

# Determination of Calcite and Dolomite Content in Soils and Paleosols by Continuous Coulometric Titration

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Quantitative determination of calcite/dolomite ratios in soil carbonate fractions is important for understanding the pedogenic history of a soil or paleosol. This is particularly relevant to stable carbonate-carbon and -oxygen isotope analyses where the presence of dolomite in a carbonate fraction can lead to erroneous results and inaccurate interpretations of the paleoenvironment. The goal of this work was to develop and test an accurate method using coulometric titration combined with differential kinetic principles for determining calcite and dolomite fractions in a sample. An automated titrator was connected to a temperature-controlled carbonate reactor where 2 M HClO<sub>4</sub> was introduced to the sample and mixed by bubbling CO<sub>2</sub>-free air at a constant rate of 100 mL min<sup>-1</sup>. Samples were ground to <53 μm to control for differences in particle size and reactive surface area. The concentration of C released from the reaction was monitored and recorded every 6 s for the length of the reaction. Data were fit with both a pseudo-first order kinetic model and a Weibull model for comparison. The latter outperformed the pseudo-first order kinetic model and the Weibull parameter, λ, fit to titration data from unknown samples was compared to λ values fit to data from mixtures of known fractions of pure calcite and dolomite to quantitatively obtain the content of the two minerals. Dolomite fractions obtained by this method qualitatively compared well with values obtained by X-ray diffraction. Our method allows a precise and accurate measurement for both total carbonate and the ratio of calcite to dolomite in a sample.

**Abbreviations:** cal, calcite; C<sub>T</sub>, total dissolved inorganic carbon; DMSO, dimethyl sulfoxide; dol, dolomite; DTA, differential thermal analysis; ETA, ethanolamine; MS<sub>residuals</sub>, mean square of the residuals; PTFE, polytetrafluoroethylene; RMSE, root mean square error; SIC, soil inorganic carbon; XRD, X-ray diffraction.

The ability to accurately determine the fraction of calcite and dolomite composing the total carbonate in a sample is important in investigations of soil genesis, determination of mineral weathering and formation rates, reconstruction of paleoenvironments, and identification of sediment source areas (Levine et al., 1989; Long et al., 1997; Capo et al., 2000; Muhs et al., 2001; Bustillo and Alonso-Zarza, 2007). This ability has aided studies in discriminating pedogenic pathways of soil inorganic carbon (SIC) accumulation from those where soil carbonates have been inherited from lithogenic sources or precipitated as a result of groundwater processes and is, thus, important for accurately inventorying true SIC sequestration (Bellanca and Neri, 1993; Wang and Anderson, 2000). In addition, investigations that use stable isotopes of paleosol carbonates—such as paleoclimatic and paleohydrologic reconstructions—depend on an accurate determination of the calcite and dolomite content in a sample.

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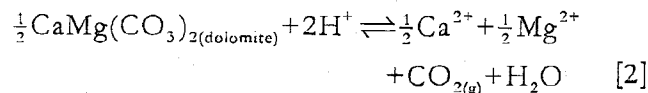
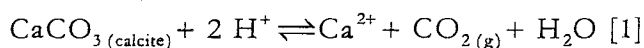
Methods for quantitatively determining calcite and dolomite in a soil sample can be distinguished on the basis of the principles they employ (Loeppert and Suarez, 1996). There are four basic categories of methods: differential kinetic, selective dissolution, X-ray diffraction (XRD), and differential thermal analysis (DTA). Unlike selective dissolution, XRD, or DTA methods, differential kinetic methods monitor the CO<sub>2</sub> gas liberated from carbonate minerals when reacted with a strong acid using manometric or volumetric techniques (Skinner and Halstead, 1958; Skinner et al., 1959; Dreimanis, 1962; Evangelou et al., 1984). Many laboratories can readily adapt standard manometric procedures to quantify calcite and dolomite fractions in a sample using the principle employed in differential kinetic methods because such procedures are often used to determine total carbonate in a sample. As a result, these methods tend to be commonly used over methods that require more expensive instrumentation and time-consuming procedures (e.g., XRD or DTA).

