

Soil and Sediment Carbonate Quantification by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

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Background

- Carbonates are the most abundant form of carbon in the crust. Their mineralogy and abundance provide information about surficial processes.
- The most abundant carbonate minerals are calcite (CaCO_3) and dolomite ($\text{MgCa}(\text{CO}_3)_2$).¹
- A quantification method was created using Diffuse Reflectance Infrared Fourier-Transform spectroscopy (DRIFTS).
- DRIFTS provides a constant sample volume, making it amenable for quantification purposes.

Methods

- Absorbance spectra recorded using Bruker Tensor 37 FTIR spectrometer with Harrick Praying Mantis DRIFT attachment.
- Samples freeze-dried and milled before analysis.
- Two sets of calibration standards with 0%-40% carbonate made by mixing carbonate-free lake sediment and powdered carbonate (calcite or dolomite).
- Calibration curves generated by integrating peak area at $\sim 2500 \text{ cm}^{-1}$ carbonate band.
- DRIFTS estimates compared to acidification-headspace estimates made with a Thermo Scientific GasBench II coupled to a Thermo Scientific Delta V IRMS.
- GasBench-IRMS samples reacted with 100% phosphoric acid at 70°C for 6 hours.
- Study site: Soil samples (18) from Sangamon River stream bank in Illinois, and sediment samples (20) from adjoining Lake Decatur.

