

A Simple Method to Determine the Reactivity of Calcium Carbonate in Soils

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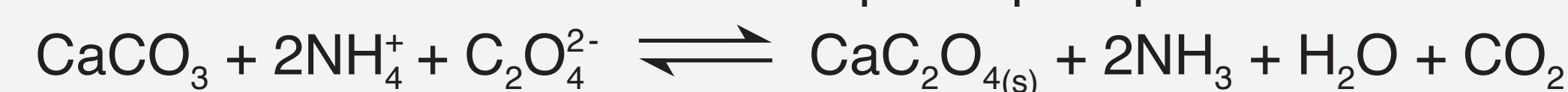
BACKGROUND

The reactive quantity of calcium carbonate—that is, active CaCO_3 or ACC—in soils influences adsorption and precipitation reactions, volatilization of ammonia, micronutrient availability, and water retention, and is important for pedogenic interpretations. Several procedures have been proposed in the literature for estimating ACC including methods that characterize particle-size distribution of the carbonate fraction, rely on acid dissolution kinetics, or involve the surface complexation of Ca. Perhaps the most common of the surface complexation procedures accounts for the difference in concentrations of an oxalate solution measured by titration with potassium permanganate before and after reaction with a sample. However, KMnO_4 takes approximately 24 hours to prepare, requires