**13C MAS NMR spectroscopy of inorganic and biogenic carbonates**

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**ABSTRACT**

This paper presents the results of a 13C 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 13C chemical shifts for different carbonates is small, varying from 166.3 ppm for a synthetic magnesian calcite (~41 mol% MgCO3) 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. 13C NMR methods allow quantitative determination of calcite/aragonite ratios in physical mixtures. For calcites, the 13C peak width increases with increasing Mg content.

**INTRODUCTION**

13C NMR spectroscopy has been a routine tool of organic chemistry for many years, but there has been little investigation of the 13C NMR behavior of inorganic phases. This paper presents the first reported systematic 13C MAS NMR study of carbonates. Phases investigated include reagent alkali (Li, Na, Cs) carbonates, synthetic calcium carbonates, natural calcites and aragonites of biogenic and non-biogenic origin, and natural magnesite and cerussite. 13C NMR spectroscopy is particularly attractive because 13C has nuclear spin \( J = \frac{1}{2} \) and, thus, does not suffer from quadrupolar effects. Its natural abundance, however, is only 1.1%, making spectrum acquisition slow.

Previous 13C NMR studies of carbonates include a study of calcite (Lauterbur, 1958) and reported 13C 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 13C 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% MgCO3), calcite (<4 mol% MgCO3), and dolomite can be investigated via 13C 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 13C 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 Clandrall (1986; except that no CoCl2 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 [Mg₅(CO₃)₄(OH)₄·4H₂O or Mg₅(CO₃)₄(OH)₃·3H₂O, 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). 13C NMR spectroscopy methods

The 13C 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...
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 13C 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, T1 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 Al2O3 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 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 Receder 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 1123 nonordering and the 0115 ordering reflections (1123/(1123 + 0115) = 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 13C 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, Li2CO3 (space group C2/c; Effenberger and Zemann, 1979), Na2CO3 (space group C2/m; Ehrhardt et al., 1980), and Cs2CO3 (space group P21/c; van Aalst et al., 1976) yield 13C chemical shifts that increase slightly with increasing cation atomic radius. Their chemical shifts vary from 168.4 ppm for Li2CO3 (Fig. 1a) to 169.8 ppm for Na2CO3 to 169.9 ppm for Cs2CO3 (effective ionic radii: 