Although the use of coulometric titration appears to be somewhat limited in soil or paleosol investigations, it has been a common method used in other Earth sciences for determining the total inorganic C of rock and water samples (Herrmann and Knake, 1973; Engleman et al., 1985; Chan, 1986; Dickson and Goyet, 1994). As with standard manometric procedures, coulometric titration measures the CO<sub>2</sub> evolved from the reaction of a sample with a strong acid. By measuring the CO<sub>2</sub> coulometrically, however, it overcomes the problem inherent in manometric or volumetric determinations of CO<sub>2</sub> by not requiring an empirically based calibration (Jackson and Roof, 1992). Moreover, unlike other titrimetric methods, coulometric titration has the advantage of not requiring the standardization of a titrant (Huffman, 1977).

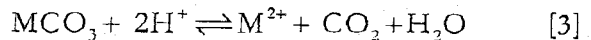
The objective of our study was to quantify calcite and dolomite fractions using continuous coulometric titration and, thus, expand the techniques used in differential kinetic methods. We are aware of only one study that has attempted to quantify various fractions of carbonate using coulometric titration where the CO<sub>2</sub> evolved in the reaction with acid was continuously monitored (Morrison et al., 1990). Although Morrison et al. (1990) were able to distinguish and quantify siderite from the total carbonate in the rock samples used in their study, they were not successful in distinguishing calcite from dolomite. Our aim was to overcome the limitations in Morrison et al. (1990) by grounding the description of the reaction rates of calcite and dolomite in a more theoretically based kinetic model.

## THEORY

Differential kinetic methods take advantage of the difference in reaction rates between calcite and dolomite in quantifying the relative abundance of the two minerals. Soil carbonate dissolution can be described by the following reactions (Loeppert and Suarez, 1996):



or expressed more generally following Evangelou et al. (1984):



where M represents either Ca or Ca and Mg with the appropriate stoichiometric coefficients (i.e., Eq. [1] and [2]). Given that the concentration of the acid greatly exceeds that of total dissolved inorganic carbon (C<sub>T</sub>) throughout a dissolution experiment (i.e., [H<sup>+</sup>] >> C<sub>T</sub>), a pseudo-first order rate law can be written in integrated form for the general reaction in Eq. [3] as:

$$Q_\infty - Q_t = C_0 \exp[-kt] \quad [4]$$

where Q<sub>∞</sub> is the total inorganic carbon in the sample, Q<sub>t</sub> is the inorganic carbon released as CO<sub>2</sub> at time *t*, *k* is the pseudo-first order rate constant, and C<sub>0</sub> represents the total inorganic carbon initially in the sample (i.e., C<sub>0</sub> = Q<sub>∞</sub>) but can be treated as a fitting parameter. This equation holds only for pseudo-first order kinetics; a departure from linearity in the ln[Q<sub>∞</sub> - Q<sub>t</sub>] vs. *t* plot would severely limit its application in describing the kinetics of the reaction. Reasons for a linear departure include a reaction order different from unity (i.e., the reaction is actually fractional, higher, or mixed order), the existence of a surface-controlled mechanism in the reaction, or the presence of multiple particle sizes (Stumm, 1992; Sparks, 2003). This is especially important for samples containing both calcite and dolomite since the extent to which transport-controlled or surface-controlled mechanisms govern the dissolution of dolomite remains uncertain (Morse and Arvidson, 2002). A more general expression than Eq. [4] is, thus, needed to describe systems with kinetics of heterogeneous processes.

One such expression is the Weibull model which has been used to describe the kinetics of crystal growth (Kolar-Anic et al., 1975). A generalized form of this model can be written as:

$$Q_t / Q_\infty = A - D \exp[-(t/\lambda)^n] \quad [5]$$

where *A* represents the asymptote of the reaction, *D* is the difference between the asymptote and the intercept, λ and *n* are fitting parameters that represent the scale and shape of the curve, respectively, and the rate parameter of the curve is equal to λ<sup>-*n*</sup> (Kolar-Anic et al., 1975; Ratkowsky, 1983). Although *A* and *D* in Eq. [5] may be treated as fitting parameters, their values should both be close to unity since Q<sub>t</sub>/Q<sub>∞</sub> ranges from zero at the beginning of the experiment to unity at the termination of the experiment.

