Quantitative Identification of Metastable Magnesium Carbonate Minerals by Solid-State $^{13}$C NMR Spectroscopy

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Supporting Information

ABSTRACT: In the conversion of CO$_2$ to mineral carbonates for the permanent geosequestration of CO$_2$, there are multiple magnesium carbonate phases that are potential reaction products. Solid-state $^{13}$C NMR is demonstrated as an effective tool for distinguishing magnesium carbonate phases and quantitatively characterizing magnesium carbonate mixtures. Several of these mineral phases include magnesite, hydromagnesite, dypingite, and nesquehonite, which differ in composition by the number of waters of hydration or the number of crystallographic hydroxyl groups. These carbonates often form in mixtures with nearly overlapping $^{13}$C NMR resonances which makes their identification and analysis difficult. In this study, these phases have been investigated with solid-state $^{13}$C NMR spectroscopy, including both static and magic-angle spinning (MAS) experiments. Static spectra yield chemical shift anisotropy (CSA) lineshapes that are indicative of the site-symmetry variations of the carbon environments. MAS spectra yield isotropic chemical shifts for each crystallographically inequivalent carbon and spin–lattice relaxation times, T$_1$, yield characteristic information that assist in species discrimination. These detailed parameters, and the combination of static and MAS analyses, can aid investigations of mixed carbonates by $^{13}$C NMR.

INTRODUCTION

Many CO$_2$ capture and sequestration studies have focused on the formation of magnesium carbonate minerals from mafic and ultramafic protoliths as a permanent storage solution for CO$_2$. These reaction products are often imprecisely described as magnesite (MgCO$_3$), the energetically favored magnesium carbonate. There are, however, additional thermodynamically metastable phases that include waters of crystallization and hydroxyl groups in the crystal structure. These metastable minerals form due to kinetic trapping along the reaction pathway to magnesite. The lifetime of the metastable magnesium carbonate minerals can be long, even relative to geologic time scales, since the energy needed to remove a water from the crystal structure is not always available to the system. These metastable minerals form due to kinetic trapping along the reaction pathway to magnesite. The lifetime of the metastable magnesium carbonate minerals can be long, even relative to geologic time scales, since the energy needed to remove a water from the crystal structure is not always available to the system.

There are many possible forms of these hydroxy-hydrated magnesium carbonates: some examples, listed from least hydrated to most, include hydromagnesite [4MgCO$_3$·Mg(OH)$_2$·4H$_2$O], dypingite [4MgCO$_3$·Mg(OH)$_2$·(5–8)H$_2$O], and nesquehonite [Mg(OH)·(HCO$_3$)·2H$_2$O].

In CO$_2$ sequestration reactions, it has been reported that Mg-containing minerals react with CO$_2$ to form products consisting of a mixture of hydroxy-hydrated magnesium carbonates and magnesite. The specific composition of these product mixtures is dependent on the reactant minerals and reaction conditions, such as temperature and pH.

The ability to distinguish and quantify the product minerals in a mixture of magnesium carbonate phases is difficult due to a combination of factors. One complicating factor is that reaction products often form mixtures of amorphous and crystalline species, and current methods such as powder X-ray diffraction (pXRD) cannot identify the amorphous components. Additionally, multiple possible hydrated magnesium carbonates can be produced as well as adducts that form with ions, such as Na$^+$ and Ca$^{2+}$. Here we will demonstrate the ability of NMR to identify these mineral phases and quantitatively characterize these species in mixtures, thereby facilitating the study of sequestration reactions and their kinetics.

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Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for identification of various carbonate species, despite having relatively small structural differences between them. Pure MgCO₃ phases are needed as standards for rigorous NMR characterization, and we present synthesis methods to obtain these for each of the metastable minerals. The NMR signatures of magnesite, hydromagnesite, dyopite, and nesquehonite are established through a suite of minerals which allow, for example, the study of compositional analysis from in situ and ex situ NMR experiments. The ¹³C NMR signatures of magnesite, hydromagnesite, and nesquehonite are established through a suite of minerals. The NMR narrows resonances that are broadened by dipolar coupling, as well as chemical shift anisotropy (CSA). As a result, narrow resonances are observed at a species’ isotropic chemical shift (δ_iso). MAS NMR allows the minerals to be distinguished by both the chemical shift and the number of peaks which corresponds to the number of crystallographically inequivalent ¹³C sites. Static ¹³C NMR yields a characteristic line shape from broadening of the NMR resonance through the CSA. These broad ‘powder patterns’ can be used to distinguish the symmetry of the chemical environment of the ¹³C in the product mineral. Static ¹³C NMR resonances are defined by components evident in the CSA line shape—namely, their isotropic chemical shift (δ_iso), chemical shift anisotropy (Δiso), and asymmetry (η). These parameters are determined by the shape of the static NMR CSA powder pattern and are unique for each metastable magnesium carbonate mineral based on the carbon atoms’ nearby environments.