standardization, and has a relatively short shelf life making the procedure cumbersome for routine analysis. Also, one of the major sources of error is the presence of exchangeable Ca which reacts with oxalate in the extractant.

Objective: We sought to develop a simple and reliable method for determining ACC in soils by modifying the oxalate procedure. This modification should remove both the need for KMnO_4 and the interference from exchangeable Ca.

THEORY

Dissolved ammonium oxalate will react with ACC in a soil sample to precipitate calcium oxalate via the reaction:



Conventional Approach: Oxalate used up in the reaction is determined as the difference between the initial and final concentrations of oxalate in the extracting solution. Potassium permanganate is used to determine the final concentration in the solution through the following reaction:



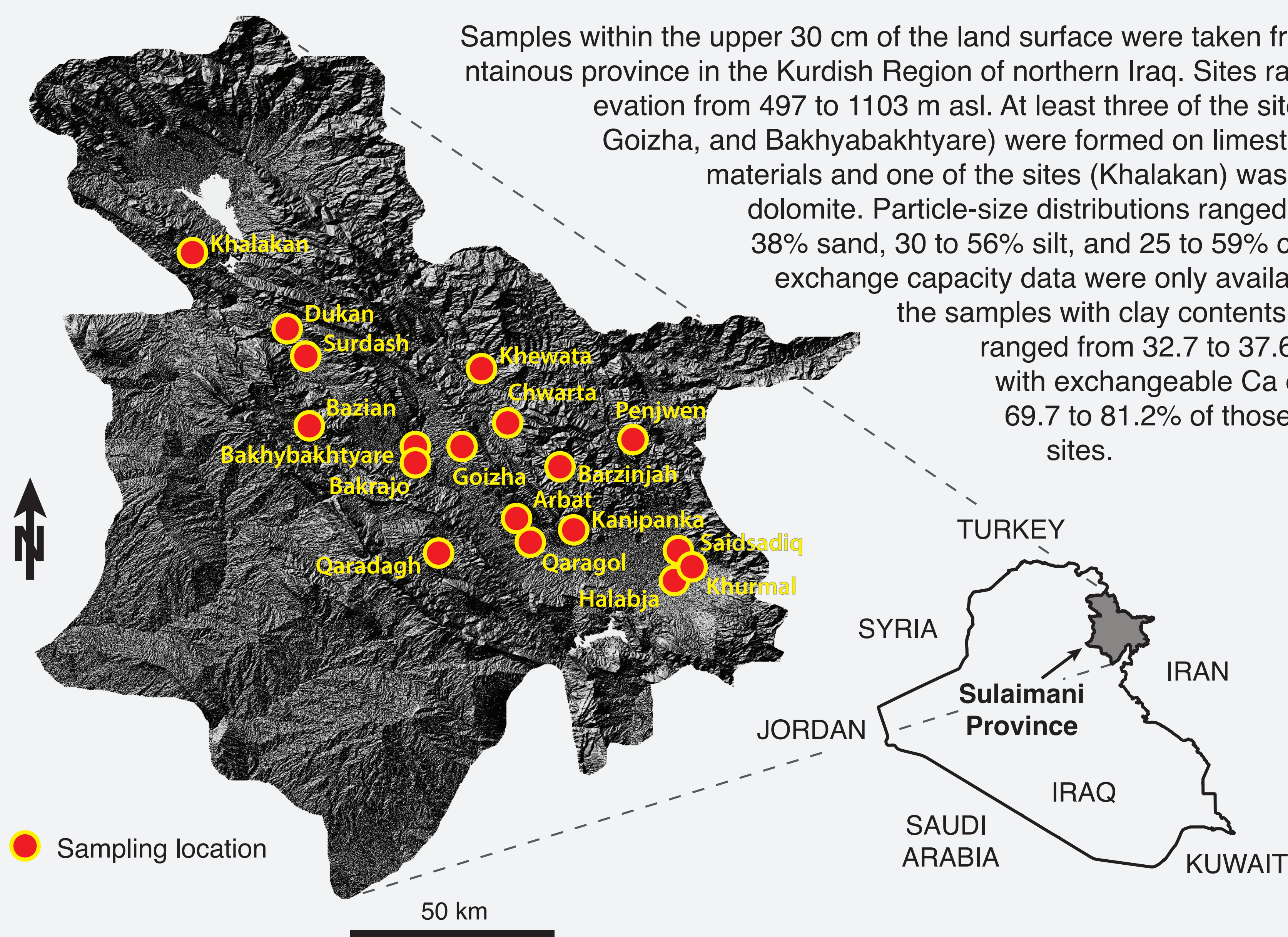
The mass fraction of ACC (f_{ACC}) in the sample is determined as:

$$f_{\text{ACC}} = \frac{100 V_{\text{el}} [C_{\text{e}} V_{\text{a}} - V_{\text{i}} C_{\text{i}} (5/2)]}{V_{\text{a}} M_{\text{s}}}$$

where V_{e} = volume of the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ extractant solution used in the procedure, C_{e} = extractant molar concentration, V_{i} = volume of KMnO_4 used to titrate an aliquot volume (V_{a}) of the extractant after reaction with ACC, C_{i} = titrant molar concentration, M_{s} = sample mass, $5/2$ = stoichiometric molar ratio of $\text{C}_2\text{O}_4^{2-}:\text{Mn}^{2+}$ in the previous reaction, and 100 = formula weight of CaCO_3 .

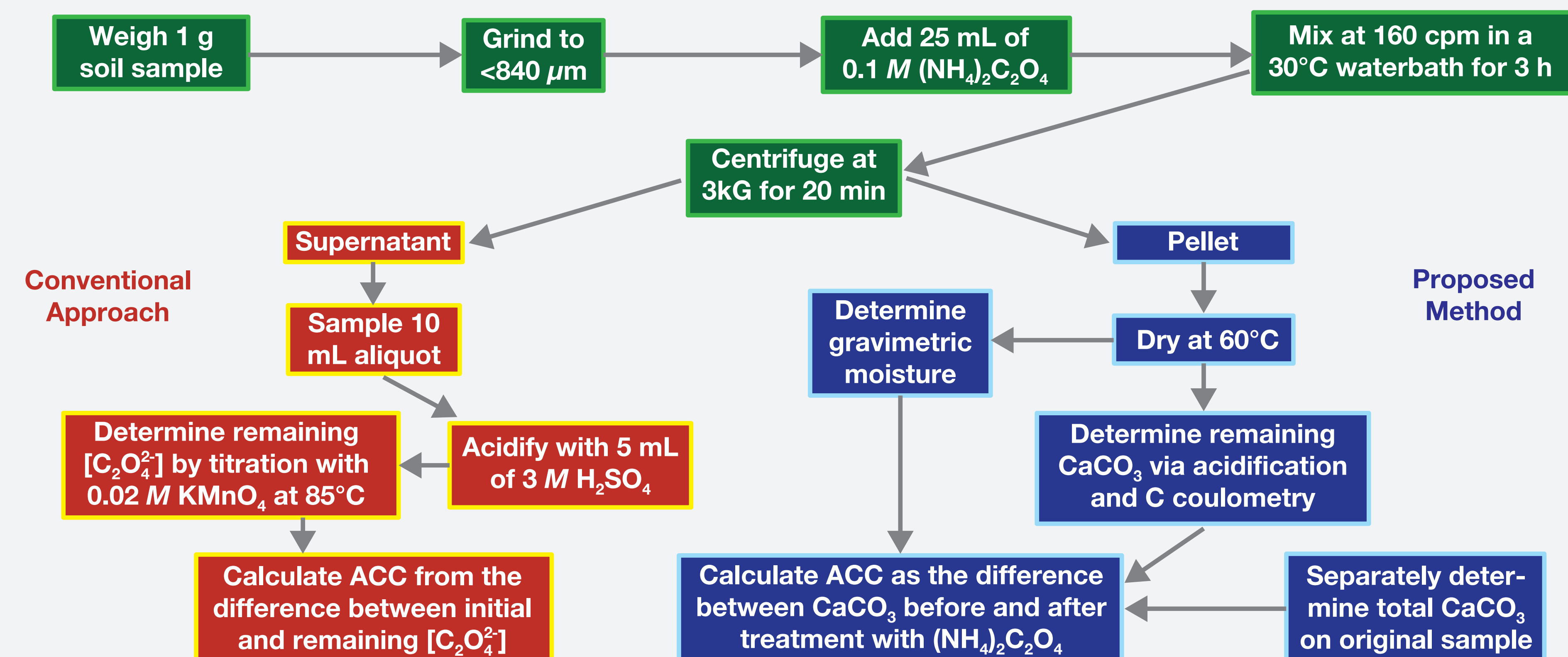
Proposed Method: The mass fraction of ACC is calculated as the difference between the mass fractions of CaCO_3 determined from an acidification and coulometric titration procedure in samples reacted and unreacted with $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

