XRD) for quantitative mineralogical analysis. In particular, we hoped that the linear response of the relative NMR peak intensities with atom abundances of ^{13}C in different phases and the simplicity of sample preparation would make NMR a useful quantitative method for determination of calcite : aragonite ratios. NMR spectroscopy is especially attractive because results are not influenced by preferred orientation and other factors that complicate quantitative analysis with powder XRD.

SAMPLES AND EXPERIMENTAL METHODS

Sample preparation and origin

Synthetic calcite and vaterite were produced using the methods described in Easton and Claughter (1986; except that no $CoCl_2$ was used) and in Turnbull (1973), respectively. A mixture of amorphous and crystalline magnesian calcite was produced using the procedure described by Glover and Sippel (1967, prep. no. 66) except that the two solutions were mixed dropwise at 22 °C over 8 h. Minor amounts of aragonite and hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ or $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$, see Lippmann, 1973] are also present.

Most of the biogenic samples were collected from Florida Bay and the Florida reef tract. The "Arcacea" sample is a mixture of shells of the genera *Arca, Anadara,* and *Barbatia.* Biogenic samples that contained significant amounts of organic material (e.g., *Halimeda opuntia, Melobesia* sp., etc.) were treated with 5 wt% NaOCl.

Most of the nonbiogenic natural phases are from the University of Illinois at Urbana-Champaign mineral collection. The Andros Island (Rb-8) and Sugarloaf Key dolomites (Su-1) were supplied by Zakaria Lasemi (Miami University, Oxford, Ohio). Additional information on those dolomites can be found in Lasemi et al. (1989).

^{13}C NMR spectroscopy methods

The ^{13}C NMR spectra were collected at 90.5 MHz under magic-angle-spinning (MAS) conditions. The spectrometer is based on an 8.45-T superconducting solenoid magnet (Oxford Instruments, Osney Mead, Oxford, England) and a Nicolet (Madison, Wisconsin) 1280 automation system as previously described by Smith et al. (1983). The ex-

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citing pulses were typically 4 μs long, yielding a 45° spin-system flip angle. TMS was used as an external chemical-shift standard.

The MAS probe is "home-built" and uses an Andrew-Beams spinning assembly and delrin rotors. The ^{13}C signal from the delrin was routinely subtracted from the final spectrum. MAS speeds were typically 3.0 kHz. Samples were ground with an agate mortar and pestle.

Recycle times of 120 or 150 s were typically sufficient to prevent further spectral changes with increasing delay. For the alkali carbonates and some of the aragonites and synthetic carbonates, however, T_1 appears to be longer, and recycle times up to 650 s were needed. A recycle time of 600 s was needed to yield a quantitative spectrum of a 1:1 mixture of aragonite and calcite. Line broadening due to exponential multiplication (EM) of 25, 50, or 100 Hz was used, but has been subtracted from the reported peak breadths. The reported peak breadths do, however, contain about 0.5 ppm due to the field inhomogeneity.

Powder XRD methods

Each sample for XRD was wet ground with an Al_2O_3 mechanical mortar and pestle until the suspension passed through a 25-μm screen (500 mesh). Ethanol was used to provide cooling to reduce structural damage (Milliman, 1974). The suspensions were dried at 50 °C, and powders were side-packed into Al sample holders.

All XRD work was carried out on a DACO-MP computer-automated Siemens D-500 powder diffractometer using Ni-filtered Cu radiation and a diffracted-beam graphite monochromator. Reconnaissance runs of samples were made using 0.02° 2θ steps and 1.2-s counting times (1° 2θ/min). Additional runs were made for cell refinements and quantitative analysis using 0.01° 2θ steps and 2.4-s counting times (0.25° 2θ/min) to collect integrated intensities over specific reflections. To investigate the minimum detection limit of aragonite in calcite, an extremely slow run (0.002° 2θ/min) was made on a physical mixture of 99:1 vein-fill calcite : *Halimeda opuntia* aragonite using 0.01° 2θ steps and 300-s counting times.

