



ELSEVIER

Contents lists available at ScienceDirect

## Solid State Nuclear Magnetic Resonance

journal homepage: [www.elsevier.com/locate/ssnmr](http://www.elsevier.com/locate/ssnmr)

# On the crystal structure of the vaterite polymorph of $\text{CaCO}_3$ : A calcium-43 solid-state NMR and computational assessment



Kevin M.N. Burgess, David L. Bryce\*

Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie Private, Ottawa, Ontario, Canada K1N 6N5

## ARTICLE INFO

## Article history:

Received 14 May 2014

Accepted 29 August 2014

Available online 8 September 2014

## Keywords:

Vaterite

Calcium carbonate

Double-rotation NMR

Calcium-43

GIPAW DFT

Polymorph

## ABSTRACT

The vaterite polymorph of  $\text{CaCO}_3$  has puzzled crystallographers for decades in part due to difficulties in obtaining single crystals. The multiple proposed structures for the vaterite polymorph of  $\text{CaCO}_3$  are assessed using a combined  $^{43}\text{Ca}$  solid-state nuclear magnetic resonance (SSNMR) spectroscopic and computational approach. A combination of improved experimental and computational methods, along with a calibrated chemical shift scale and  $^{43}\text{Ca}$  nuclear quadrupole moment, allow for improved insights relative to our earlier work (Bryce et al., *J. Am. Chem. Soc.* 2008, 130, 9282). Here, we synthesize a  $^{43}\text{Ca}$  isotopically-enriched sample of vaterite and perform high-resolution quadrupolar SSNMR experiments including magic-angle spinning (MAS), double-rotation (DOR), and multiple-quantum (MQ) MAS experiments at magnetic field strengths of 9.4 and 21.1 T. We identify one crystallographically unique  $\text{Ca}^{2+}$  site in vaterite with a slight distribution in both chemical shifts and quadrupolar parameters. Both the experimental  $^{43}\text{Ca}$  electric field gradient tensor and the isotropic chemical shift for vaterite are compared to those calculated with the gauge-including projector-augmented-wave (GIPAW) DFT method in an attempt to identify the model that best represents the crystal structure of vaterite. Simulations of  $^{43}\text{Ca}$  DOR and MAS NMR spectra based on the NMR parameters computed for a total of 18 structural models for vaterite allow us to distinguish between these models. Among these 18, the  $P3_221$  and  $C2$  structures provide simulated spectra and diffractograms in best agreement with all experimental data.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