In the carbonate dissolution experiment described here, a strong acid is introduced to a sample containing a mixture of calcite and dolomite and the CO<sub>2</sub> evolved from the reaction is monitored with time via coulometry (Fig. 1). Unlike manometric or volumetric methods, coulometry directly measures CO<sub>2</sub>

released from the reaction by titration (Sixta, 1977). Parameters from the kinetic model (i.e., Eq. [4] or [5]) fit to the data are compared to a standard curve—prepared by reacting known mixtures—and the fraction of calcite and dolomite summing to the total carbonate in the sample is determined.

## MATERIALS AND METHODS

### Carbonate Standards

The calcite standard used in this study was obtained from Alfa Aesar (Production no. 44520) and the dolomite was a sample of the Lower Ordovician Cotter Dolomite collected from southwest Missouri. Both standards were crushed to  $<53\ \mu\text{m}$  with an agate mortar and pestle to homogenize the sample and minimize effects of differing particle sizes.

We checked the purity of these standards by XRD and by quantifying their total C. Standards were analyzed with an X-ray diffractometer equipped with a graphite crystal monochromator using  $\text{CuK}\alpha$  radiation. The XRD analyses of the powdered standards show that these are, indeed, sufficiently pure samples of calcite and dolomite; only small but detectable amounts of plagioclase and zircon are observed in the calcite pattern (Fig. 2). The dolomite pattern shows minor components of calcite, Mg-calcite, and quartz. The effect of these impurities is assumed to be negligible on the kinetics of the reaction because the intensities of these peaks are small relative to the intensity of the primary dolomite peak ( $<3\%$ ). Total carbon, analyzed by coulometry (Chan, 1986), for the calcite and dolomite standards were  $0.122$  and  $0.129\ \text{kg C kg}^{-1}\ \text{mineral}^{-1}$  (corresponding to impurity concentrations of  $<2$  and  $<1\%$ ), respectively, and supported the conclusion that these were sufficiently high purity standards.

A set of known mixtures of the standards was prepared to contain approximately 0, 0.1, 0.25, 0.5, 0.75, 0.9, and 1 mass fraction of calcite per combined total of calcite and dolomite. Approximately 10 mg were prepared before each run in polytetrafluoroethylene (PTFE) cups and used to create the standard curve from which calcite and dolomite fractions could be determined in the unknown samples.

### Samples

Samples used in this study were collected from an outcrop exposure of the Upper Jurassic Morrison Formation in Shooting Canyon, Garfield County, Utah. The canyon wall exposes lacustrine and lake-margin sandstones, siltstones, and mudstones, fluvial sandstones, and interbedded crevasse-splay and levee sandstones and mudstones, all of which are pedogenically modified to immature paleosols of the Tidwell and lower Salt Wash members of the Morrison Formation (Hasiotis, 2004; Demko et al., 2005). Paleosols are interpreted as Protosols and Argillisols (sensu Mack et al., 1993), and carbonate is present as nodules and cements, though it is not particularly abundant (Demko et al., 2004; Hasiotis, 2004). We targeted this local-

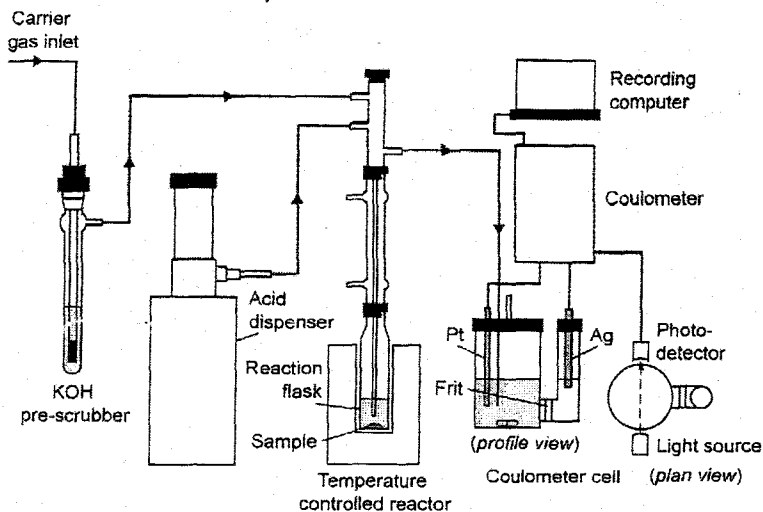


Fig. 1. Diagram of the acidification module and coulometer system (CM5230 and CM5015, UIC Inc., Joliet, IL) used in this study. Modified from Banisek (2009).