Cell refinements of the calcite and magnesian calcite samples were done using peak centroids (determined with DACO-MP) and a modified version of Garvey's (1988) implementation of Appleman and Evans (1973) program with 9 to 20 reflections, including $\bar{1}012$, $10\bar{1}4$, 0006, $11\bar{2}0$, $11\bar{2}3$, $20\bar{2}2$, $\bar{2}024$, $\bar{1}018$, $11\bar{2}6$, $21\bar{3}1$, $\bar{1}\bar{2}32$, $21\bar{3}4$, $20\bar{2}8$, $11\bar{2}9$, $\bar{2}\bar{1}35$, $30\bar{3}0$, 000.12, $\bar{2}02.10$, $\bar{2}\bar{1}38$, and $11\bar{2}.12$.

Mg composition of calcites was calculated from the *a*, *c*, and *V* cell parameters (and their standard errors) by using the regression equations of Bischoff et al. (1983) for synthetic magnesian calcites. Mg composition values and errors represent the averages of the three values calculated using the *a*, *c*, and *V* cell parameters and standard errors. Mg compositions calculated by using the *c/a* ratio and that regression equation of Bischoff et al. (1983) for synthetic calcites did not produce reasonable results because of the cumulative effect of dividing the typically distorted cell parameters of biogenic calcites.

For samples composed of mixtures of carbonates, cell refinements were not practical because of peak overlap or because calcite peak intensities were too small. Instead, Mg composition was estimated from the calcite $d_{10\bar{1}4}$ peak position by using the iterative solution of the *a* and *c* regression equations of Bischoff et al. (1983). For the synthetic amorphous and crystalline magnesian calcite sample, the Mg content exceeded the maximum limit (24 mol% $MgCO_3$) suggested by Bischoff et al. (1983) for their regression equations.

Therefore, the Mg composition was determined by using a line fitted to the data for cation-disordered, synthetic magnesian calcites in Goldsmith et al. (1961, Table 3A).

Accurate cell refinements of the Sugarloaf Key and Andros Island dolomites required that the interference from aragonite, calcite, and magnesian calcite reflections be eliminated. Therefore, for powder XRD, these samples were ground to ~53 μm (270 mesh) and soaked for several 6-h intervals in 0.5 vol% formic acid (88%) until nearly all of the aragonite, calcite, and magnesian calcite was dissolved. The reflections listed in Reeder and Sheppard (1984) were used in the cell refinements of all the dolomites. Composition of the St. Louis Formation (Mississippian) "saddle" dolomite was determined by energy-dispersive electron-microprobe analysis.

The Sugarloaf Key and Andros Island dolomites were determined to be disordered on the basis of the integrated intensities of the $11\bar{2}3$ nonordering and the $01\bar{1}5$ ordering reflections ($11\bar{2}3/(11\bar{2}3 + 01\bar{1}5) = 0.95$ and 0.97 ± 0.01 for Sugarloaf Key and Andros Island dolomites, respectively; see Bathurst, 1975, Fig. 358).

Approximate concentrations of aragonite, calcite, magnesian calcite, and dolomite were determined by using integrated intensities and the calibration curves in Davies and Hooper (1963) and Ebanks (1967). The approximate vaterite : aragonite ratio (wt%) was determined by using peak heights and the equation from Wilbur and Watabe (1963).

RESULTS

Table 1 lists the ^{13}C NMR chemical shifts (peak maxima) and peak widths (FWHH), sample, source or locality, and unit-cell parameters and Mg composition for calcites and magnesian calcites. Figure 1 shows representative NMR spectra.

Reagent monoclinic alkali carbonates

The three monoclinic, alkali carbonates analyzed, Li_2CO_3 (space group *C*2/*c*; Effenberger and Zemann, 1979), Na_2CO_3 (space group *C*2/*m*; Ehrhardt et al., 1980), and Cs_2CO_3 (space group $P2_1/c$; van Aalst et al., 1976) yield ^{13}C chemical shifts that increase slightly with increasing cation atomic radius. Their chemical shifts vary from 168.4 ppm for Li_2CO_3 (Fig. 1a) to 169.8 ppm for Na_2CO_3 to 169.9 ppm for Cs_2CO_3 (effective ionic radii: $^{[4]}Li^+ = 0.590$ Å, $^{[6]}Na^+ = 1.02$ Å, and $^{[6]}Cs^+ = 1.67$ Å;

TABLE 1. Sample information, ^{13}C NMR chemical shift and peak width, and powder XRD results