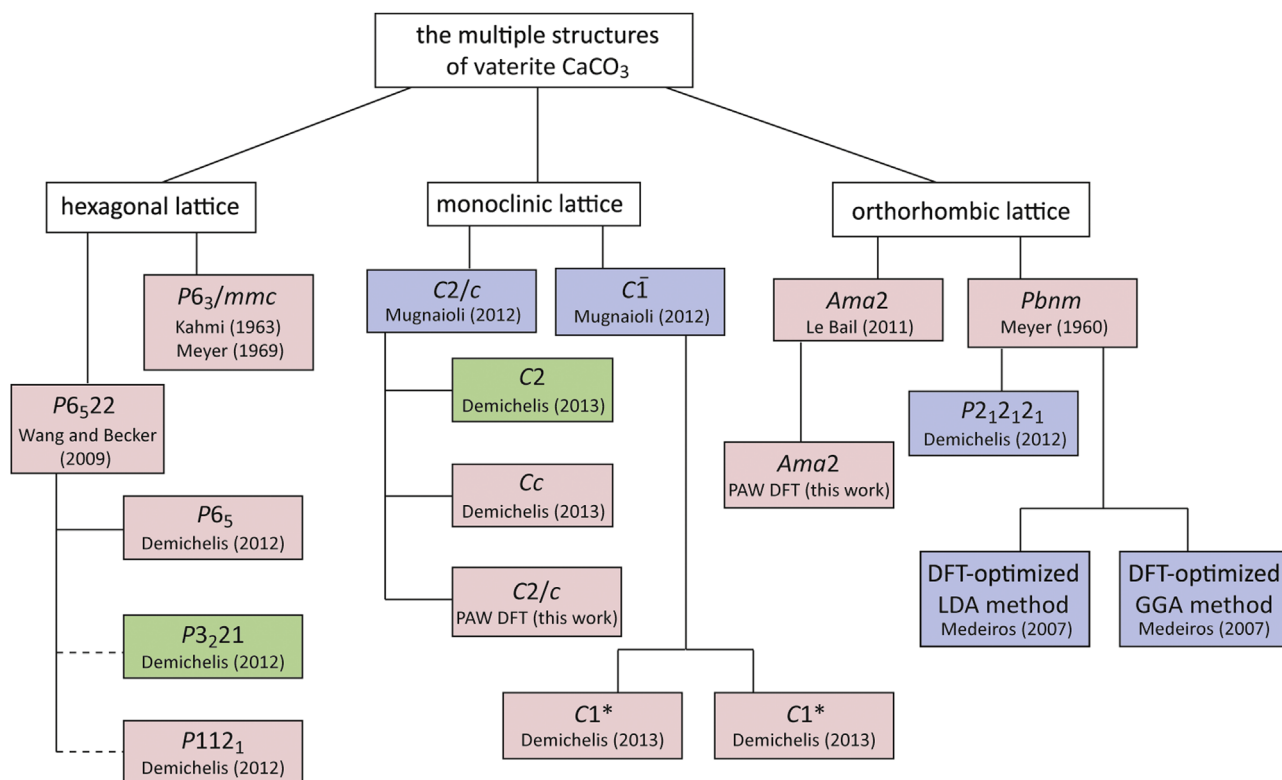
The crystalline phases of calcium carbonate ( $\text{CaCO}_3$ ) are important biomaterials and minerals which have been identified in various living organisms and in the Earth's crust [1–3]. Much recent research has focused on amorphous forms of  $\text{CaCO}_3$  and their transformation to one or many of the three polymorphs of this material: calcite, aragonite, and vaterite [4–8]. Despite these studies, the crystal structure of the vaterite polymorph still remains puzzling in part due to challenges in growing suitably large single crystals for accurate diffraction experiments. It is of great importance to fully characterize vaterite to better study the various crystallization mechanisms of amorphous  $\text{CaCO}_3$  as well as measure its role in biological systems. Recently, Pokroy and co-workers [9] characterized vaterite as having at least two interspersed structures. The major structure is proposed to exhibit hexagonal symmetry consistent with the original single crystal X-ray structure reported by Kahmi [10,11], whereas a minor

structure with unknown structural symmetry is suggested to also be present. In addition, many research groups have proposed various alternate structural models for vaterite via a range of characterization methods including powder X-ray diffraction (PXRD) [12], Raman spectroscopy [13], and ab initio calculations [14]. Shown in Scheme 1 is a chart of the proposed vaterite structures available in the literature. They are organized in such a way so as to identify the parent vaterite structures along with some newly proposed models from Demichelis et al. by DFT computations [15,16]. Given the great interest in this field of research and the many hypothesized structures, we submit that  $^{43}\text{Ca}$  NMR experiments should provide unique information for the determination of the crystal structure of vaterite.

It is well understood that, even with the very low natural abundance of  $^{43}\text{Ca}$  (0.14%), calcium NMR observables such as the quadrupolar coupling constant,  $C_Q$ , and the isotropic chemical shift,  $\delta_{\text{iso}}$ , are very sensitive to subtle differences about the  $\text{Ca}^{2+}$  centers in crystal structures [17–19]. We have shown in the past with natural abundance  $^{43}\text{Ca}$  SSNMR experiments that it was possible to distinguish between the three polymorphs of  $\text{CaCO}_3$  via  $^{43}\text{Ca}$  SSNMR at multiple magnetic field strengths under magic-angle spinning (MAS) conditions [20]. More recently, we [21], and others

\* Fax: +1 613 562 5170.

E-mail address: [dbryce@uottawa.ca](mailto:dbryce@uottawa.ca) (D.L. Bryce).