ity because previous investigations into economically recoverable uranium and vanadium identified co-occurring calcite and dolomite (Northrop et al., 1990). For the present study, hand specimens were collected at 0.5-m intervals in a vertical section measured along the canyon wall. Samples and standards were prepared similarly. Hand specimens were cut and polished to reveal fresh surfaces from which residue was removed by drilling. Sample residues were crushed to  $<53\ \mu\text{m}$ , homogenized, and weighed in PTFE cups before introduction into the coulometer.

### Continuous Coulometric Titration

A coulometer (CM5015, UIC Inc., Joliet, IL) was used to continuously monitor the C arising from the reaction of acid with the sample in a detachable reaction flask (Fig. 1). Weighed

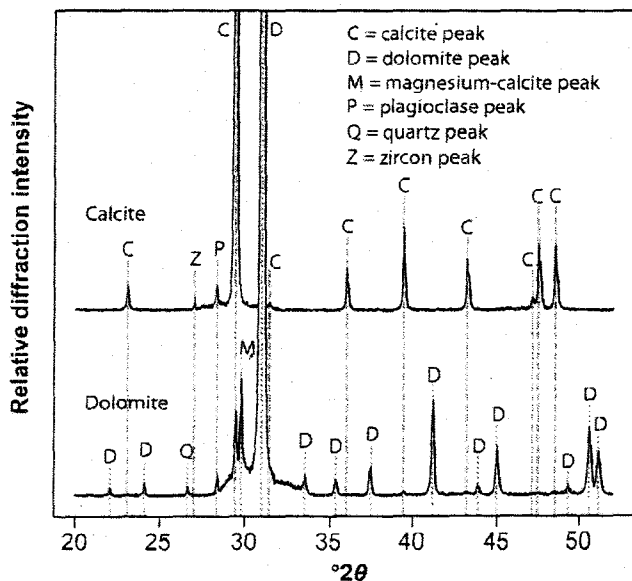
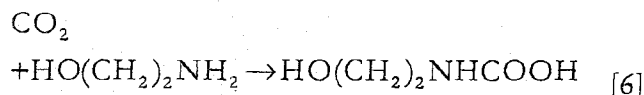
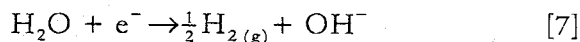


Fig. 2. X-ray diffraction patterns of the pure calcite and dolomite standards used in this study. *d*-Spacings for the calcite, dolomite, Mg-calcite, quartz, and zircon peaks are given by Brown and Brindley (1980) and the plagioclase peak by Jackson (2005).

and recorded samples containing approximately 10 mg of carbonate were introduced to the flask in 250  $\mu$ L PTFE cups. The sides of the flask were rinsed with 10 mL of deionized water to ensure that no sample residue adhered to the sides of the flask. The flask was reattached to the instrument and the system purged of  $\text{CO}_2$  for 60 s with a gas stream initially scrubbed of  $\text{CO}_2$  with 8 M KOH. After the appropriate purge time, 10 mL of 2 M  $\text{HClO}_4$  was dispensed in the reaction flask and the  $\text{CO}_2$  evolved from the reaction was carried by the gas stream at a constant rate of 100  $\text{mL min}^{-1}$  to the cathode compartment of a coulometer cell. The compartment was separated from an anode by a glass frit and contained a Pt-cathode and mixture of water, ethanolamine (ETA), thymolphthalein (a colorimetric pH indicator), and tetraethylammonium bromide in dimethyl sulfoxide (DMSO) (Engleman et al., 1985; Dickson and Goyer, 1994). The  $\text{CO}_2$  is absorbed by reaction with ETA:



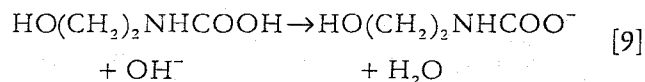
and the hydroxyethylcarbamic acid produced causes the color indicator of the cathode solution to fade (Dickson and Goyer, 1994). The fade in the color indicator, detected as an increase in percent transmittance at 612 nm using a photodetector (Huffman, 1977), triggers an electric current to be passed through the solution to generate titrant according to the reaction (Dickson and Goyer, 1994):



while silver is dissolved at the anode:



in a saturated solution of potassium iodide in water and DMSO to form  $\text{AgI}_2^-$ . The reaction in Eq. [6] is neutralized by the production of base in Eq. [7] as the reaction:



and the gram equivalent weight of  $\text{CO}_2$  is calculated from the quantity of electricity needed to titrate the hydroxyethylcarbamic acid using Faraday's laws of electrolysis (Johnson et al., 1985). Micrograms of C were recorded at intervals of 6 s for at least 8 min and until the reaction was determined to be complete. The end point was signaled when readings separated by 24 s were consistently  $<0.1\%$  different.

## Statistics

Linear and nonlinear regression analyses were conducted with the R 2.10.1 statistical language (R Development Core Team, Vienna, Austria). Nonlinear Weibull parameter fits were conducted with the SSweibull function following Ratkowsky (1983). We used the root mean square error (RMSE) to quantify the uncertainty associated with the prediction of mass fraction of calcite:

$$\text{RMSE} = \sqrt{\frac{(f_{\text{cal}}^{\text{p}} - f_{\text{cal}}^{\text{a}})^2}{n}} \quad [10]$$

where  $f_{\text{cal}}^{\text{a}}$  and  $f_{\text{cal}}^{\text{p}}$  are actual and predicted fractions of calcite, respectively, and  $n$  is the number of samples.

## RESULTS AND DISCUSSION

### Kinetic Model Comparisons

The pseudo-first order kinetic model expressed in Eq. [4] appears to represent pure calcite (i.e.,  $f_{\text{cal}} = 1$ ) adequately ( $R^2 = 0.990$ ;  $P < 0.001$ ) although the curve moves noticeably away from approximately 10% of the points at the start of the reaction (Fig. 3a). A plot of  $\ln[Q_\infty - Q_t]$  vs.  $t$  (not shown) does exhibit a strong linear relationship for pure calcite over most of its