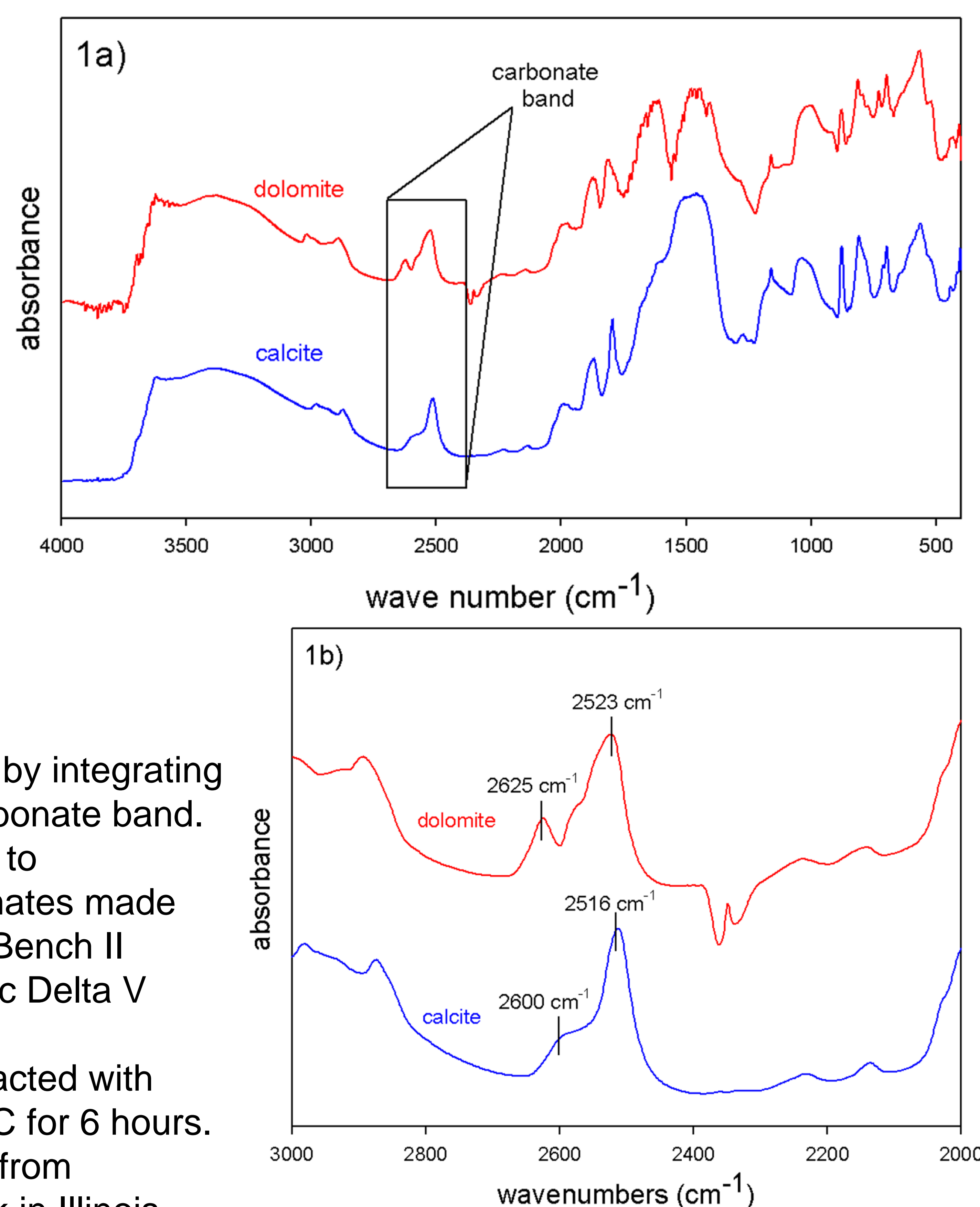


Figure 1. 1a) DRIFT spectra of calcite and dolomite calibration standards with 25% carbonate. 1b) 1a spectra with carbonate bands enlarged and peak wavenumbers shown.

Results and Discussion

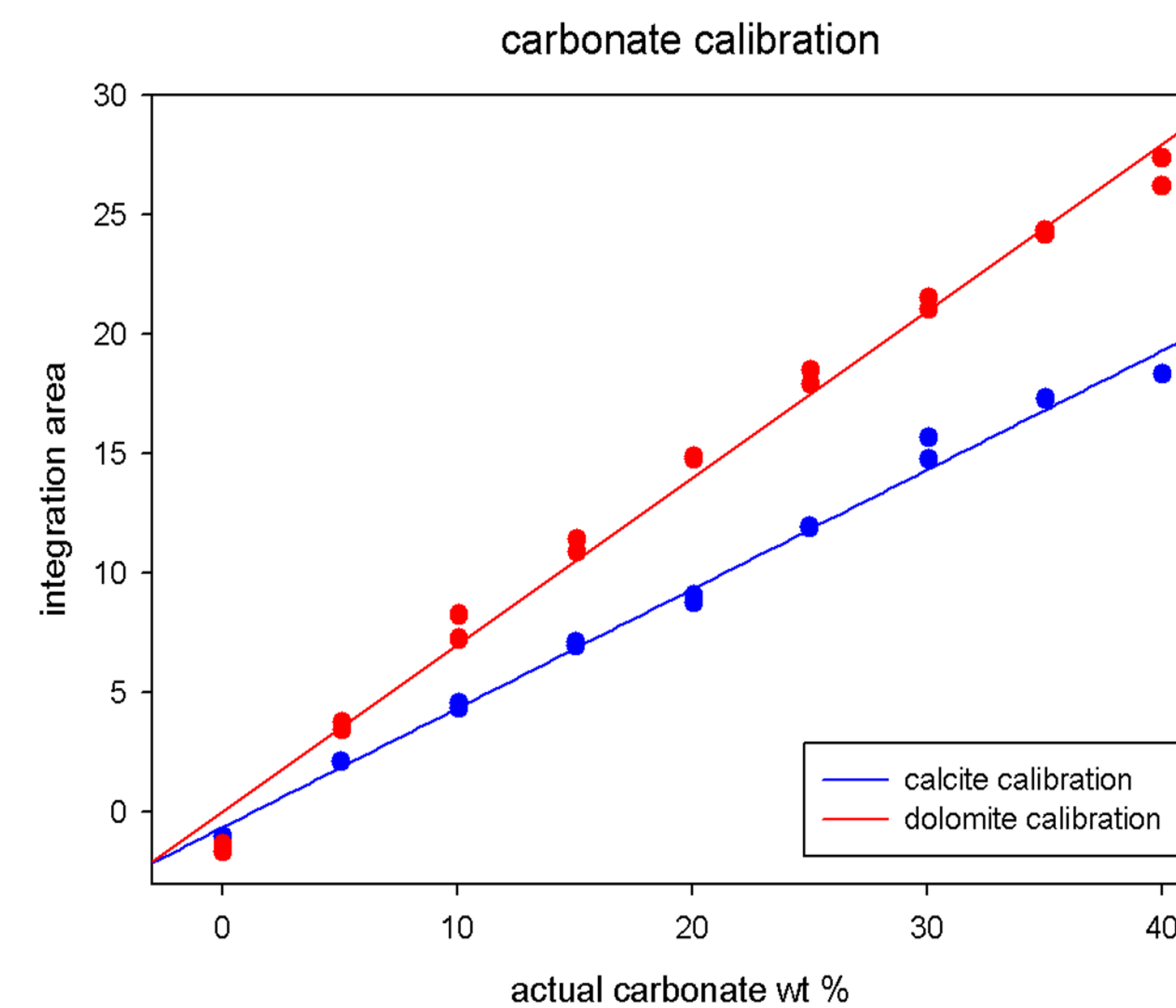


Figure 2. Calibration functions for calcite and dolomite based on the integrated peak area for the carbonate band at $\sim 2500 \text{ cm}^{-1}$.

