Carbonate mineral identification and quantification in sediment matrices using diffuse reflectance infrared Fourier transform spectroscopy

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Carbonate mineral identification and quantification in sediment matrices using diffuse reflectance infrared Fourier transform spectroscopy

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Abstract
Carbonate minerals are a major reservoir in the global carbon cycle and a key player in the sequestration and emission of atmospheric CO_2. In addition to the minerals' frequent use in agriculture and construction, carbonate formation has been targeted for anthropogenic CO_2 sequestration. Due to carbonate's importance in geological and anthropogenic realms, research on carbonate characterization and quantification is of interest. Here, we demonstrate a method to identify and quantify calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) in sediment matrices using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Needing only a few minutes per sample, DRIFTS is a rapid technique that does not require hazardous chemicals and does not destroy samples during analysis. We selected the 2515 ± 9 cm^{-1} absorbance bands for quantification as they exhibited little interference from sediment matrix minerals and large peak areas relative to other bands. The DRIFTS technique was compared to the traditional acidification headspace analysis method on artificial mixtures of sediment and carbonate as well as natural lake bed and river bank samples from the Upper Sangamon River Basin in Illinois, USA. DRIFTS offers an additional advantage over acidification in that it permits carbonate mineral identification simultaneously with its quantification. Though DRIFTS estimates were higher, a good correlation was found between DRIFTS and acidification estimates for both lake sediments ($R^2 = 0.99$) and bank samples ($R^2 = 0.92$), indicating DRIFTS is a reliable method for carbonate quantification in sediment matrices.

Keywords Carbonate quantification · Calcite · Dolomite · DRIFTS · FTIR · Sediments

Introduction

At 60 million Pg C, carbonate rocks are the largest carbon reservoir in Earth's lithosphere (Sharp 2007). It has a key role in long-term climate regulation as carbonate dissolution/precipitation leads to the sequestration/emission of the greenhouse gas CO_2 (Berner et al. 1983). Mirroring the natural system, prominent anthropogenic carbon sequestration approaches rely on carbonate formation (Oelkers et al. 2008; Wang et al. 2020). Two of the most abundant carbonate minerals are calcite ($CaCO_3$) and dolomite ($MgCa(CO_3)_2$), both commonly used by humans in agriculture, construction, and carbon sequestration schemes (Biasi et al. 2008; Legodi et al. 2001; Oelkers et al. 2008; Sun et al. 2014; Wang et al. 2020). Due to its prominence in the carbon cycle and in anthropogenic activities, carbonate mineral identification and quantification is a frequent need. Quantitative methods have relied on FTIR spectroscopy (Bruckman and Wriessnig 2013; Grunenwald et al. 2014; Legodi et al. 2001; Smidt et al. 2010; Tatzber et al. 2007; Vagenas et al. 2003), Raman spectroscopy (Kontoyannis and Vagenas 2000; Smith et al. 2013), X-ray powder diffraction (Bruckman and Wriessnig 2013; Kontoyannis and Vagenas 2000), and acid-released CO_2 quantification (Morera-Chavarria et al. 2016; Tatzber et al. 2007).

Transmission FTIR of samples in KBr pellets is one of the most common methods. FTIR is rapid (a few minutes per sample), does not require hazardous chemicals, has a small sample requirement (~ 1 mg), and produces several distinguishable carbonate bands in its spectrum. However, it

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is challenging to be quantitative with KBr pellets as obtaining reproducible path lengths is difficult. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a form of FTIR with additional advantages compared to transmission FTIR. DRIFTS does not require sample dilution in infrared transparent material, thus reducing sample preparation time, its sample-holding microcells allow for fixed volumes, and the sample is recoverable after analysis.

Here, we demonstrate a method for identifying and quantifying calcite and dolomite in natural sediments using DRIFTS. Not many previous studies have used spectroscopic techniques to quantify carbonate in non-carbonate geological matrices (Bruckman and Wriessnig 2013; Du et al. 2013; Tatzber et al. 2007). As geological field samples rarely feature carbonate in its pure form, developing a reliable technique for carbonate quantification in matrices will be particularly valuable.