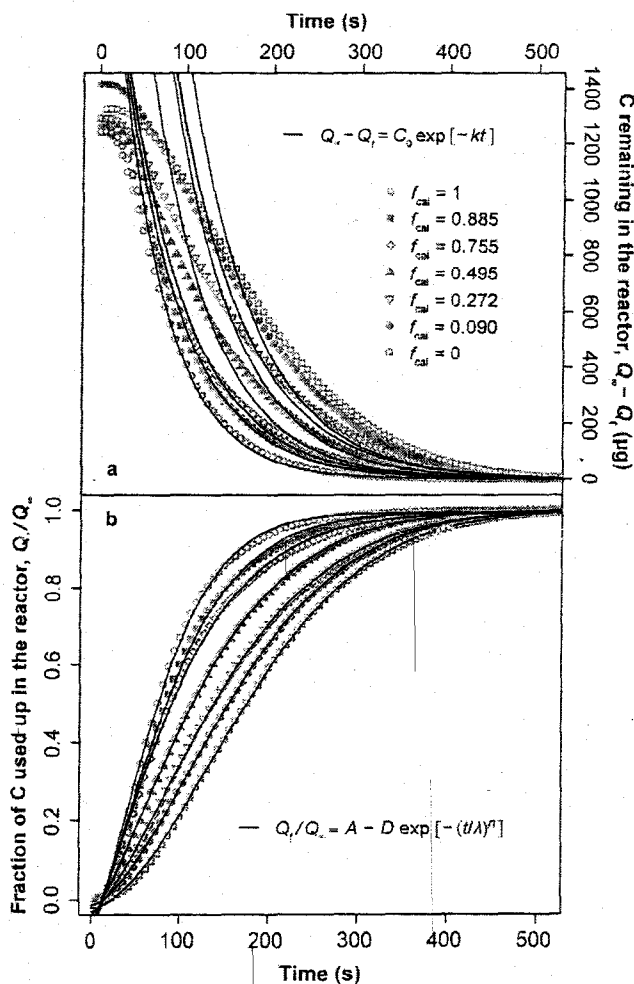


Fig. 3. (a) Pseudo-first order kinetic model (Eq. [4]) fit to the plot of inorganic C remaining in the reactor vs. time for seven mass fractions of calcite in the calcite-dolomite mixture ( $f_{\text{cal}}$ ). Ability of the model to describe the data worsens with decreasing  $f_{\text{cal}}$  values (i.e., increased dolomite content). The condition that  $C_0 = Q_\infty$  is relaxed to improve the fit. (b) Plot showing the fraction of inorganic C used up in the reaction vs. time. Significant improvement in fit is obtained with the Weibull kinetic model for all  $f_{\text{cal}}$  (Eq. [5]). Although  $A$  and  $D$  are treated as fitting parameters, they are not significantly different from unity.

range suggesting that a pseudo-first order expression is appropriate for samples where a large fraction of the carbonate is calcite. The model, however, performs progressively worse at predicting the reaction as the dolomite content of the sample is increased (i.e.,  $f_{\text{cal}}$  decreases; Fig. 3a). For example, when calcite comprises less than about 75% of the calcite-dolomite mixture by mass (i.e.,  $f_{\text{cal}} < 0.75$ ), only a few points, representing the middle and end of the reaction, fall on the curve. We observed a curvilinear relationship for plots of  $f_{\text{cal}} < 0.75$  using the linearized form of Eq. [4]. This suggests that when dolomite makes up more than 25% of the carbonate in a sample, pseudo-first order kinetics no longer describes the reaction. This may be due to the slow kinetics of dolomite dissolution making the reaction more complex, perhaps by addition of a surface-controlled mechanism (Stumm, 1992; Morse and Arvidson, 2002).

The Weibull model is a considerable improvement over the pseudo-first order kinetic model in describing the reaction from samples composed entirely of calcite to samples composed entirely of dolomite (Fig. 3b). The model performance actually improves slightly with increased dolomite content in the sample: for  $f_{\text{cal}} = 1$ , the mean square of the residuals ( $MS_{\text{residuals}}$ ) was  $9.37 \times 10^{-5}$ ; for  $f_{\text{cal}} = 0$ ,  $MS_{\text{residuals}}$  was  $1.10 \times 10^{-5}$  (lower  $MS_{\text{residuals}}$ -values reflect improvement; Logan, 2010). This drop in unexplained variation likely reflects the model's ability to be used in contexts where heterogeneous processes are responsible for the kinetics of the reactions—for example, where transport and surface-controlled kinetics are both operating.

The parameter,  $\lambda$ , in the Weibull model, which contains most of the nonlinearity in the function (Ratkowsky, 1983), showed the strongest correlation with  $f_{\text{cal}}$  ( $r^2 = 0.990$ ;  $P < 0.001$ ; Fig. 4). This parameter represents the scale or spread of the curve. As Fig. 3b displays, the more dolomite in the sample, the more spread is exhibited by the data, which is represented by increas-

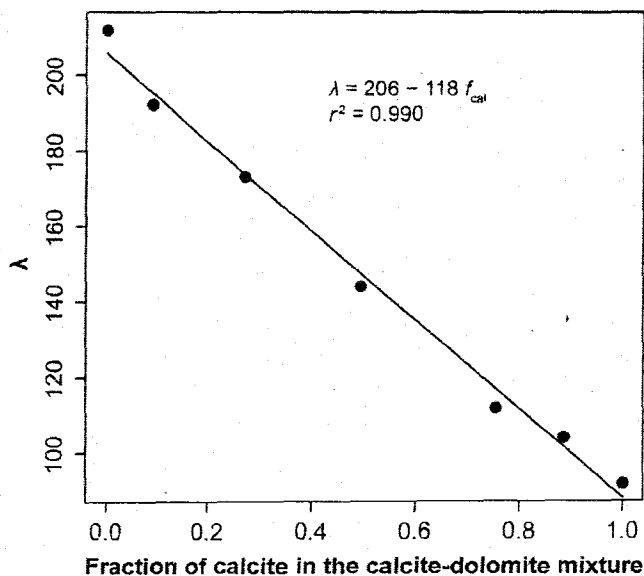


Fig. 4. Plot of the parameter,  $\lambda$ , obtained from the nonlinear least squares regression of the Weibull model in Fig. 3b against the fraction of calcite in the calcite-dolomite mixture,  $f_{\text{cal}}$ .

ing  $\lambda$  values. Figure 4 shows the plot of  $\lambda$  against  $f_{\text{cal}}$  for the fit Weibull curves in Fig. 3b and represents a single set of standards prepared and run on the same day. Thus, Fig. 4 illustrates a typical standard curve constructed from mixtures of calcite and dolomite that can be used to quantitatively determine  $f_{\text{cal}}$  in an unknown sample from the relationship between  $\lambda$  and  $f_{\text{cal}}$  (e.g.,  $f_{\text{cal}} = [\lambda - 206]/118$ ).

