Pulsed Terahertz Radiation for Sensitive Quantification of Carbonate Minerals

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* Supporting Information

ABSTRACT: Quantification of natural carbonate minerals, namely, aragonite, high- and low-Mg calcite, and dolomite provides essential information about biomineralization, carbon cycling on Earth, and the evolution of ocean chemistry, and is also useful in many other scientific, pharmaceutical, and industrial fields. However, X-ray diffractometer has previously been the only practical tool to identify and quantify carbonate minerals, including calcium carbonate (CaCO3) polymorphs. We propose new fingerprint terahertz (THz) absorption and reflective index spectra in the 1–6 THz range that probe the lattice phonon modes and can be used for sensitive quantification of these four carbonate minerals, including polymorphs. In THz time-domain spectroscopy with our unique attenuated total reflection system, high- and low-Mg calcite and aragonite show different absorbance and reflective index amplitudes at 3.32 THz, which corresponds to the transverse optic mode. Dolomite shows a distinct absorbance peak and reflective index at 4.82 THz because its space group (R3) is different from that of calcite (R3c). THz absorbance and reflective index curves of the mixed carbonate materials, which typically occur in natural environments, correspond well to the curves calculated from the results of single-mineral samples (R2 > 0.98). Remarkably, the absorbance and reflective index can quantify small fractions (<1%) of low-Mg calcite in an aragonite matrix with high linearity (R2 = 0.99). Our findings provide a new method for screening low-Mg calcite diagenetic overprints on primary aragonite fossil skeletons such as corals, which is crucial for climate reconstructions using the isotopic analyses because a 1% overprint can cause estimated temperature deviations of ~1 °C. THz spectra of carbonate minerals offer not only a new high-sensitivity quantification tool for interdisciplinary fields, but also safer light-source handling than X-ray diffractometer.

1. INTRODUCTION

Carbonate minerals have provided essential information in diverse fields of scientific, pharmaceutical, and industrial researches such as the Earth’s climate and history, oil and gas reservoir detection,1,2 planetary systems, and identification of the origin of aeolian dust.3 In pharmaceuticals and industries, differentiating and imaging different carbonate minerals are important for assuring sufficient quality of the active pharmaceutical ingredient for analyzing coatings and/or filler pigments and extenders in the paper making and printing industries4 and for reinforcing rubber and plastic. Carbonate minerals have been also used as the most common pigments and substrates for wall painting since ancient times.5 Therefore, determining the original composition of the carbonate minerals is important for the conservation of art and cultural property.6

Calcium carbonate (CaCO3) is the most common carbonate mineral and exists as the crystal polymorphs, calcite, aragonite, and vaterite. Vaterite is rare in nature and is likely to occur only as a transient intermediate from an amorphous calcium carbonate reservoir detection,2,3 planetary systems, and identification of the origin of aeolian dust.4 In pharmaceuticals and industries, diagenetic overprint can cause estimated temperature deviations of ~1 °C. THz spectra of carbonate minerals offer not only a new high-sensitivity quantification tool for interdisciplinary fields, but also safer light-source handling than X-ray diffractometer.

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Calcite is divided into high- and low-Mg calcite, according to its Mg content (>4 mol %). In the modern marine environment, aragonite and high-Mg calcite are two major constituents that form biominerals and cement. Dolomite, CaMg(CO3)2, is another common carbonate mineral that frequently forms depositional and diagenetic layers in ancient shallow-water sediments.