Experimental

Field site and sample collection

Field samples were collected from the Upper Sangamon River Basin in central Illinois, USA. This region is dominated by intensive row crop (corn and soybean) agriculture. The Sangamon watershed is part of the NSF-supported Intensively Managed Landscapes Critical Zone Observatory (IML-CZO)—established to study the impacts of long-term land use on the critical zone environment (Blair et al. 2018).

River bank samples, alluvial sediments with developing soils, were collected in 2016 from two locations along the Sangamon River: Saybrook (lat: 40.426690, lon: − 88.526514), an upland portion of the watershed, and Allerton Park (lat: 39.998273, lon: − 88.650671), in the lowland floodplains (Blair et al. 2018). Bank exposures were scraped clean of external debris and sampled from the surface down to stream level. Samples were stored frozen at − 20 °C until analysis. Likely provenances of collected samples include oxbow or lacustrine sediments, post-settlement floodplain alluvium, glacial outwash, and glacial till.

Lake bed sediment samples were collected in 2015 from Lake Decatur (lat: 39.826115, lon: − 88.924801), a reservoir at the terminus of the Upper Sangamon River Basin. The current lake is the result of a dam emplaced in 1922, and agriculturally driven erosion caused rapid filling of the lake with sediment (Blair et al. 2018). Sediment cores were obtained from the lake bed using a vibracorer. The core used in this study reached a depth of 105 cm, estimated to be ~ 55 years of sediment accumulation from ^{137}Cs and ^{210}Pb data (Blair et al. 2018). The core was subsampled at 5 cm intervals, and sediment from each interval was centrifuged to separate the solid phase from the pore water. Afterward, the sediment was stored frozen at − 20 °C until analysis.

Prior to FTIR analysis, all samples were lyophilized. To obtain the well-resolved and consistent spectra needed for quantification, samples were homogenized by grinding with a Crescent Wig-L-Bug ball mill for 2 min.

Carbonate reference materials and standard mixtures

Standard mixtures were prepared with agricultural calcitic lime obtained from the Alden quarry near Alden, Iowa, and dolomite purchased from Thermo Scientific Chemicals (Ward Hill, MA, USA). The identities of the carbonates were verified through analysis of the 877 ± 6 cm^{-1} and 721 ± 9 cm^{-1} carbonate bands in their DRIFTS spectra for which Pezzolo (2013) reported peak wavenumbers for calcite at 877 cm^{-1} and 713 cm^{-1}, and dolomite at 883 cm^{-1} and 729 cm^{-1}. Four sets of calibration standards were made, two with calcite and two with dolomite. Standards were mixtures of known carbonate quantities (calcite or dolomite) and lyophilized, low-carbonate Lake Decatur sediment (initially thought to be carbonate-free from the absence of a peak complex in the 2515 ± 9 cm^{-1} spectral region, but headspace analysis of acidified samples recorded 0.24 ± 0.1 wt% carbonate). Two sets of standard mixtures (one calcite, one dolomite) spanned 0–40 wt% carbonate at 5% intervals. The other two spanned 0–5% at 1% intervals. All mixtures were milled for homogeneity.

Carbonate quantification by DRIFTS

Absorbance DRIFTS spectra were recorded using a Bruker Tensor 37 FTIR spectrometer with a Harrick Praying Mantis DRIFTS attachment. Each spectrum was recorded from 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution and an average of 16 scans. All spectra were corrected against a KBr background. A 3-mm-diameter sampling cup capable of holding ~ 30 mg of sample was used. Samples were gently tamped down into the cup, and the sample surface was leveled to the cup rim. A minimum of two spectra were recorded per sample.