### Predicting Calcite and Dolomite Fractions

Prepared standard mixtures of calcite and dolomite were run on the coulometer at various times over approximately a 3-mo period. The plot of predicted calcite fraction against actual calcite fraction using the  $\lambda$  value along with the 95% confidence interval is displayed in Fig. 5. The regressed line through the plot is not significantly different from the 1:1 line ( $P_{\text{slope}} = 0.197$ ;  $P_{\text{intercept}} = 0.294$ ). In addition, the plot shows a very strong correlation ( $r^2 = 0.958$ ) indicating that the fit from the Weibull model can be used to quantify fractions of dolomite and calcite. The RMSE value for the regression was 0.0732 making the uncertainty of the prediction approximately  $\pm 7.3\%$ .

Seventy-nine samples taken from a section of both lithified sediments and paleosols at Shootaring Canyon, Utah, were run using the continuous coulometric titration procedure outlined earlier. The majority of samples is dominated by quartz and contains minor fractions of feldspars and rock fragments (Goldhaber et al., 1990). Clay minerals present include smectite, kaolinite, and chlorite (Goldhaber et al., 1990). Results from the run were compared to a nearby core (<2 km away from the outcrop) that was run for dolomite fraction (i.e., dolomite/[dolomite+calcite]) using a semiquantitative XRD technique (Northrop et al., 1990). The intensities of the primary dolomite and calcite peaks on the XRD pattern from prepared powdered mounts were used to form a ratio representing respective fractions of the two minerals in the sample (Northrop, 1982; Northrop et al., 1990).

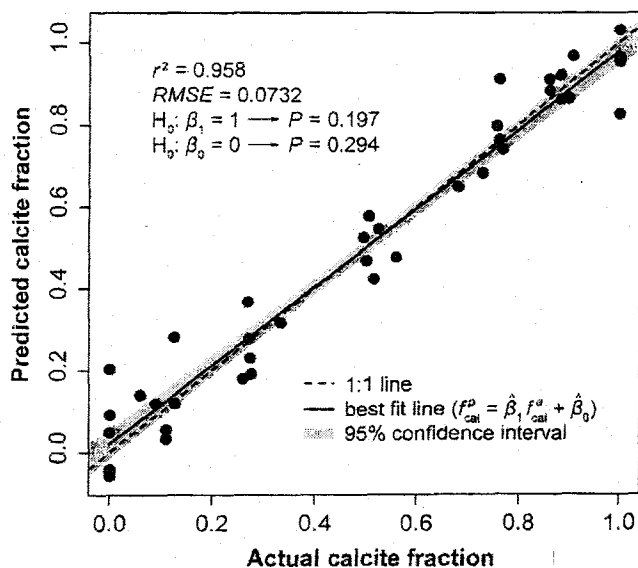


Fig. 5. Plot of calcite fraction predicted from the Weibull parameter  $\lambda$  against actual calcite fraction. Slope and intercept of the regressed line do not significantly differ from 1 and 0, respectively.

Figure 6 plots the data for comparison. We correlated samples taken from the section in this study with the core samples of Northrop et al. (1990) using the contact between the Salt Wash and Tidwell members as a stratigraphic marker. Our method captured the overall  $f_{\text{dol}}$ -depth function through the range of comparison. Exact peak matching is tenuous at best, however, because Northrop's (1982) semiquantitative procedure makes direct comparison difficult. In addition, some variation in the  $f_{\text{dol}}$ -depth function is expected because lateral variations in fluvial landscapes can alter vertical profiles over even short distances. Nevertheless, the range of variability with depth is in very good agreement with the results reported by Northrop et al. (1990). For example, between 20 and 70 m, our percent dolomite values range from 0 to 27 whereas Northrop et al. (1990) found the values to range from 7 to 36 using their XRD technique. Similarly, between -10 and 20 m, our values range from 10 to 87% compared with a range of 16 to 100% found by Northrop et al. (1990) in the same depth interval.