With this detailed characterization, it is possible to distinguish these products in a variety of settings, including analysis from in situ and ex situ NMR experiments. The ¹³C MAS NMR, pXRD, and Raman spectroscopy each lend themselves to ex situ characterization of subsets of the product minerals which allow, for example, the study of compositional gradients within a reactor. The ¹³C static NMR gives the capability for in situ monitoring of the mineral and CO₂ reaction ensemble that forms these mixtures of metastable magnesium carbonates. Using the magnesium carbonate phases and the quantitative characterization afforded by solid-state NMR, the capability of distinguishing and quantifying kinetically trapped magnesium carbonate minerals is possible in both in situ and ex situ NMR experiments.

### MATERIALS AND METHODS

Magnesite, MgCO₃, was synthesized in a high temperature, elevated pressure vessel for use in analyzing the reaction in situ with ¹³C static NMR as described previously. Samples were prepared by adding 1.60 g of forsterite, Mg₂SiO₄, powder and 2.77 mL deionized (DI) water into the reaction vessel. The vessel was then pressurized with 110 atm of ¹³CO₂ generated by adding 0.221 g of 99% ¹³C enriched NaHCO₃ to a solution of 0.251 g of MgCl₂ in 3.25 mL of DI water. This solution reacted for 24 h at room temperature, followed by 48 h of reaction at 62 °C, finally reacting for 24 h at 72 °C. The precipitate was then filtered and dried under vacuum at 24 h at room temperature.

Dyopite, [MgCO₃·Mg(OH)₂·(5–8)H₂O], was synthesized by adding 0.146 g of 99% ¹³C enriched NaHCO₃ to a solution of 0.164 g of MgCl₂ in 3.25 mL of deonized (DI) water. The solution was stirred for 1 min, and the glass beaker was sealed. The solution reacted for 3 days at room temperature. The precipitate was collected by filtering the sample, drying under vacuum at 40 °C for 10 min, followed by air drying overnight. The powder was then rinsed with DI water before repeating the filtering and drying procedure. The mineral assignments were confirmed by pXRD and ¹³C NMR.

The NMR measurements were acquired on a 7 T magnet with a ¹H frequency of 299.673 MHz and a ¹³C frequency of 75.365 MHz with a commercial HX MAS Chemagnetics probe. ¹³C¹H MAS and static NMR spectra were acquired in a single scan by a Bloch decay sequence with decoupling during acquisition (28.4 kHz typical decoupling strengths) spinning frequency (ν/3, MAS only) of 5 kHz, using a π/2 pulse length of 8.8 μs, and allowing the sample to reach thermal equilibrium in the magnetic field over 44 min. ¹³C¹H CPMAS cross-polarization “build-up” curves and spectra were acquired with ν/3 of 5 kHz, a recycle delay of 5 s, and recording 32 transients. The B1 field strengths were 27.8 kHz which gave a ¹H π/2 pulse length of 9 μs. The matching condition for the contact period was found by the Hartmann–Hahn match and the B₁ fields were not modulated during the contact time. Typical cross-polarization contact times (τ_c) of 100 μs to 15 ms were used to obtain the “build-up” curves. Chemical shifts were referenced to adamantane at 29.45 ppm. The isotropic chemical shifts for the static spectra were assigned via peak fitting and confirmed with slow spinning MAS NMR. Some samples were comixed with a carbon-free powder, forsterite, due to limited sample quantity (for the purpose of filling a NMR rotor volume).

The relaxation time T₁ was measured by ¹³C¹H MAS NMR saturation recovery pulse sequence and fitting the peak area versus delay time curve. The T₂ and T₂* were measured with ¹³C¹H CPMAS NMR and fitting the cross-polarization “build-up” curve. The peak areas were collected from the fits of the data.