\[
{}^{10}\text{Li}^+ = 0.590 \text{ Å}, \quad {}^{16}\text{Na}^+ = 1.02 \text{ Å}, \quad \text{and} \quad {}^{136}\text{Cs}^+ = 1.67 \text{ Å}.
\]
## Table 1. Sample information, \(^{13}\)C NMR chemical shift and peak width, and powder xRD results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source or locality</th>
<th>Phase*</th>
<th>(^{13})C (ppm)</th>
<th>(^{13})C FWHH (ppm)</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(V) (Å(^3))</th>
<th>(\text{MgCO}_3) (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reagent monoclinic alkali carbonates</strong></td>
<td></td>
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<tr>
<td>(\text{Li}_2\text{CO}_3)</td>
<td>Mallinckrodt Chemical Works</td>
<td>100% A</td>
<td>154.8</td>
<td>1.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(\text{Na}_2\text{CO}_3)</td>
<td>Fisher Scientific Co.</td>
<td>99% A + 2% A + 3% MC</td>
<td>154.9</td>
<td>0.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(\text{Ca}_2\text{CO}_3)</td>
<td>Aldrich Chemical Co., Inc.</td>
<td>100% A</td>
<td>154.7</td>
<td>1.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
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</tr>
<tr>
<td><strong>Orthorhombic carbonates (aragonite and cerussite)</strong></td>
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<tr>
<td>Cave aragonite</td>
<td>UIUC collection</td>
<td>100% A</td>
<td>169.9</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ooids</td>
<td>Recent, Joulters Cay, Bahamas</td>
<td>99% A + 2% A + 3% MC</td>
<td>169.9</td>
<td>0.9</td>
<td>—</td>
<td>—</td>
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<tr>
<td>&quot;Arcacea&quot; (3 genera),</td>
<td>Recent, Bimini, Bahamas</td>
<td>99% A + 2% A + 3% MC</td>
<td>169.8</td>
<td>0.9</td>
<td>—</td>
<td>—</td>
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<td>—</td>
</tr>
<tr>
<td>Acropora cervicornis,</td>
<td>Recent, Florida reef, Florida trach, Florida</td>
<td>99% A + 2% A + 3% MC</td>
<td>169.9</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Porites divaricata, coral</td>
<td>Recent, Florida reef, Florida trach, Florida</td>
<td>99% A + 2% A + 3% MC</td>
<td>169.8</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
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</tr>
<tr>
<td>Halimeda opuntia, green algae,</td>
<td>Recent, off Key Largo, Florida</td>
<td>99% A + 2% A + 3% MC</td>
<td>169.8</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cerrussite (PbCO(_3))</td>
<td>UIUC collection</td>
<td>100% cerussite</td>
<td>169.9</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
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<tr>
<td><strong>Rhombohedral carbonates (calcite, magnesian calcite, magnesite, and dolomite)</strong></td>
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<tr>
<td>Miami Limestone</td>
<td>Pleistocene, Miami, Florida</td>
<td>95% C + 5% A + 2% quartz</td>
<td>168.1</td>
<td>1.0</td>
<td>4.991(2)</td>
<td>17.07(1)</td>
<td>368.3(4)</td>
<td>0.0(3)</td>
</tr>
<tr>
<td>Vein-fill calcite</td>
<td>UIUC collection</td>
<td>100% C</td>
<td>167.9</td>
<td>1.0</td>
<td>4.988(4)</td>
<td>17.06(1)</td>
<td>367.3(4)</td>
<td>0.0(3)</td>
</tr>
<tr>
<td>Lagueus sp., brachiopod</td>
<td>Recent, off Catalina Island, California</td>
<td>100% C</td>
<td>167.5</td>
<td>1.1</td>
<td>4.991(4)</td>
<td>17.07(1)</td>
<td>368.4(4)</td>
<td>0.0(3)</td>
</tr>
<tr>
<td>Belemnite, cephalopod</td>
<td>Cretaceous, Wyoming</td>
<td>100% C</td>
<td>167.4</td>
<td>1.0</td>
<td>4.989(5)</td>
<td>17.07(1)</td>
<td>368.4(4)</td>
<td>0.0(3)</td>
</tr>
<tr>
<td>Clupea sp., echinoderm</td>
<td>Recent, off Key Largo, Florida</td>
<td>99% MC + 1% A</td>
<td>167.5</td>
<td>1.1</td>
<td>4.942(4)</td>
<td>16.8(4)</td>
<td>356.4(4)</td>
<td>10.9(4)</td>
</tr>
<tr>
<td>Archaeas sp., foraminifer</td>
<td>Recent, Florida Bay, Florida</td>
<td>98% C + 2% A</td>
<td>167.2</td>
<td>1.9</td>
<td>4.940(7)</td>
<td>16.8(2)</td>
<td>356.4(4)</td>
<td>11.0(5)</td>
</tr>
<tr>
<td>Melobesia sp., red algae</td>
<td>Recent, Rodriguez Key, Florida</td>
<td>97% C + 3% A</td>
<td>167.2</td>
<td>1.7</td>
<td>4.936(7)</td>
<td>16.8(2)</td>
<td>356.4(4)</td>
<td>12.4(6)</td>
</tr>
<tr>
<td>Goniolithon strictum, red algae</td>
<td>Recent, Rodriguez Key, Florida</td>
<td>99% MC + 1% A</td>
<td>167.3</td>
<td>2.4</td>
<td>4.916(3)</td>
<td>16.7(2)</td>
<td>349.9(2)</td>
<td>18.6(9)</td>
</tr>
<tr>
<td>Magnesite</td>
<td>UIUC collection</td>
<td>100% magnesite</td>
<td>169.7</td>
<td>8.6</td>
<td>—</td>
<td>—</td>
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</tr>
<tr>
<td>Sugarloaf Key dolomite</td>
<td>Recent, Sugarloaf Key, Florida</td>
<td>55% MC (11.2 mol% MgCO(_3) + 41% D (calcian, disordered) + 4% A</td>
<td>169.1</td>
<td>5.1</td>
<td>4.253(5)</td>
<td>16.2(4)</td>
<td>327.0(4)</td>
<td>—</td>
</tr>
<tr>
<td>Andros Island dolomite</td>
<td>Recent, Andros Island, Bahamas</td>
<td>50% D (calcian, disordered) + 34% A + 13% MC (11.2 mol% MgCO(_3) + 3% C)</td>
<td>168.0</td>
<td>2.1</td>
<td>4.833(6)</td>
<td>16.2(2)</td>
<td>328.4(4)</td>
<td>—</td>
</tr>
<tr>
<td>St. Louis Formation dolomite</td>
<td>Mississippiian, southern Illinois</td>
<td>100% D (&quot;saddle&quot;) + 1000 ppm Mn, &lt;1000 ppm Fe</td>
<td>167.7</td>
<td>5.0</td>
<td>4.818(4)</td>
<td>16.0(1)</td>
<td>323.0(2)</td>
<td>—</td>
</tr>
<tr>
<td>Calcite, synthetic</td>
<td>see text</td>
<td>100% C</td>
<td>167.5</td>
<td>1.0</td>
<td>4.993(4)</td>
<td>17.08(1)</td>
<td>368.8(3)</td>
<td>0.0(3)</td>
</tr>
<tr>
<td>Amorphous and crystalline MC</td>
<td>see text</td>
<td>100% C + 3% A(MC) + 3% A</td>
<td>168.1</td>
<td>7.7</td>
<td>—</td>
<td>—</td>
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<td>—</td>
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<tr>
<td>Vaterite</td>
<td>see text</td>
<td>91% vaterite + 9% C</td>
<td>168.7</td>
<td>1.9</td>
<td>—</td>
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<tr>
<td><strong>Synthetic carbonates</strong></td>
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<tr>
<td>Vein-fill calcite + H. opuntia (99:1)</td>
<td>see above</td>
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</tr>
<tr>
<td>Iceland spar + calcite (ca. 1:1)</td>
<td>UIUC collection</td>
<td>100% C and 100% A, respectively</td>
<td>168.7</td>
<td>0.9 (A)</td>
<td>167.5</td>
<td>1.2 (C)</td>
<td>328.4(4)</td>
<td>0.0(3)</td>
</tr>
</tbody>
</table>