**Scheme 1.** Chart summarizing the multiple proposed structures for the vaterite polymorph of CaCO<sub>3</sub>. Models are based on hexagonal, monoclinic, or orthorhombic lattices. We indicate as well that many DFT structures are optimized from diffraction structures. Note that the *P3<sub>2</sub>21* and *P112<sub>1</sub>* DFT structures, while not hexagonal, were optimized from a parent hexagonal structure. An asterisk (\*) denotes that two different optimized structures were proposed with the same *C1* space group. These structures are referred to as *C1<sub>1</sub>* and *C1<sub>2</sub>* in the main text. Structures highlighted in blue are eliminated by comparing simulations of PXRD diffractograms to experiment. Rose colored structures are eliminated based on disagreement with experimental <sup>43</sup>Ca SSNMR experiments reported herein. Vaterite models in best simultaneous agreement with <sup>43</sup>Ca SSNMR and PXRD data are in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[22–24], have shown that gauge-including projector-augmented-wave density functional theory (GIPAW DFT) calculations reproduce quite accurately experimental  $I_{CQ}(^{43}\text{Ca})$  values especially when using the recently updated quadrupole moment for <sup>43</sup>Ca of  $-44.4$  mbarn [21,25].

We will use an NMR crystallography approach in order to evaluate the validity of each of the vaterite structures in Scheme 1 as possible models in representing this CaCO<sub>3</sub> polymorph. NMR crystallography is a growing field wherein SSNMR observables alongside DFT ab initio computations, molecular mechanics, crystal structure prediction, or powder diffraction experiments are used to elucidate the crystal structure of a given sample [26–32]. Its application in SSNMR has begun to find widespread usage specifically for polycrystalline samples that do not readily form single crystals suitable for X-ray analysis [33–35]. Firstly, we will employ our recently established [21] calibration curve for  $I_{CQ}(^{43}\text{Ca})$  in order to appropriately scale the GIPAW DFT calculated quadrupolar parameters obtained from calculations performed on all proposed structures in Scheme 1. Secondly, these values are used to analytically simulate the <sup>43</sup>Ca NMR spectra corresponding to each structural model, which are compared to new <sup>43</sup>Ca SSNMR data acquired on a <sup>43</sup>Ca isotopically-enriched vaterite sample. We note here that many structural models for vaterite reported to date, particularly the DFT-based structures, contain multiple crystallographically unique Ca sites. We employ a range of techniques including MAS, double-rotation (DOR) [36,37], and multiple quantum (MQ) MAS NMR experiments at magnetic field strengths of 9.4 and 21.1 T in attempts to resolve various possible Ca sites. Finally, we assess the differences in the simulated <sup>43</sup>Ca NMR spectra and attempt to identify the structure that is most consistent with all of the available <sup>43</sup>Ca SSNMR data and powder XRD.

## 2. Materials and methods

### 2.1. Preparation of a <sup>43</sup>Ca isotopically-enriched sample of vaterite

The vaterite polymorph of CaCO<sub>3</sub> was synthesized according to a previously reported literature procedure [38] wherein 6.11 g of glycine (Sigma-Aldrich) were dissolved in 100 mL of distilled water. 10 mL of a 0.5 M aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (Sigma-Aldrich) were added dropwise over 5 min and the resulting solution was stirred for 20 min. A <sup>43</sup>CaCl<sub>2</sub> solution was prepared by dissolving 0.17 g of <sup>43</sup>Ca isotopically-enriched <sup>43</sup>CaCl<sub>2</sub> (see Ref. 21 for more details) and 0.38 g of natural abundance CaCl<sub>2</sub> (Sigma-Aldrich) for a total of 0.55 g in 10 mL of distilled water. The resulting solution of <sup>43</sup>CaCl<sub>2</sub> was added dropwise over a 10 min period to the Na<sub>2</sub>CO<sub>3</sub>/glycine mixture. After one hour of stirring, the vaterite <sup>43</sup>CaCO<sub>3</sub> precipitate was filtered and dried under vacuum (0.237 g, 47% yield). We estimate the level of <sup>43</sup>Ca isotopic enrichment of the final product to be 5%.

### 2.2. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) experiments on the powdered <sup>43</sup>Ca isotopically-enriched vaterite sample were carried out on a Rigaku Ultima IV instrument with Cu K $\alpha$ <sub>1</sub> radiation ( $\lambda = 1.54060$  Å) and  $2\theta$  ranging between 10° and 70° at a rate of 0.5°/min and an increment of 0.02°. Simulations of the powder patterns from the available crystal structures of vaterite were generated with the Mercury software (v. 3.1) available from the Cambridge Crystallographic Data Centre.

Download English Version:

<https://daneshyari.com/en/article/5420350>

Download Persian Version:

<https://daneshyari.com/article/5420350>

[Daneshyari.com](https://daneshyari.com)