All NMR spectra were fit with DMFIT. The isotopic chemical shift is defined as 1/3(δ_X+δ_Y+δ_Z). The principal values of the CSA powder pattern are defined as |δ_Z|>|δ_Y|>|δ_X|. The anisotropic chemical shift is defined as δ_aniso = δ_Z - δ_iso. Finally, the asymmetry is defined as η = (δ_YY−δ_ISO)/δ_ISO. The Raman spectra were acquired on a HoloLab Series 5000 Laser Raman Microprobe with a 532 nm laser beam at 11 mW of power. The resolution was approximately 3 cm⁻¹, and sampled regions were approximately 5 μm in diameter. The reproducibility of the Raman data were better than 1 cm⁻¹.

The pXRD data were obtained on a Rigaku Geigerflex D-MAX/A diffractometer with Cu–Kα radiation at 35 kV and 35 mA. Values of 2θ ranged from 6° to 60° with a step size of 0.02°.
0.04° and 1 s intervals. Samples were held in a standard pXRD slide. Samples that had been comixed with forsterite, for the NMR studies, have peaks for this mineral in the pXRD patterns (as seen in Supporting Information (SI) Figures S2 and S3).

### RESULTS AND DISCUSSION

The NMR spectrum of each mineral, both static and MAS, will be discussed individually, while the nuclear relaxation data will be discussed at the end, as to easily compare the minerals. All the relaxation data and CSA parameters are summarized in Table 1 and the CSA parameters are defined in the Materials and Methods section. The assignment of MAS NMR peaks was confirmed by slow spinning MAS NMR, which is discussed in the SI and shown in Figure S1. Schematics of the carbon sites present in the metastable magnesium carbonates are shown in Scheme 1. Shown are an axially symmetric CO$_3^{2-}$ carbonate (D$_{3h}$ point group) and a lower symmetry HCO$_3^-$ bicarbonate species. Distinguishing between CO$_3^{2-}$ and HCO$_3^-$ is possible via their $^{13}$C $\delta$iso chemical shifts, which have shifts of 170 and 160 ppm, respectively, in solution. Alternatively, the CSA line shape can be unambiguous for characterization in static $^{13}$C NMR.

**Magnesite.** Magnesite, MgCO$_3$, precipitates during sequestration reactions on the surface of forsterite, the reactant mineral phase. It forms directly in solutions with Mg$^{2+}$ and CO$_3^{2-}$ ions at temperatures above 120 °C but will form via an intermediate, hydromagnesite (that will be discussed later), even when the temperature is under 120 °C if given sufficient time. Magnesite is the only nonhydrated magnesium carbonate and has a single $^{13}$C NMR resonance at 169.9 ppm as seen in static $^{13}$C{1H} NMR (Figure 1A) and $^{13}$C{1H} MAS NMR with $\nu_R = 5$ kHz. (D) Expanded view of $^{13}$C{1H} MAS NMR. * denotes spinning sideband.
Proton-containing
MgCO₃

Figure 2. ¹³C{¹H} MAS NMR of a mineral containing magnesite and magnesite with nearby protons with €R = 5 kHz.

(see in SI Figure S2). It is also possible to cross-polarize the proton-containing magnesite peak with CPMAS proving that there are indeed protons nearby the magnesite carbon (CO₃²⁻) in the higher frequency peak. The shift to higher frequency was reported in a hydrated calcium carbonate. Other evidence used in assigning the higher frequency peak to the proton-containing magnesite species is comparing the peak fwhm. The fwhm of the peak in Figure 1 is 0.46 ppm. The peak at 169.5 ppm in Figure 2 has a fwhm of 0.57 ppm while the fwhm of the peak at 170.2 ppm is 1.08 ppm. Since the low frequency peak in Figure 2 and the peak in Figure 1 have a similar fwhm, the structures have similar crystallinity which can be dictated by the presence of protons. The high frequency peak in Figure 2, however, is broadened, presumably by nearby protons.