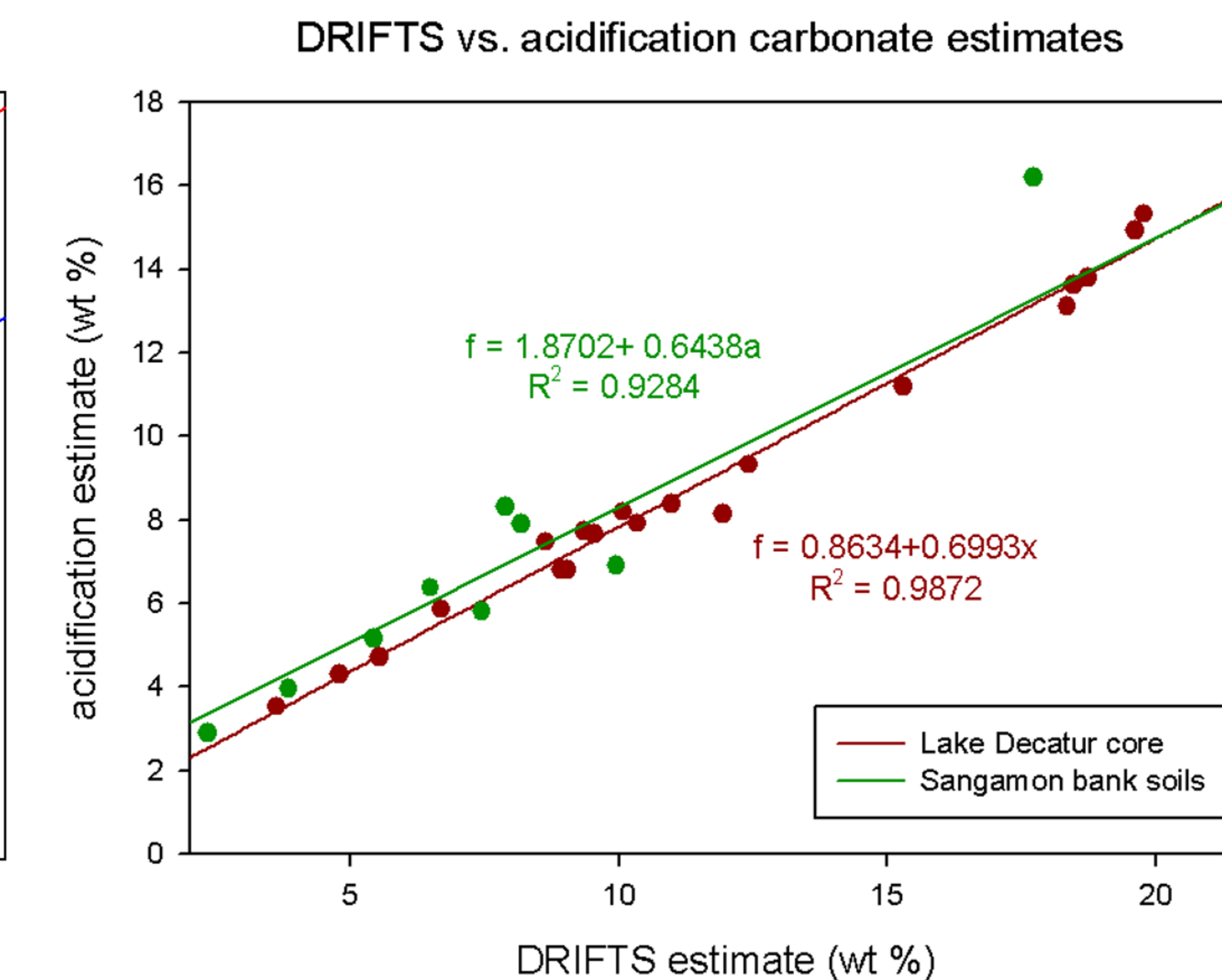


Figure 3. Correlation between DRIFTS and acidification estimates for Lake Decatur sediments (calcite) and Sangamon bank soils (dolomite).

- Peak shape at the $\sim 2500 \text{ cm}^{-1}$ band can distinguish between calcite and dolomite.
- Previous studies identified three main bands associated with carbonate: 1440 cm^{-1} , 880 cm^{-1} , and 720 cm^{-1} .² During this study, attempts to use them in calibration have been unsuccessful due to interferences from other minerals.
- Sangamon bank soils contained naturally occurring dolomite. Lake Decatur sediments contained calcite.
- Bank soil dolomite likely originated from the Potosi dolomite formation underlying the region.³
- The source of the calcite has not been identified yet.
- Positive linear correlations were found between the DRIFTS method and the more conventional acidification technique (Fig. 3, 4). The method worked equally well for calcite and dolomite in soils and sediments.