Sample	Source or locality	Phase[*]	$\delta^{13}C$ (ppm)	^{13}C FWHH (ppm)	a (Å)	c (Å)	V (Å^3)	$MgCO_3$[**] (mol%)
Reagent monoclinic alkali carbonates								
Li_2CO_3	Mallinckrodt Chemical Works		168.4	1.8	—	—	—	—
Na_2CO_3	Fisher Scientific Co.		169.8	0.8	—	—	—	—
Cs_2CO_3	Aldrich Chemical Co., Inc.		169.9	1.4	—	—	—	—
Orthorhombic carbonates (aragonite and cerussite)								
Cave aragonite	UIUC collection	100% A	169.9	1.2	—	—	—	—
Ooids	Recent, Joulters Cay, Bahamas	96% A + 2% C + 3% MC	169.9 167.6	1.0 (A) n.m. (C + MC)	—	—	—	—
"Arcacea" (3 genera), pelecypod	Recent, Bimini, Bahamas	99% A + tr. C + tr. MC	169.8	0.9	—	—	—	—
Acropora cervicornis, coral	Recent, Florida reef tract, Florida	99% A + tr. C	169.9	1.3	—	—	—	—
Porites divaricata, coral	Recent, Florida reef tract, Florida	100% A + tr. C	169.9	1.2	—	—	—	—
Halimeda opuntia, green algae	Recent, off Key Largo, Florida	99% A + tr. C + tr. MC	169.6 167.7	1.0 (A) n.m. (C + MC)	—	—	—	—
Cerrussite ($PbCO_3$)	UIUC collection	100% cerussite	166.4	1.8	—	—	—	—
Rhombohedral carbonates (calcite, magnesian calcite, magnesite, and dolomite)								
Miami Limestone	Pleistocene, Miami, Florida	95% C + 5% A + tr. quartz	168.1 170.3	1.0 (C) 0.9 (A)	4.9912(5)	17.07(1)	368.3(4)	0.0(3)
Vein-fill calcite	UIUC collection	100% C	167.9	1.0	4.9888(4)	17.06(1)	367.7(3)	0.3(3)
Laqueus sp., brachiopod	Recent, off Catalina Island, California	100% C	167.5	1.1	4.9914(3)	17.07(1)	368.3(3)	0.0(2)
Belemnite, cephalopod	Cretaceous, Wyoming	100% C	167.4	1.0	4.9897(5)	17.07(1)	386.0(4)	0.1(4)
Clypeaster sp., echinoderm (test)	Recent, off Key Largo, Florida	99% MC + 1% A	167.5	1.7	4.9428(4)	16.84(1)	356.4(3)	10.9(4)
Archaias sp., foraminifer	Recent, Florida Bay, Florida	98% MC + 2% A	167.2	1.9	4.9407(6)	16.85(2)	356.3(4)	11.0(5)
Melobesia sp., red algae	Recent, Rodriguez Key, Florida	97% MC + 3% A	167.2	1.7	4.9363(7)	16.82(2)	355.5(5)	12.4(6)
Goniolithon strictum, red algae	Recent, Rodriguez Key, Florida	99% MC + 1% A	167.3	2.4	4.9163(8)	16.72(2)	349.9(2)	18.8(9)
Magnesite	UIUC collection	100% magnesite	169	8.6	—	—	—	—
Sugarloaf Key dolomite (Su-1)	Recent, Sugarloaf Key, Florida	55% MC (11.2 mol% $MgCO_3$) + 41% D (calcian, disordered) + 4% A	167.7	2.1 (D + MC)	4.8282(5)	16.20(1)	327.0(4)	—
Andros Island dolomite (Rb-8)	Recent, Andros Island, Bahamas	50% D (calcian, disordered) + 34% A + 13% MC (11.2 mol% $MgCO_3$) + 3% C (1.7 mol% $MgCO_3$)	168.0 170.1	2.1 (D + MC + C) 1.1 (A)	4.8331(6)	16.23(2)	328.4(4)	—
St. Louis Formation dolomite	Mississippian, southern Illinois	100% D ("saddle") ~4100 ppm Mn, <1000 ppm Fe	167.7	5.0	4.8181(4)	16.07(1)	323.0(2)	—
Synthetic carbonates								
Calcite, synthetic	see text	100% C	167.5	1.0	4.9931(4)	17.08(1)	368.8(3)	0.0(3)
Amorphous and crystalline MC	see text	amorphous MC + MC (ca. 41 mol% $MgCO_3$) + A + hydromagnesite	166.3	7.7	—	—	—	—
Vaterite	see text	91% vaterite + 9% C (0.0 mol% $MgCO_3$)	168.7	1.9	—	—	—	—
Physical mixtures								
Vein-fill calcite + *H. opuntia* (99:1)	see above	see above	167.5	1.0	—	—	—	—
Iceland spar + cave aragonite (ca. 1:1)	UIUC collection	100% C and 100% A, respectively	169.7 167.5	0.9 (A) 1.2 (C)	—	—	—	—