**Hydromagnesite.** Hydromagnesite forms in sequestration reactions as a mixture with dypingite, described below, in solutions with high concentrations of Mg²⁺, HCO₃⁻, and CO₃²⁻ and temperatures between 40 and 120 °C. However, hydromagnesite can be synthesized in isolated form in benchtop reactions. There are two crystallographically inequivalent carbons in the crystal structure of hydromagnesite, seen in the ¹³C NMR spectra of Figure 3, and the assignment has been confirmed with pXRD (SI Figure S3). Hydromagnesite is the least hydrated metastable magnesium carbonate, the H₂O/Mg ratio being 0.8, the composition of hydromagnesite being [4MgCO₃-Mg(OH)₂·4H₂O].

The two resonances have isotropic ¹³C chemical shifts of 165.2 and 163.0 ppm. These peaks, respectively, account for 51.8% and 48.2% of the integrated area signifying that the two sites are approximately equally populated in the mineral, as expected. The asymmetry of the CSA line shape shows one peak (δiso = 165.2 ppm) as nearly axially symmetric and the other (δiso = 163.0 ppm) as more asymmetric with η values of 0.16 and 0.55 respectively. These CSA parameters indicate that one of the carbon sites in the crystal structure is similar to that of magnesite, which is axially symmetric, while the other site has an asymmetry similar to the asymmetric nesquehonite carbon, as will be seen below.

When using CPMAS NMR, the resonance at 163.0 ppm split into two resonances (as seen in SI Figure S4) with different values for the time constants T₁ρ and T₁S for each resonance. This split resonance reveals why the peak at 163.0 ppm is shorter and broader than the peak at 165.2 ppm: the peak at lower frequency appears to be made up of at least two resonances. These data indicate the nesquehonite-like carbon, 163.0 ppm, has more disorder caused by multiple configurations, likely due to nearby waters of crystallization.

Figure 3. ¹³C NMR of a hydromagnesite, [4MgCO₃-Mg(OH)₂·4H₂O], mineral. (A) Static ¹³C{¹H} NMR. (B) Fit of the static ¹³C NMR with the overall fit in black and the individual sites fitted in red and green and parameters listed in Table 1. (C) ¹³C{¹H} MAS NMR with €R = 5 kHz. The peak at 165.2 ppm is the green powder pattern and the peak at 163.0 ppm is the red powder pattern. (D) Expanded view of ¹³C{¹H} MAS NMR.

**Dypingite.** Dypingite forms in sequestration reactions as a mixture with hydromagnesite in solutions with high concentrations of Mg²⁺, HCO₃⁻, and CO₃²⁻ and temperatures between 40 and 120 °C. Here we were able to isolate a nearly pure dypingite mineral. There is no known crystal structure for dypingite, but the mineral has a unique pXRD pattern (SI Figure S5). The current convention is that dypingite is any hydroxy-hydrated magnesium carbonate with 5 to 8 waters of hydration and the formula [MgCO₃·Mg(OH)₂·x·H₂O], (where x = 5–8) giving a H₂O/Mg ratio of 1–1.6. This makes a pure phase difficult to synthesize; nevertheless, this mineral still has distinguishable NMR features. Figure 4 shows the static and MAS ¹³C{¹H} NMR of the dypingite sample.

Two NMR resonances are apparent in the ¹³C MAS NMR spectrum (see Figure 4C and 4D) with isotropic chemical shifts of 165.3–163.5 ppm, and each has a unique CSA line shape. There is a small impurity resonance (Figure 4D) at 166.5 ppm (which notably does not match the δiso chemical shift of any other species we’ve observed so far). These resonances indicate the presence of two crystallographically inequivalent carbons. The difference is apparent in the asymmetry of the powder patterns, where the peak at δiso = 165.3 ppm is magnesite-like with an η value of 0.17 and a δaniso value of −47.3 ppm, while...
the peak at δiso = 163.5 ppm is more asymmetric with an η value of 0.57 and a δaniso value of −53.9 ppm. Even without a known crystal structure, the appearance of two crystallographically inequivalent carbon sites in dypingite is encouraging because the composition only differs from hydromagnesite (with two unique carbons) by the number of waters of hydration. The resonance at 165.3 ppm comprises 60.7% of the integrated area of the spectrum, meaning that approximately 3 out of every 5 carbon sites are in the magnesite-like electronic environment. To identify dypingite with 13C NMR it is important to check the area ratio of the peaks since this area ratio of 3:2 for the resonances at 165.3 and 163.5 ppm is different from that of hydromagnesite (with its 1:1 ratio for the two sites), since the two chemical shift values are very close.