### Practicality of the Method

The Weibull model considerably improved the description of the carbonate dissolution reaction over the pseudo-first order kinetic model especially where dolomite made up a signif-

icant fraction of the carbonate in the sample. Although the model we employ is more sophisticated and requires the use of nonlinear regression compared to the simpler linear transformation of the pseudo-first order kinetic model, our model is relatively straightforward to use because nonlinear regression techniques are implemented in most of the common statistical software packages (e.g., R, S-PLUS, SAS, SPSS). In general, more accurate results are obtained using nonlinear regression as opposed to linear regression on transformed data because of estimator and standard error bias associated with reparameterization of the model (Glantz and Slinker, 1990). If, however, access to nonlinear regression techniques is limited, Eq. [5] can easily be linearized by assuming that the parameters  $A$  and  $D$  are equal to unity and taking the double logarithm of both sides.

Initial setup costs for our method are considerable and associated with the purchase of the coulometric titrator. Thus, we expect that the method would be most applicable where coulometric titration is already being used to determine inorganic C content of soils or paleosols. Preparation time to setup the entire standard curve (seven mixtures of calcite and dolomite) was approximately 1.5 h after the instrument was initially warmed-up (~2 h) and blanks and internal standards run (~1 h). A typical sample run time was between 10 and 12 min.

### CONCLUSIONS

We report, apparently for the first time, that continuously monitored coulometric titration can be successfully used to determine calcite and dolomite fractions in soil and paleosol samples. The Weibull model outperformed the pseudo-first order model in describing the kinetics of the reaction. The parameter,  $\lambda$ , obtained by fitting the Weibull model to the data, easily distinguished between calcite and dolomite and can be used to quantify carbonate fractions in an unknown sample when compared against a standard curve. As with other differential kinetic methods, our procedure allows for the simultaneous determination of total inorganic C and the quantity of calcite and dolomite in a sample (i.e., provided the calcite and dolomite are the only significant minerals comprising the carbonate fraction). Thus, to the list of methods for quantitatively determining calcite and dolomite fractions in a sample, we add continuous coulometric titration.

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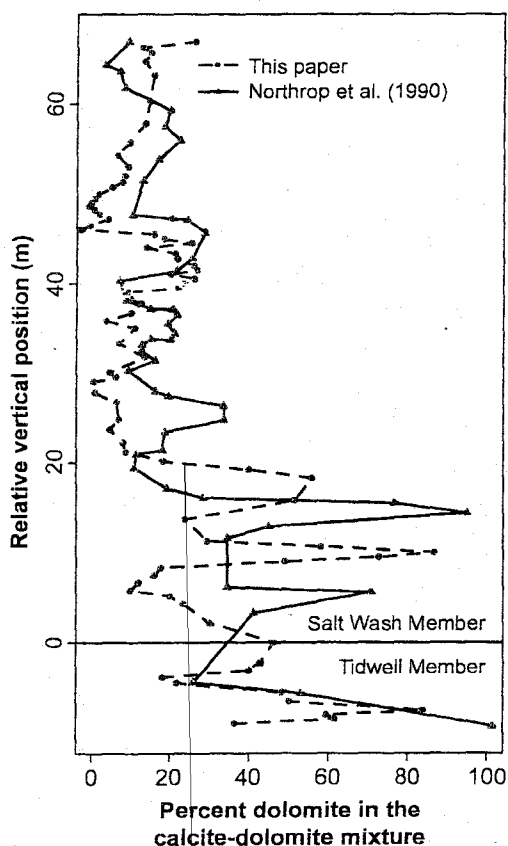


Fig. 6. Comparison of percent dolomite with depth measured by continuous coulometric titration in this study on samples taken in Shooting Canyon, Utah, against percent dolomite measured using the ratio of the primary dolomite to calcite X-ray diffraction peaks in a core taken by Northrop et al. (1990). The core was taken <2 km away from the samples taken in this study.

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