Note: C = calcite (<4 mol% $MgCO_3$); MC = magnesian calcite (>4 mol% $MgCO_3$); D = dolomite; A = aragonite; FWHH = full width at half height (background corrected); UIUC collection = University of Illinois at Urbana-Champaign mineral collection, locality unknown; tr. = <1 wt%; n.m. = not measurable.

[*] Mg compositions for calcites listed here were determined using the calcite $d_{10\bar{1}4}$ powder XRD peak position and iterative solution of the a and c regression equations of Bischoff et al. (1983). For the amorphous and crystalline magnesian calcite sample, the Mg content was determined using the calcite $d_{10\bar{1}4}$ powder XRD peak position and the data from Goldsmith et al. (1961; see text).

[**] Mg compositions represent the average of the results from the a, c, and V regression equations of Bischoff et al. (1983).

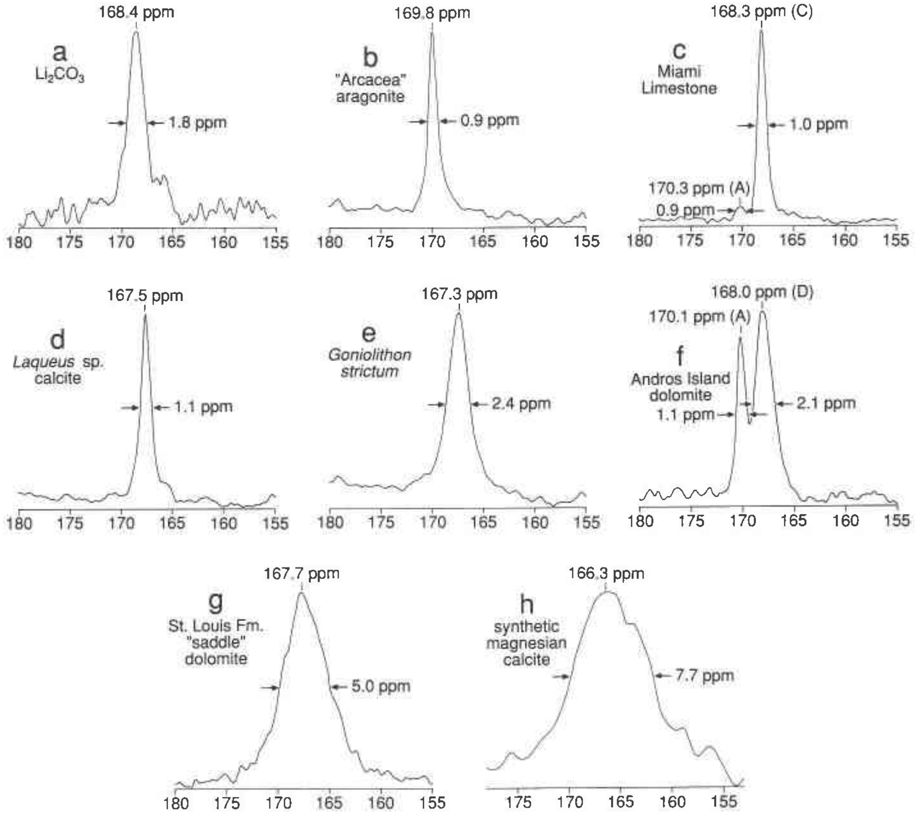

Fig. 1. Representative ^{13}C MAS NMR spectra: (**a**) reagent Li_2CO_3 (EM = 25; recycle time = 600 s); (**b**) "Arcacea" aragonite (EM = 50; recycle time = 120 s); (**c**) Miami Limestone (EM = 25; recycle time = 150 s); (**d**) *Laqueus* sp. calcite (EM = 50; recycle time = 120 s); (**e**) *Goniolithon strictum* magnesian calcite (EM = 50; recycle time = 120 s); (**f**) Andros Island dolomite (calcian, disordered) (EM = 50; recycle time = 120 s); (**g**) St. Louis Formation "saddle" dolomite (EM = 25; recycle time = 150 s); (**h**) synthetic amorphous and crystalline magnesian calcite (EM = 100; recycle time = 650 s) (C = calcite, A = aragonite, D = dolomite). Scales are in ppm from TMS.