Each spectrum was analyzed using the OPUS Quant 6.5 software (Bruker Optics). Due to the different shapes and wavenumber ranges for the 2515 ± 9 cm^{-1} bands of calcite and dolomite, different calibrations were needed for each mineral. For samples with more than 5% carbonate, the peak complex was integrated from 2647 to 2452 cm^{-1} for calcite and 2679 to 2455 cm^{-1} for dolomite. For samples with less than 5% carbonate, it was integrated from 2637 to 2466 cm^{-1} for calcite and 2662 to 2468 cm^{-1} for dolomite. The integration baseline is a line connecting the left and right edges of the peak between the wavenumbers to be integrated.

Carbonate quantification by acidification

Carbonate concentrations measured with DRIFTS were compared to estimates made via headspace analyses of acidified samples using a Thermo Scientific GasBench II coupled to a Thermo Scientific Delta V Isotope Ratio Mass Spectrometer. Samples were reacted with anhydrous (103%) phosphoric acid (H_3PO_4) for 6 h at 70 °C. The instrument was calibrated and analytical uncertainty estimated with the international calcite standards NBS 18 and NBS 19. The precision of the carbonate concentration measurements is ± 0.1 wt%.

Results and discussion

Carbonate in the DRIFTS spectrum

Carbonate bands with potential for quantification were identified in the 2515 ± 9 cm^{-1}, 1805 ± 9 cm^{-1}, 877 ± 6 cm^{-1}, and 721 ± 9 cm^{-1} spectral regions of the DRIFTS spectra (Fig. 1a). A peak or peak complex at these regions suggests carbonate presence with the exact peak wavenumbers varying by carbonate mineral. For the 1805 ± 9 cm^{-1}, 877 ± 6 cm^{-1}, and 721 ± 9 cm^{-1} regions, calcite had peaks at 1796 cm^{-1}, 875 cm^{-1}, and 712 cm^{-1}, while dolomite had peaks at 1814 cm^{-1}, 880 cm^{-1}, and 730 cm^{-1}. For both minerals, peak complexes were observed in the 2515 ± 9 cm^{-1} region. The maximum peak of calcite is at 2516 cm^{-1} with a shoulder at 2600 cm^{-1}, while that of dolomite occurs at 2523 cm^{-1} with a smaller shouldering peak at 2625 cm^{-1} (Fig. 1b). Calibrations were explored for all four spectral regions. The statistical performance of all 0–40% calibrations was similar (most $R^2 > 0.95$, and slope and intercept $p < 0.05$), but not the 0–5% calibrations. For both minerals, the 1805 ± 9 cm^{-1}, 877 ± 6 cm^{-1}, and 721 ± 9 cm^{-1} bands had small peak areas or peak overlaps from matrix interference, likely reducing R^2 for some calibrations. Because the 2515 ± 9 cm^{-1} bands appeared in a region without peak overlaps, had the largest integration areas, and resulted in high R^2 values, they were selected for DRIFTS calibration.