SAMPLES

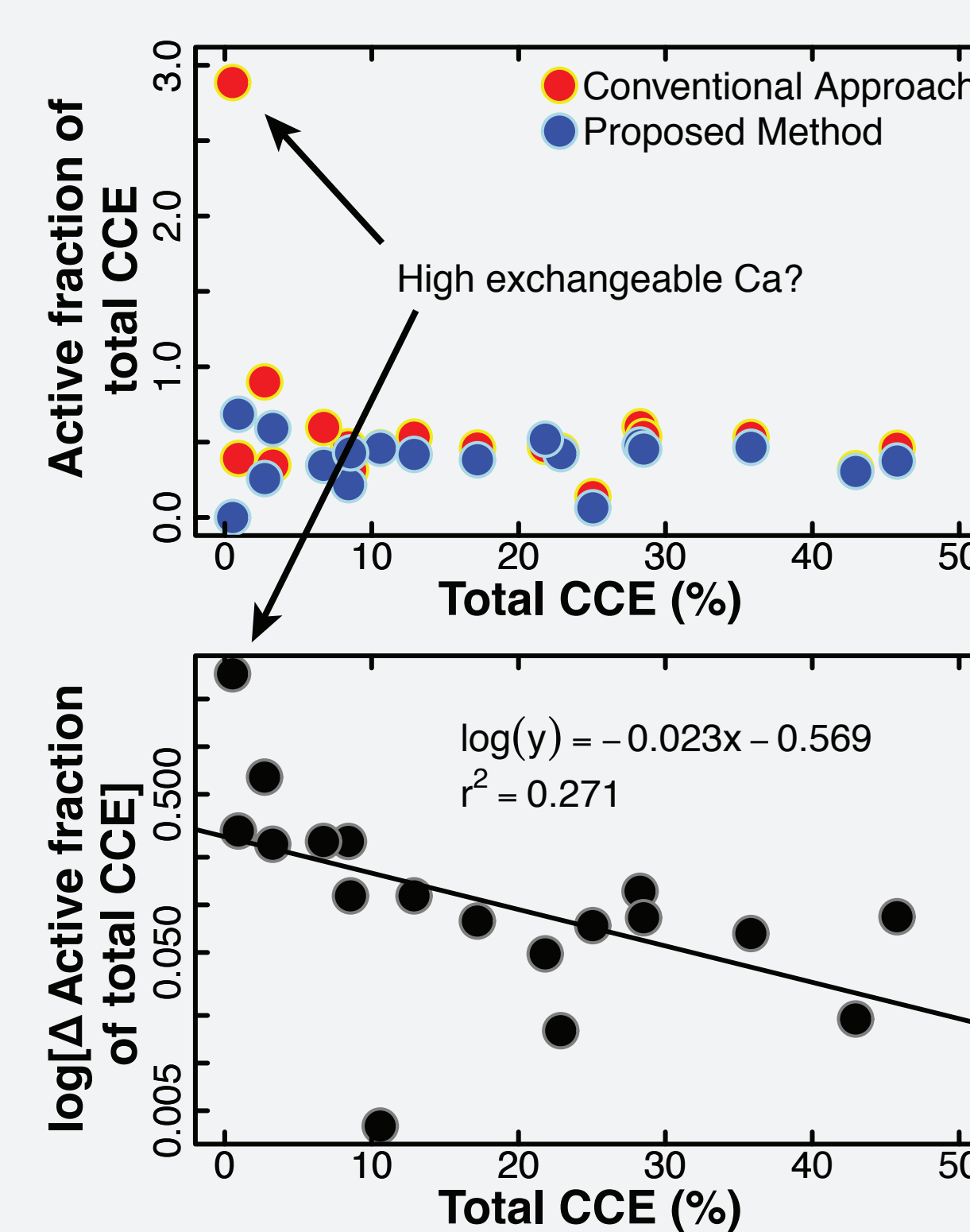


Samples within the upper 30 cm of the land surface were taken from a mountainous province in the Kurdish Region of northern Iraq. Sites ranged in elevation from 497 to 1103 m asl. At least three of the sites (Dukan, Goizha, and Bakhybakhtyare) were formed on limestone parent materials and one of the sites (Khalakan) was formed on dolomite. Particle-size distributions ranged from 27 to 38% sand, 30 to 56% silt, and 25 to 59% clay. Cation exchange capacity data were only available on 4 of the samples with clay contents >43% and ranged from 32.7 to 37.6 $\text{cmol}_c \text{kg}^{-1}$ with exchangeable Ca comprising 69.7 to 81.2% of those exchange sites.