Shannon, 1976). Peak widths are small (0.8–1.8 ppm FWHH) and show no systematic variation.

Orthorhombic carbonates (aragonite and cerussite)

The aragonite (space group *Pmcn*; Jarosch and Heger, 1986) samples include cave, ooid, coral, algal, and molluscan material and have nearly identical positions and peak widths. For the seven samples composed predominantly of aragonite, the average peak position is 169.8(1) ppm and the average peak width 1.07(16) ppm (Fig. 1b). There is no significant change in peak position with Sr content (Sr compositions from Milliman, 1974; *Arca* sp., 2500 ppm; *Porites divaricata,* 7900 ppm; *Acropora cervicornis,* 8100 ppm; *Halimeda opuntia,* 8800 ppm; Bahamian ooids, 9900 ppm).

Cerussite ($PbCO_3$, space group *Pmcn*; Sahl, 1974) yields a ^{13}C chemical shift of 166.4 ppm.

Rhombohedral carbonates

The synthetic, biogenic, and vein-fill low-magnesian calcites (space group $R\bar{3}c$; Reeder, 1983) have nearly identical peak positions and narrow peak widths (Figs. 1c–1d). For the seven samples composed predominantly of low-magnesian calcite, the average calcite ^{13}C chemical shift is 167.6(3) ppm and the average peak width (FWHH) is 1.04(8) ppm.

The average chemical shift of the four magnesian calcite samples, 167.3(1) ppm, is not significantly different from that of the calcites [167.6(3) ppm], but the peak width increases linearly with increasing Mg content (Fig. 2). The biogenic magnesian calcite sample with the highest Mg content, *Goniolithon strictum* [18.8(9) mol% $MgCO_3$], has a peak width of 2.4 ppm (Fig. 1e). The Fe and Mn contents of these four magnesian calcite samples are probably not sufficient to significantly increase the

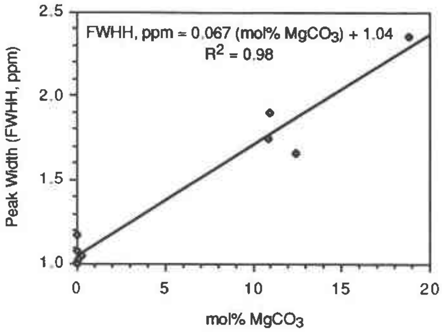

Fig. 2. Variation of ^{13}C MAS NMR FWHH peak width (ppm) with mol% MgCO$_3$ in calcites and magnesian calcites (n = 10).

peak width. According to Milliman (1974), *Goniolithon* or related genera contain ca. <200 ppm Fe and <50 ppm Mn. Magnesite (space group $R\bar{3}c$; Reeder, 1983) has the largest peak width, 8.6 ppm FWHH. Its chemical shift of 169 ppm is ca. 1.5 ppm less shielded than the calcites, but there is no overall trend in chemical shift from calcite to magnesian calcites to magnesite.

The spectra of the magnesian calcites, unfortunately, show no evidence of multiple, resolvable peaks that would allow us to investigate (Mg,Ca) order-disorder phenomena in these phases.

The ^{13}C chemical shift for dolomite (space group $R\bar{3}$; Reeder, 1983), 167.8(2) ppm (average of three samples; Figs. 1f–1g), is also very similar to that of calcite. The peak width is greater than that of calcite, averaging 2.1 ppm for the two calcian dolomites, which is less than some of the magnesian calcites and magnesite. The "saddle" dolomite has a larger peak width, 3.0 ppm (Fig. 1g), probably the result of Fe^{2+} and Mn^{2+} substitution for Ca^{2+}, which is typical in "saddle" dolomites (Radke and Mathis, 1980). This dolomite has ~4100 ppm Fe and <1000 ppm Mn (the approximate minimum detection limit for energy-dispersive microprobe). NMR peak broadening due to transition-metal impurities (caused by unpaired d- and f-orbital electrons) is a common phenomenon (Grimmer et al., 1983; Oldfield et al., 1983; Sheriff and Hartman, 1985).