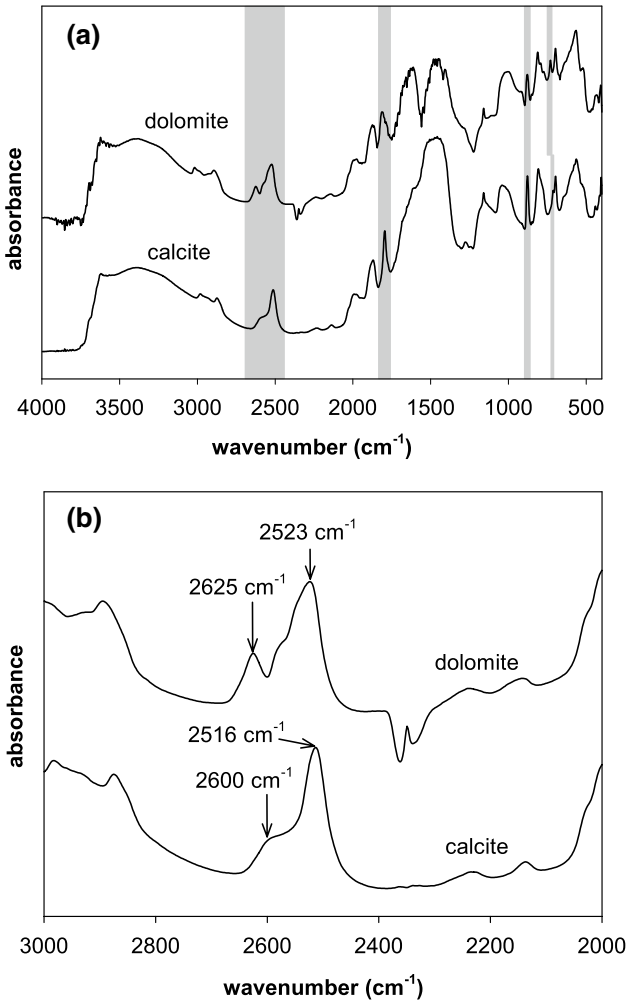

Fig. 1 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on carbonate–sediment mixtures by the analysis of internally reflected incident infrared light from powdered samples. **a** DRIFTS spectra of the 25% calcite and the 25% dolomite calibration standard mixtures. Shaded boxes indicate regions with carbonate bands considered for calibration. Single peaks were observed at 1805 ± 9 cm^{-1}, 877 ± 6 cm^{-1}, and 721 ± 9 cm^{-1}, and peak complexes at 2515 ± 9 cm^{-1}. **b** 2515 ± 9 cm^{-1} carbonate bands of the 1a spectra

Calibration for carbonate quantification

Figure 2a shows the relation between spectral peak integration area and carbonate concentration for the 0–40% calcite and dolomite calibration mixtures (both $R^2 = 0.99$). Figure 2b shows the same for the 0–5% mixtures (both $R^2 = 0.97$). All calibrations had slope and intercept $p < 0.05$ except for the dolomite 0–40% calibration (intercept $p = 0.93$).

In this study, we have focused on single-carbonate minerals within a sediment matrix. We acknowledge it is possible for geological samples to contain a mix of carbonate minerals. To our knowledge, only one study has attempted to quantify mixtures of different carbonate minerals within a matrix (Bruckman and Wriessnig 2013). However, it required two different methods, transmission FTIR and powder X-ray diffraction, and relied on the latter to distinguish different minerals. The DRIFTS approach alone should be able to resolve and quantify carbonates in such samples. The redundancy offered by multiple bands provides a means to avoid matrix interference, and the overlapping peak complexes at 2515 ± 9 cm^{-1} can be deconvoluted and deconvoluted peaks characteristic of different carbonates can be used for calibration. As the field samples in this study did not contain mixtures of different