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 \(d_400\) 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 \(d_400\) powder xRD peak position and the data from Goldsmith et al. (1961; see text). Mg compositions for calcites shown here were obtained using the calcite \(d_400\) powder xRD peak position and iterative solution of the a and c regression equations of Bischoff et al. (1983).

** 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 $\text{Li}_2\text{CO}_3$ (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) $\text{Lacqueus}$ sp. calcite (EM = 50; recycle time = 120 s); (e) $\text{Goniolithon}$ 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.

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; $\text{Arca}$ sp., 2500 ppm; $\text{Porites}$ divaricata, 7900 ppm; $\text{Acropora}$ cervicornis, 8100 ppm; $\text{Halimeda}$ opuntia, 8800 ppm; Bahamian ooids, 9900 ppm).

Cerussite ($\text{PbCO}_3$, 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 $R3c$; 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, $\text{Goniolithon}$ strictum [$18.8(9)$ mol% $\text{MgCO}_3$], 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

Shannon, 1976). Peak widths are small (0.8–1.8 ppm FWHH) and show no systematic variation.
peak width. According to Milliman (1974), Goniolithon or related genera contain ca. <200 ppm Fe and <50 ppm Mn. Magnesite (space group R3c; 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 R3; 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 $d_{104}$ 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).

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 50% 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 (Sheriff 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.
greatest effect on the chemical shifts, because for a given $A$, $d_{n}$ : 1.26 Å, calculated on the basis of the structure in Ehrhardt et al., 1981. Aragonite has about the same effect on the $^{13}$C chemical nucleus distance ($r$) as $1/(r)^{3}$. This conclusion is consistent with the ionic character of all the Me-O bonds.

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: $d_{c-o}$ = 2.3598(6) Å, $d_{n}$ = 1.2815(6) Å, Effenberger et al., 1981; magnesian calcite (10 mol% MgCO$_3$): $d_{c-o}$ = 2.3463(1) Å, $d_{n}$ = 1.2763(3) Å, Althoff, 1977; dolomite: $d_{c-o}$ = 2.3822(5) Å, $d_{n}$ = 1.2877(4) Å, Effenberger and Zemann, 1979; $\gamma$-Na$_2$CO$_3$: $d_{c-o}$ = 2.1018(4) Å, $d_{n}$ = 1.2852(4) Å, Effenberger et al., 1981]. There is a similar range of variation in orthorhombic carbonates [aragonite: $d_{c-o}$ = 2.5282(4) Å, $d_{n}$ = 1.2822(4) Å, Jarosch and Heger, 1986; cerussite: $d_{p-o}$ = 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$_2$CO$_3$: $d_{l}$ = 1.960(4) Å (tetrahedral coordination), $d_{o}$ = 1.281(2) Å, Effenberger and Zemann (1979); $\gamma$-Na$_2$CO$_3$: $d_{n}$ = 2.49 Å, $d_{o}$ = 1.26 Å, calculated on the basis of the structure in van Aalst et al. (1976), assuming octahedral coordination for Na; Cs$_2$CO$_3$: $d_{c-o}$ = 3.30 Å, $d_{n}$ = 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 ($r$) as $1/r^3$. 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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