Synthetic carbonates

The NMR spectrum of the synthetic amorphous and crystalline magnesian calcite (also containing aragonite and hydromagnesite) has poor signal/noise ratio but does contain a broad peak (7.7 ppm FWHH) with a maximum at 166.3 ppm (Fig. 1h). The powder XRD response is similar, with an anomalously high background between about 25° and 35° 2θ representing the amorphous fraction and a broad calcite $d_{10\bar{1}4}$ peak at 30.7° 2θ giving a MgCO$_3$ content of ~41 mol% for the crystalline fraction (Fig. 3). For this sample the recycle time used was 120 s, and this relatively short value has suppressed the signal for aragonite. The large breadth of the peak is probably due to broadening of both the peaks for the amorphous and crystalline magnesian calcite. As noted above, increasing Mg content in calcites causes peak broadening. Amorphous materials also typically have broader peaks than crystalline materials (see, e.g., Kirkpatrick, 1988, for a review).

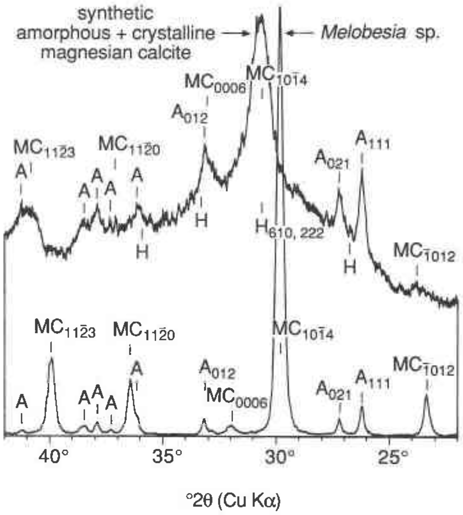

Fig. 3. Comparison of powder XRD patterns for synthetic amorphous + crystalline magnesian calcite with the *Melobesia* sp. red algae sample. The baselines of each pattern are superimposed; the high background level for the synthetic material is from the amorphous magnesian calcite (MC = magnesian calcite, A = aragonite, H = hydromagnesite).

The chemical shift of vaterite (hexagonal; see Lippmann, 1973, for a review of possible space groups) is 168.7 ppm with a peak width of 1.9 ppm.

Physical mixtures

To investigate whether ^{13}C NMR is a useful tool for quantitatively determining calcite : aragonite ratios, we examined two synthetic physical mixtures of these two phases (99:1 and ca. 1:1 calcite : aragonite) as well as several natural mixtures.

For the ca. 1:1 calcite : aragonite mixture and the Miami Limestone sample, which contains 5% aragonite (Fig. 1c), the calcite and aragonite signals are well resolved with NMR. However, the aragonite signal in the 99:1 calcite : aragonite mixture was not resolved above the background level with NMR.

DISCUSSION

Chemical-shift range

Perhaps the most interesting result of this study is the very small observed range of ^{13}C chemical shifts (166.3 to 170.3 ppm). Data for carbonate groups in scapolites extend this range to 163.8 ppm (Sherriff et al., 1987). This 6.5 ppm range is much less than the full range of ^{13}C chemical shifts (~200 ppm) for all substances. It is also less than the range for ^{29}Si in tetrahedral coordination

(~65 ppm). It is, however, comparable to the range of ^{29}Si chemical shift in Al-free orthosilicates (no bridging oxygens), ~11 ppm (Kirkpatrick et al., 1985).

This result is not surprising, given that all the phases examined have isolated CO_3^{2-} groups (like all natural carbonates) and contain no bridging oxygens. Thus, only changes in the large cations (which are next-nearest neighbors to the C atoms) and changes in structure are available to cause changes in the ^{13}C NMR chemical shifts. Furthermore, the variation in average Me–O and C–O bond distances is not great.