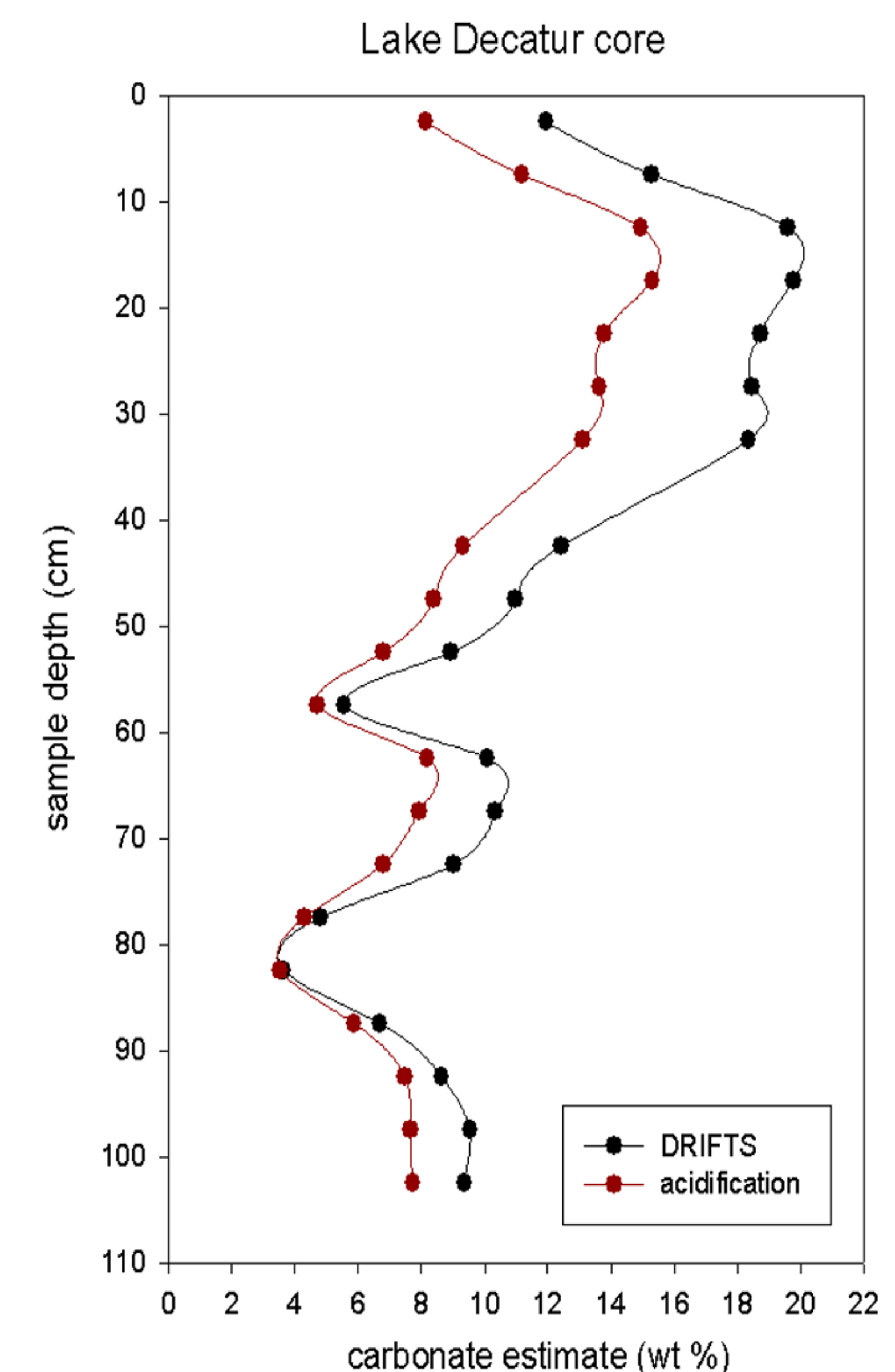


Figure 4. Changes in calcite estimates with depth for LD core samples. Both DRIFTS and acidification estimates are shown.

Conclusion

The strong correlation between the DRIFTS and acidification estimates (Fig. 3, 4) suggest DRIFTS is a reliable method for both the identification and quantification of calcite and dolomite in soils and sediments. Further investigation will be needed to determine if the quantification method will be effective for estimating calcite and dolomite in a larger variety of field samples.

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