A wide variety of analytical techniques have been used to identify Ca−Mg carbonate minerals, including X-ray diffractionmetry (XRD), differential scanning calorimetry, infrared spectroscopy, Raman spectroscopy, hyperspectral imaging, solid-state nuclear magnetic resonance measurements, a combination of X-ray photoelectron and time-of-flight secondary ion mass spectrometries, and shortwave infrared hyperspectral imaging spectroscopy. However, XRD is the only practical tool for quantifying all Ca−Mg carbonate minerals. Recently, terahertz (THz) pulsed spectroscopy has been proposed as a potential tool for characterizing crystalline properties of solid materials by probing the lattice phonon modes, which occur in the far-infrared range, especially below 18 THz (600 cm−1). Therefore, the center of the THz region, 0−10 THz, which bridges the gap between the infrared and microwave regions, covers a series of unique crystal fingerprints. The recent revolution in terahertz pulsed time-domain spectroscopy (THz-TDS) enables the direct measurement of the transient electric field of THz radiation. This method yields THz spectra with far better sensitivity, a wider dynamic range, and a higher signal-to-noise ratio compared with Fourier transform infrared (FTIR) spectroscopy. So far, only THz absorption spectra from 0 to 4 THz by THz-TDS have been reported for aragonite and calcite, but not for dolomite. In addition, the absorption spectrum of calcite does not distinguish low- and high-Mg calcite, and the reflective indices of low- and high-Mg calcite are not available.

Herein, we propose new THz absorption spectra and the reflective indices of main natural Ca−Mg carbonate minerals, aragonite, high- and low-Mg calcite, and dolomite for high-sensitivity quantification using our THz-TDS method from 1 to 6 THz. Our THz-TDS method uses a unique attenuated total reflection (ATR) system, in which the ATR prism is directly bonded to the THz detector and generator. The ATR structure of the THz-TDS instrument (Figure S1) prevents THz wave absorption by water vapor, reducing the total reflection loss and increasing the signal-to-noise ratio compared with conventional THz-TDS. Our study provides a new spectroscopic tool for the high-sensitivity quantification of carbonate minerals as an alternative to XRD.

2. RESULTS AND DISCUSSION

2.1. Absorbance and Reflective Index of Ca−Mg Carbonate Minerals. The carbonate minerals analyzed in this study were aragonite (coral Porites sp.), high-Mg calcite (11.6 mol % Mg; large foraminifera Cycloclypeus sp.), low-Mg calcite (0.6 mol % Mg; Jurassic Solnhofen limestone from Germany), and dolomite (Ediacaran Dengying Formation from China), and the mineralogies of which were confirmed by XRD (Figure S2). Elemental concentrations of the minerals were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The dolomite sample had a nearly stoichiometric ratio of Ca and Mg (51.3 mol % Ca and 48.7 mol % Mg; Table S1).

We performed 10 THz-TDS measurements of the low-Mg calcite sample. The values in the 1−6 THz range have an absorbance of less than 0.1 (1 standard error (SE)) and a reflective index of less than 0.004 (1 SE) (Figure 1a,b), although the SE of both indices increase with frequency, suggesting that our ATR technique with THz-TDS is reliable. We obtained the absorbance and reflective index spectra, which were unique for aragonite, high- and low-Mg calcite, and dolomite (Figure 1a,b). The absorbance of low-Mg calcite, the most stable calcium carbonate polymorph, shows a clear peak at 3.32 THz that corresponds to the center point of frequencies between the maximum (2.97 THz) and minimum (3.61 THz) reflective indices. Although a relevant absorbance peak at 3.32 THz appears for high-Mg calcite, patterns of the THz spectra are flattened (Figure 1). The transition from the low-Mg calcite spectrum to the high-Mg calcite spectrum is due to the change in the vibration mode caused by Mg substitution. Magnesite has a different vibration frequency from calcite, and the Mg bond probably generates no signals in the 0−6 THz range. The THz spectra are sensitive to Mg substitution, and there are distinct differences between low- and high-Mg calcite, whereas the XRD spectra only show a
slight difference in peak positioning (Figure S2). Aragonite, which has an orthorhombic system instead of a hexagonal system in calcite, shows flatter patterns for both the absorbance and reflective index, whereas its absorbance has a broad peak with the center at 3.32 THz, the same center position as peaks of high- and low-Mg calcite. The maximum absorbance at 3.32 THz is a unique characteristic of calcium carbonates that is probably reflected from an out-of-plane vibration and an in-plane vibration of the carbonate group, which correspond to the transverse optic mode in earlier studies. Dolomite has different absorption and reflective index patterns from calcium carbonate samples. Dolomite shows a clear absorbance peak at 4.82 THz that corresponds to the center point between the maximum (4.63 THz) and minimum (5.11 THz) reflective indices. Higher frequencies of the dolomite absorption peak and reflective index are likely related to the different space groups of calcite (R3c) and dolomite (R3), although calcite and dolomite belong to the same hexagonal crystal system. These results are consistent with previous studies of the far-infrared spectra using FTIR, which found a strong peak for calcite and a minor peak for aragonite at approximately the same frequency of 110 cm$^{-1}$ (3.3 THz) and a strong peak for dolomite at a slightly different frequency of 160 cm$^{-1}$ (4.8 THz). Thus, mineralogy-specific absorbance and reflective indices for Ca–Mg carbonate minerals appear from 2.0 to 5.5 THz.