**Nesquehonite.** The mineral nesquehonite is the most hydrated magnesium carbonate phase included here, with a H2O/Mg ratio of 2, and has a chemical composition of [Mg(OH)(HCO3)·2H2O].41 This species has also been described as [MgCO3·3H2O]30,42,43 which will be discussed more below. This hydroxy-hydrated magnesium carbonate is the preferential product in systems with high concentrations of Mg2+, HCO3−, and CO32− and temperatures below 40 °C.28,30,44,45 The crystal structure of nesquehonite contains only one crystallographically inequivalent carbon.35,46 Therefore, only one NMR resonance is expected, and this resonance can be distinguished in both the static (Figure 5A) and MAS 13C{1H} NMR (Figure 5C, D) spectra and is confirmed by pXRD and Raman in SI Figure S6.

The isotropic chemical shift, which can be seen in Figure 5C and 5D, is 165.4 ppm. The fit of the static spectrum gives an asymmetry (η) of 0.51, a symmetry close to that of the bicarbonate structure seen in Scheme 1, and an anisotropic shift (δaniso) of −50.64 ppm. We note that some previous studies report that nesquehonite has two 13C resonances,26,47 but the crystal structure from X-ray diffraction dictates otherwise. From further studies (as seen in SI Figure S7), we conclude that this second resonance is a northupite impurity in nesquehonite, arising from incomplete sample purification and the presence of excess Na+ from the synthesis. This assignment is confirmed by pXRD (SI Figure S8B−E), Raman (SI Figure S8A), and 23Na{1H} MAS NMR (SI Figure S9).

The large degree of asymmetry of the static line shape suggests that the symmetry of the 13C site is far from that of D3h (see Scheme 1). The chemical shift is at a lower frequency than magnesite suggesting that the complex [Mg(OH)(HCO3)·2H2O] (as opposed to MgCO3·3H2O) is the more accurate description due to its variation from the carbonate-like environment. Confirming evidence based on the relaxation times is discussed below.

**Comparison of Minerals and Techniques.** Nuclear spin relaxation times (13C T1, 1H T1ρ, and T1s) can be used to determine the carbon atom environment and the dynamics of nearby protons in the mineral species. A summary of the

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**Figure 4.** 13C NMR of a nearly pure dypingite, [4MgCO3·Mg(OH)2·(5−8)H2O], mineral. (A) Static 13C{1H} NMR. (B) Fit of the static 13C NMR with the overall fit in black and the individual sites fitted in red and green and parameters listed in Table 1. (C) 13C{1H} MAS NMR with 1kHz = 5 kHz. The peak at 165.3 ppm is the green powder pattern and the peak at 163.5 ppm is the red powder pattern. (D) Expanded view of 13C{1H} MAS NMR. * denotes spinning sideband.

**Figure 5.** 13C NMR of a nesquehonite mineral. (A) Static 13C{1H} NMR. (B) Fit of the static 13C NMR with parameters listed in Table 1. (C) 13C{1H} MAS NMR with 1kHz = 5 kHz. (D) Expanded view of 13C{1H} MAS NMR. * denotes spinning sideband.
nuclear spin time constants is presented in Table 1 in addition to the principal values of the $^{13}$C CSA tensor and CSA parameters previously discussed. The isotropic chemical shifts were determined from the $^{13}$C{[H]} MAS NMR spectra.

The $^{13}$C $T_1$ (spin–lattice) relaxation times across all four minerals reveal a trend that may prove predictive for other mineral phases. The $T_1$ time increases from nesquehonite to dypingite to hydromagnesite. This trend indicates that the more hydrated the mineral phase, the faster the $T_1$ relaxation, due to coupling with the H$_2$O in the crystal structure. The $T_1$ for magnesite is shorter than the hydrous-hydrated carbonates despite the expectation of a longer $T_1$ relaxation time in this nonhydrated mineral. Possible explanations are that para-magnetic impurities dominate the $T_1$ relaxation in magnesite or that the proximity of the $^{13}$C enriched carbonates in magnesite will enhance the effects of the homonuclear dipole–dipole spin–lattice relaxation mechanism. (Note: the homonuclear dipole–dipole $T_1$ mechanism is not present in natural abundance magnesite and therefore, is expected to have a longer $T_1$.) The relaxation time trend is important information when studying new mineral phases since the $T_1$ analysis ensures quantitative characterization in both in situ and ex situ CO$_2$ mineralization reactions and is informative of the level of hydration of the mineral phase.