For the rhombohedral carbonates examined, the average Me–O distances vary by only 0.3 Å and the average C–O distance by less than 0.01 Å [calcite: $d_{Ca-O} = 2.3598(6)$ Å, $d_{C-O} = 1.2815(6)$ Å, Effenberger et al., 1981; magnesian calcite (10 mol% $MgCO_3$): $d_{Ca,Mg-O} = 2.331(1)$ Å, $d_{C-O} = 1.276(3)$ Å, Althoff, 1977; dolomite: $d_{Ca-O} = 2.3822(5)$ Å, $d_{Mg-O} = 2.0877(4)$ Å, $d_{C-O} = 1.2853(4)$ Å, Effenberger et al., 1981; magnesite: $d_{Mg-O} = 2.1018(4)$ Å, $d_{C-O} = 1.2852(4)$ Å, Effenberger et al., 1981]. There is a similar range of variation in orthorhombic carbonates [aragonite: $d_{Ca-O} = 2.5282(4)$ Å, $d_{C-O} = 1.2822(4)$ Å, Jarosch and Heger, 1986; cerussite: $d_{Pb-O} = 2.69$ Å, $d_{C-O} = 1.27$ Å, Sahl, 1974].

Although the vaterite structure has not yet been completely resolved, satisfactory solutions can be produced with Me–O and C–O distances similar to calcite and aragonite (see Lippmann, 1973, and references therein).

The reagent alkali carbonates have C–O distances similar to the carbonates discussed above, but greater variation in Me–O distances (~1.3 Å). For the phases examined, their values are the following: Li_2CO_3: $d_{Li-O} = 1.960(4)$ Å (tetrahedral coordination), $d_{C-O} = 1.281(2)$ Å, Effenberger and Zemann (1979); γ-Na_2CO_3: $d_{Na-O} = 2.49$ Å, $d_{C-O} = 1.26$ Å, calculated on the basis of the structure in van Aalst et al. (1976), assuming octahedral coordination for Na; Cs_2CO_3: $d_{Cs-O} = 3.30$ Å, $d_{C-O} = 1.30$ Å, calculated on the basis of the structure in Ehrhardt et al. (1980), assuming eightfold coordination for Cs.

Thus, substantial changes in the number of electrons in the alkali cation and the Me–O distances have an almost negligible effect on the electron distribution and the occupation of electronic excited states within the CO_3^{2-} group. These changes within the group should have the greatest effect on the chemical shifts, because for a given nearest-neighbor configuration, variations in the paramagnetic (deshielding) term according to classical chemical-shift theory dominate changes in the chemical shift (Tossell, 1984; see Kirkpatrick, 1988, for a brief review). This term increases with increasing occupancy of excited states and, thus, increasing covalent character in the bond. It depends on the expectation value of the electron-nucleus distance ($\langle r \rangle$) as $1/\langle r \rangle^3$. This conclusion is consistent with the ionic character of all the Me–O bonds.

For $CaCO_3$, a change in the structure from calcite to aragonite has about the same effect on the ^{13}C chemical shift as the change for Li to Na or Cs in the monoclinic carbonates (~1.5 ppm). Thus, the changes from 6-coordinated Ca and 3-coordinated oxygen in calcite (Reeder, 1983) to 9-coordinated Ca and 4-coordinated oxygen in aragonite (Speer, 1983) also have little effect on the electron distribution in the CO_3^{2-} group.

The increase in peak breadths (FWHH) resulting from Mg substitution in calcite is also about 1.5 ppm and must be due to small changes in the electronic structure in the CO_3^{2-} group similar to those caused by different alkali cations or the change from calcite to aragonite. Each CO_3^{2-} group in calcite is coordinated to six large cations, and the increased peak breadth must be due to different numbers of Ca and Mg atoms coordinated to different individual CO_3^{2-} groups. Unfortunately, the range of chemical shifts is so small that we cannot determine whether these Ca and Mg atoms are ordered in any way.

Quantitative determination of calcite : aragonite ratio

Unfortunately, a minimum concentration of about 5 wt% aragonite appears to be necessary for adequate quantitative determination of calcite : aragonite ratios via NMR. For samples with less than 5 wt% aragonite, powder XRD is probably a more suitable analytical technique. Even for samples containing significantly greater concentrations of aragonite, the slow ^{13}C-spectrum acquisition time because of long T_1 values and the low ^{13}C concentration probably make ^{13}C MAS NMR an impractical method for routine quantitative mineralogy determination.

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