2.2. Quantification of Mixtures of Aragonite, High- and Low-Mg Calcite, and Dolomite. Four sets of mixtures of different minerals were prepared to examine the suitability of THz-TDS for quantifying mineral composition (Figure 2). The first and second sets were mixtures of two minerals selected from aragonite and low- and high-Mg calcite, which are common biomineralization products, paper coating, and filler pigment. The third set was mixtures of low-Mg calcite and dolomite, which is typically found in ancient carbonate rocks. The fourth set was mixtures of aragonite and high- and low-Mg calcite, and the main combination in modern shallow marine carbonate environments, especially coral reef regions. Figure 2 shows the absorbance and reflective index curves of these four sets of mixtures, and the theoretical curves calculated by adding the value of the single carbonate mineral (Figure 1) to the mixing ratio. The measured spectra correspond well with the calculated spectra in all four cases (coefficient of determination: $R^2 > 0.98$; Figure 2).

Since the 1970s, powder XRD has been the only widely used method for identifying and quantifying carbonate miner-
In particular, XRD has been the only method capable of differentiating high- and low-Mg calcite through the difference in peak positions (Figure S2). The Mg content of calcite shifts the peak position at $2\theta$ of 29.6° of low-Mg calcite to a slightly higher $2\theta$ value by decreasing the lattice spacing.13,15,16 Our THz-TDS method is as sensitive as or better than XRD for quantifying low- and high-Mg calcite. Infrared spectroscopic quantification, in which the linear relationship between the ratio of the transmittance peaks to the absorption peaks of the mixture of aragonite−calcite and calcite−dolomite is used, has been reported; however, the method showed a substantial error for minor components of less than $\approx 20\%$ because of the resolution limit of the spectrometer.6,23 Therefore, our quantification using THz-TDS is the first high-precision spectroscopic method for determining the concentration of all major natural carbonate minerals.

2.3. Quantification of Trace Amounts of Low-Mg Calcite in Aragonite. The sensitivity of our THz-TDS was confirmed by analyzing mixtures of aragonite and low-Mg calcite (0, 50, 90, 95, 98.5, 99.4, and 100% aragonite). The maximum absorbance (3.32 THz) of 100% low-Mg calcite decreases linearly with increasing aragonite content (Figure 3a,b). The difference in reflective index between the maximum at 2.97 THz and the minimum at 3.60 THz (Figure 3c,d) of 100% low-Mg calcite also decreases linearly with increasing aragonite content. The absorbance and reflective index both show excellent linearity with a high correlation coefficient ($R^2 > 0.97$). Thus, our THz-TDS method can determine trace concentrations of the mixture, in this case low-Mg calcite ($0.6\%$).

This experiment is important, for example, for the screening of low-Mg calcite diagenetic overprints on primary aragonitic skeletons such as coral, which is critical because altered aragonite samples are unsuitable for age dating or climate reconstructions using chemical and isotopic analyses (e.g., a 1% alteration to a low-Mg calcite overprint causes estimated deviations of $\approx 1$ °C).24 XRD analysis has been widely used for screening diagenetic alterations, and the detection limit for low-Mg calcite is $<1\%$.25,26 Recently, a thermoluminescence (TL) spectroscopy technique that detects the differences in TL emission efficiency and in the partition coefficient of manganese between calcite and aragonite was proposed to achieve a lower or comparable detection limit of secondary calcite in coral skeletons.24 The TL spectroscopic technique is potentially useful for analyzing the diagenetic alteration of aragonite; however, this technique cannot yet identify high-Mg calcite and dolomite. Our THz-TDS enables quantification of a small proportion of low-Mg calcite ($0.6\%$ or even less), which is far better than FTIR11 and comparable with XRD25 and TL spectroscopy.24