The $^1$H $T_1$ relaxation time is in the rotating frame, and $T_{1p}$ is the CP-buildup time governed by $^{13}$C–$^1$H dipolar coupling. In nesquehonite, the relatively long $T_{1p}$ time constant could indicate that the protons near the carbon in this mineral have little motion. As stated before, this structure has been published as both [MgCO$_3$·3H$_2$O] and [Mg(OH)(HCO$_3$)·2H$_2$O]. For the nearest proton to be relatively static, the latter of these, the magnesium bicarbonate structure, is the one most consistent with the $T_{1p}$ data (and is consistent with the $^{13}$C line shape shown in Figure 5A). The shorter $T_{1p}$ in dypingite and hydromagnesite, may reflect nearby proton dynamics from the waters of crystallization; however, it is also possible that the purity and crystallinity of the sample could lead to the shorter $T_{1p}$.

We are able to see two types of carbon symmetries in these minerals based on the values of $\eta$. Asymmetry values close to 0.5 are structures that resemble the bicarbonate-like carbon environment, while values close to 0.1 are structures close to the $D_{3h}$ magnesite carbon environment (both seen in Scheme 1). Static NMR CSA powder patterns are therefore seen to be helpful in determining local carbon structure.

Dypingite and hydromagnesite have very similar structures seen in the chemical shift and asymmetry. One key differentiating factor is the relative fraction of carbons in each type of structure. Dypingite has a 3:2 ratio of carbons, with three of the carbon sites having an $\eta$ value close to 0.1 and two carbon sites with an $\eta$ value close to 0.5. However, hydromagnesite has a 1:1 ratio of these two sites. Another difference is seen in the $T_1$ relaxation times: the hydromagnesite $T_1$ relaxation is longer by approximately 50 s. By measuring the $T_1$ relaxation time and the area of the two peaks, dypingite and hydromagnesite are able to be distinguished. These differences will aid in quantifying a mixture of these products since a mixture will exhibit a weighted average of these values. Knowing the relaxation times and integrated areas for each mineral species allows quantification of dypingite and hydromagnesite individually from a mixture.

The information on each of these minerals is relevant to future NMR studies, both in situ and ex situ. The in situ NMR technique gives the full complement of the reacting system while ex situ analysis has the ability to characterize subsets of the reaction mixture.

In situ NMR measurements are of significant interest because these reactions can be completed in a reactor that mimics CO$_2$ sequestration processes. In situ NMR provides a spectroscopic “window” into the product mineral formation, which is important because the pH, reactant minerals, and temperature all affect the product outcome. Such techniques have been used to observe the speciation of $^{13}$C as it is introduced from enriched $^{13}$CO$_2$ gas under geologic sequestration conditions (i.e., $\sim$ 80 °C, $\sim$80 atm). These experiments benefit from methods that allow a high pressure of CO$_2$ to remain on the reacting system which forces the CO$_2$ to remain in solution and thus accessible for reaction. This high pressure reaction environment is easily achievable with static $^{13}$C NMR, therefore this technique can monitor the reaction continuously.

Ex situ NMR measurements involve collecting the reacted mineral sample and running $^{13}$C{[H]} MAS (or CPMAS) NMR experiments on the product. The reaction products are then distinguished by their crystallographically inequivalent $^{13}$C sites, which are each indicated by an individual $^{13}$C chemical shift. This technique can therefore be used to characterize spatial product gradients that form during the sequestration reactions, by sectioning the product as a function of depth in a fixed bed reactor or sample chamber. When in situ and ex situ $^{13}$C NMR techniques are used together, the combined information can be integrated to give a full picture of the reaction and its associated products.

## ASSOCIATED CONTENT

### Supporting Information

Included are Raman spectra, powder X-ray diffraction (pXRD) patterns, $^{13}$C{[H]} MAS at slow spinning speeds, and $^{23}$Na{[H]} magic angle spinning (MAS) NMR spectra that confirm the NMR assignments in this article. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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