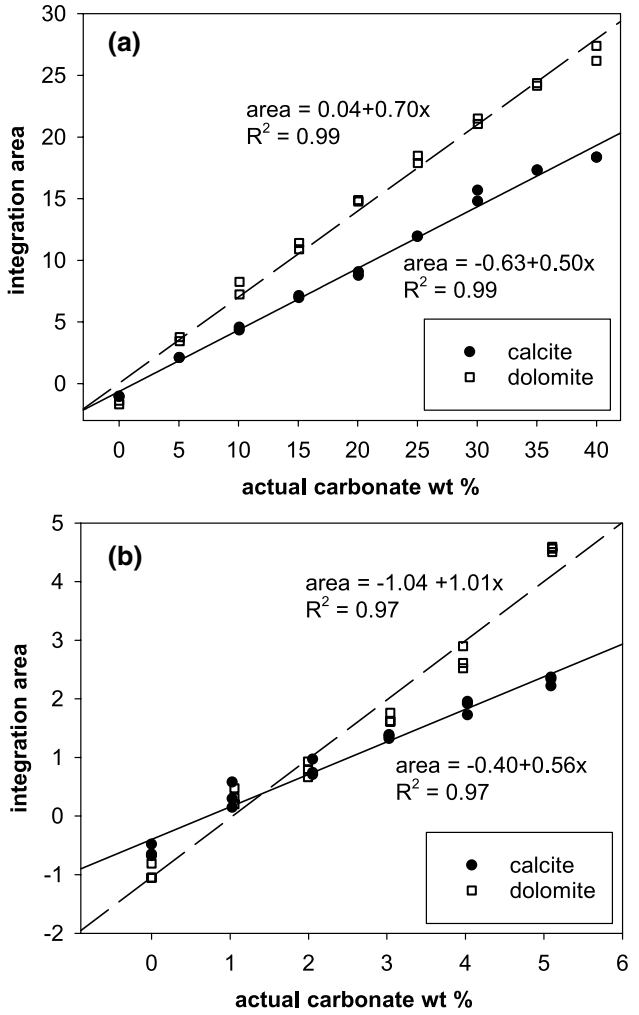

Fig. 2 Calibration curves for quantifying calcite and dolomite using the 2515 ± 9 cm^{-1} carbonate bands for **a** 0–40% standard mixtures, and **b** 0–5% standard mixtures. Both 0–40% calibrations had $R^2 = 0.99$, and both 0–5% calibrations had $R^2 = 0.97$. In both cases, the dolomite calibration had a steeper slope, indicating a larger peak area for the same carbonate wt% compared to calcite

carbonate minerals, single-carbonate calibrations were sufficient.

Comparison of DRIFTS and acidification estimates

Analysis of peak wavenumbers in the 2515 ± 9 cm^{-1}, 877 ± 6 cm^{-1}, and 721 ± 9 cm^{-1} bands indicated Lake Decatur contained only calcite, while Sangamon bank samples contained only dolomite (Table 1). In lake sediments, acidification estimates commonly fell below DRIFTS estimates, with larger differences for samples with higher calcite contents. On average, DRIFTS estimates were 1.26 times higher than acidification. Tatzber et al. (2007) found a similar result when comparing calcite estimates made through transmission FTIR and HCl acidification, the former having estimates 1.56 that of the latter. The same trend appeared in bank samples with DRIFTS estimates being 1.09 times higher on average.

It is notable that the DRIFTS–acidification discrepancy appears only for field samples, not calibration mixtures (Table 1). Longer sample incubation periods in the GasBench (48 h, data not shown) did not remove the discrepancy suggesting acidification reaction times were not the issue. That calibration mixtures had similar DRIFTS and acidification estimates also suggests instrumental calibrations were not the issue. Two possible explanations are a matrix effect (wherein interactions between the carbonate and matrix in field samples resulted in an incomplete acidification reaction) or a physical difference between calibration standard carbonates and field sample carbonates. Despite the discrepancy, the two sets of estimates had a good correlation (Fig. 3). Lake Decatur samples had $R^2 = 0.99$ (slope and intercept $p << 0.05$), while Sangamon bank samples had $R^2 = 0.92$ (slope $p << 0.05$, intercept $p = 0.05$).

Conclusion

Carbonate mineral analysis, once primarily the purview of geological studies, has gained a new importance due to efforts to artificially sequester carbon for climate control. Rapid, nondestructive analytical methods requiring modest sample preparation and providing qualitative and quantitative information would be of value. The proposed DRIFTS method can both identify and quantify calcite and dolomite minerals in sediment matrices using multiple spectral regions. The 2515 ± 9 cm^{-1} spectral window shows promise for quantification in samples where matrix interference may preclude the use of other bands. Though field sample DRIFTS estimates systematically differed from acidification estimates, the good correlation between the two methods ($R^2 = 0.99$ for Lake Decatur sediments, $R^2 = 0.92$ for Sangamon bank samples) suggests DRIFTS is a reliable method for quantifying calcite and dolomite in sediment matrices.