Figure 3. Absorbance and reflective index of mixtures of different proportions of aragonite and low-Mg calcite (0, 50, 90, 95, 98.5, 99.4, and 100% aragonite). (a) Intensity of absorbance and (c) reflective index decrease with increasing aragonite content. (b) Maximum absorbance peak (3.32 THz) and (d) the difference between the two extreme reflective index peaks (2.95 and 3.60 THz) are highly correlated with aragonite concentration (%).
3. CONCLUSIONS

Our ATR method using THz-TDS in the 1–6 THz range revealed new mineral-specific absorption peaks and reflective indices at 3.32 THz for calcium carbonate polymorphs of aragonite, high- and low-Mg calcite, and at 4.82 THz for dolomite. These results allow us to identify and quantify the main natural Ca–Mg carbonate minerals with high accuracy. The sensitivity of this method is sufficient to quantify a small fraction (~1%) of low-Mg calcite in aragonite, comparable with or lower than the detection limits of XRD and TL spectroscopy. Our findings may provide a new method for the screening of low-Mg calcite diagenetic overprints on primary aragonitic skeletons such as corals, which is crucial for climate reconstructions using isotopic analyses because a 1% overprint can cause estimated temperature deviations of ~1 °C. Further experiments will expand applications of THz-TDS, for example, quantifying Mg contents in calcium carbonates. In addition, the technique only requires a class-1 laser, which improves the safety of the measurements compared with XRD. Many areas, such as astronomical observations of cosmic dust, testing pharmaceutical homogeneity, paper making, conservation and restoration of archeological materials, and THz imaging applications, will benefit from our new THz fingerprint spectra.

4. METHODS

4.1. THz Time-Domain Spectroscopy. All materials were ground into powder less than 5 μm in diameter using a mixer mill (MM 400, Retsch) and homogenized. Measurements were performed by ATR (Figure S1), which can obtain the THz spectral signatures from smaller amounts of samples than the standard transmission technique.11 The sample weight was adjusted to between 1.0 and 1.1 mg, and the sample was placed in a circular hole 3 mm in diameter in a 1 mm thick rubber, which was attached to the ATR prism. The powdered sample was homogenized by adding ethanol (10 μL) and gently stirred with a polypropylene microspatula. The powder was allowed to dry on the surface of the ATR prism for 10 min, and then the sample was irradiated with the THz laser (~1 mm in diameter). The laser frequency was scanned from 0.5 to 7.0 THz with a resolution of 55 GHz (0.05 THz), and 10 cumulative measurements were taken (1 min, 30 s). The THz generator and detector in our THz-TDS are directly attached to the total reflection prism. Therefore, the system does not require purging with dry nitrogen to avoid water vapor absorption unlike to a conventional THz spectrometer.

4.2. XRD. Powder diffraction data were collected using an X-ray diffractometer (Empyrean, Malvern Panalytical). Powder samples were packed into zero-background silicon sample holders. Antiscatter slits, divergence slits, and masks were chosen on the basis of sample area and starting θ. Data were collected between 2θ of 24 and 32° using data collector software (Panalytical). Search/Match phase identification was performed using HighScore software (Panalytical) and ICDD PDF+ database.

4.3. ICP-AES. Powder samples (0.1–5 mg) were placed in centrifugal tubes and dissolved by adding 2% HNO₃ (~5 mL). The samples were filtered through a 0.2 μm membrane (Minisart, Sartorius) and diluted with 2% HNO₃ if needed. The Ca and Mg concentrations were then measured by an ICP-AES (iCAP7200, Thermo Fisher Scientific). The resulting data were used to calculate the elemental content of carbonate minerals.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03311.

Side view of the integrated prism system for ATR in THz-TDS; powder XRD data for the analyzed carbonate minerals; and Mg and Ca concentrations in Ca–Mg carbonate minerals (PDF)

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### Notes

The authors declare no competing financial interest.

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