Table 1 Carbonate contents of select calibration standards and field samples from the Upper Sangamon River Basin

Sample ID	Carbonate mineral	Estimated carbonate content		Actual carbonate content
		DRIFTS (wt%)	Acidification (wt%)	Mass (wt%)
Calibration standard mixtures				
CCS 25%	Calcite	25.15	24.00	25.00
CCS 40%	Calcite	37.92	40.75	40.01
DCS 5%	Dolomite	5.25	5.34	5.07
DCS 25%	Dolomite	25.93	26.82	25.03
DCS 40%	Dolomite	38.13	39.96	40.00
Lake Decatur core				
LDC 0–5 cm	Calcite	11.95	8.13	
LDC 5–10 cm	Calcite	15.30	11.19	
LDC 10–15 cm	Calcite	19.62	14.94	
LDC 15–20 cm	Calcite	19.76	15.32	
LDC 20–25 cm	Calcite	18.75	13.79	
LDC 25–30 cm	Calcite	18.48	13.63	
LDC 30–35 cm	Calcite	18.36	13.10	
LDC 40–45 cm	Calcite	12.43	9.32	
LDC 45–50 cm	Calcite	10.98	8.38	
LDC 50–55 cm	Calcite	8.94	6.80	
LDC 55–60 cm	Calcite	5.54	4.70	
LDC 60–65 cm	Calcite	10.08	8.19	
LDC 65–70 cm	Calcite	10.35	7.92	
LDC 70–75 cm	Calcite	9.03	6.79	
LDC 75–80 cm	Calcite	4.12	4.30	
LDC 80–85 cm	Calcite	3.42	3.53	
LDC 85–90 cm	Calcite	6.69	5.86	
LDC 90–95 cm	Calcite	8.63	7.47	
LDC 95–100 cm	Calcite	9.54	7.65	
LDC 100–105 cm	Calcite	9.36	7.72	
Sangamon bank samples				
AP 151030-1, 0–5 cm	Dolomite	0.60	0.90	
AP 151030-4, mud drape	Dolomite	2.79	2.90	
SB8 151030-1, 0–5 cm	Dolomite	7.89	8.30	
SB8 151030-2, 25–30 cm	Dolomite	5.43	5.14	
SB8 151030-3, 40–45 cm	Dolomite	17.74	16.21	
SB8 151030-4, 70–75 cm	Dolomite	8.19	7.90	
SB8 151030-5, 95–100 cm	Dolomite	7.45	5.80	
SB8 151030-6, 113–118 cm	Dolomite	9.96	6.91	
SB10 151030-5, 250–255 cm	Dolomite	25.55	16.48	
SB11 151030-2, 50–55 cm	Dolomite	3.62	3.96	
SB11 151030-3, 65–70 cm	Dolomite	6.49	6.37	

LDC samples had 3–20% calcite with shallower samples occupying the higher end of the range. SB and AP samples had 0–25% dolomite

CCS calcite calibration standard, *DCS* dolomite calibration standard, *LDC* Lake Decatur core, *AP* Allerton Park, *SB* Saybrook

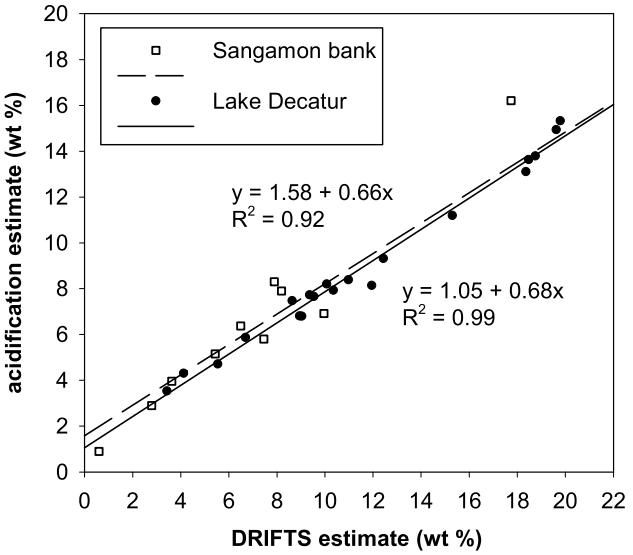

Fig. 3 Correlation between DRIFTS and acidification estimates for Lake Decatur sediments (calcite) and Sangamon bank samples (dolomite). Both correlation lines are very similar indicating similar degrees of DRIFTS–acidification discrepancies for all samples. DRIFTS: Diffuse reflectance infrared Fourier transform spectroscopy

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