PROCEDURE

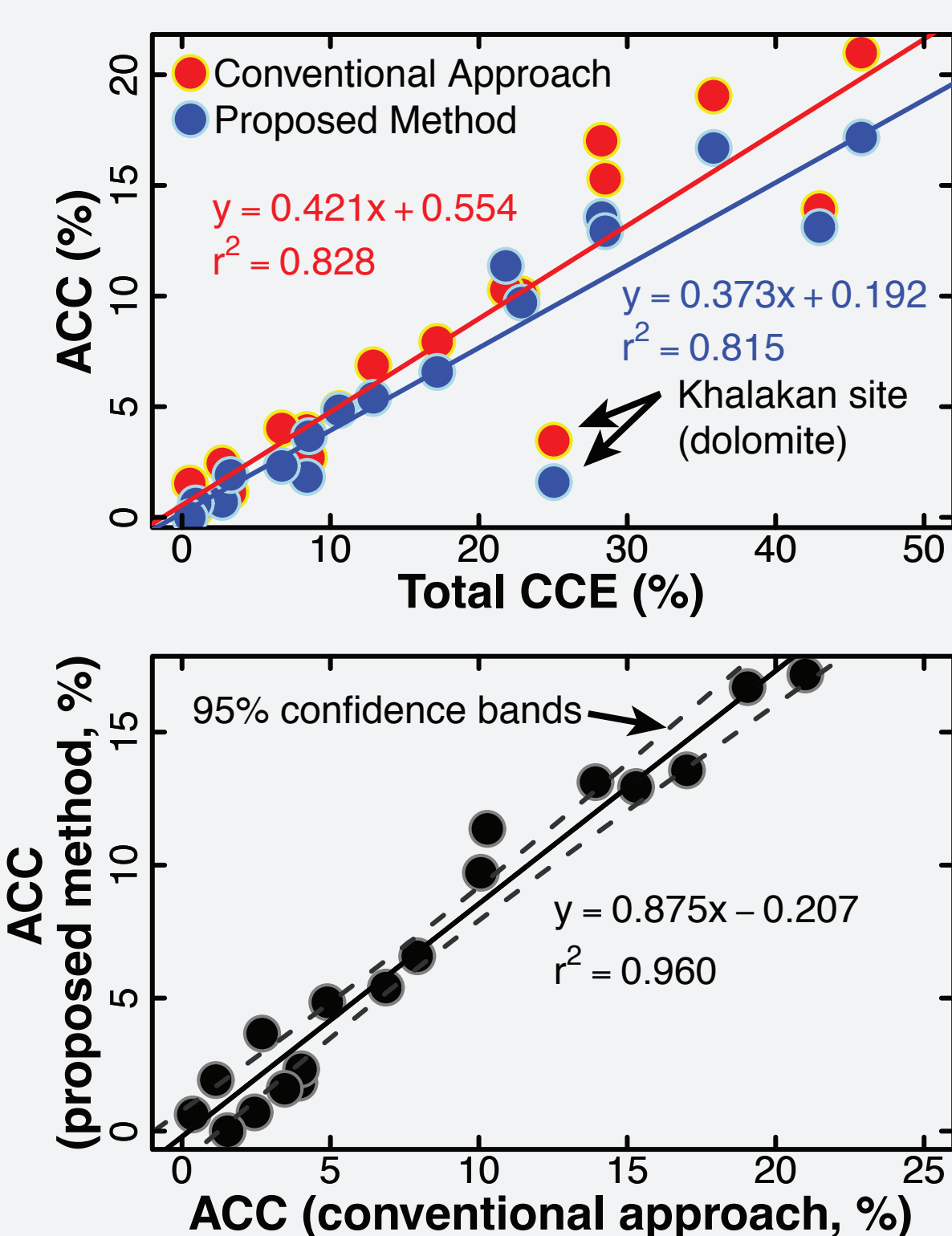


RESULTS



The active fraction of the total calcium carbonate equivalent (CCE) in the samples remained relatively constant across the wide range of CCEs (0.4 to 46% CCE). One notable deviation from this trend was the Barzinjah sample with a non-sensical value of nearly 3 times the total CCE in the sample. One plausible explanation for this high value is the likely presence of high exchangeable Ca; this sample contained approximately 59% clay.

With respect to the active fractions of total CCE, the largest differences between the two procedures occurred at the lowest CCE contents. This is due to the increasing sensitivity of the low range of total CCE due to the effect of small deviations in ACC on the fraction of total CCE. In this range (i.e., <20% CCE), significant errors in the conventional approach can occur due to the presence of exchangeable Ca. The deviation in ACC between the two procedures also suggests the presence of exchangeable Ca in the samples: ACC values determined by the conventional approach had a higher slope (0.421) than those determined by the proposed method (0.373) suggesting the new method is insensitive to the presence of exchangeable Ca. Values from the two procedures were highly correlated and exhibited a large coefficient of determination (0.960).



CONCLUSIONS

The proposed method performed as well as the conventional approach with ACC determined from the difference between the carbonate fractions of samples before and after reaction with ammonium oxalate showing a high correlation with the ACC determined from titration of the remaining oxalate using potassium permanganate. The method was considerably faster than the conventional approach and was unaffected by the assumed presence of exchangeable Ca which can significantly affect final oxalate concentrations especially in samples with modest amounts of carbonate. Thus, the proposed method is particularly well suited for samples with relatively low amounts of ACC or CCE.

Future work: Oxalate should be reacted with the active carbonate during coulometric titration to continuously monitor the CO_2 evolved during the precipitation of calcium oxalate to further simplify and expedite the procedure. Because the reaction of oxalate and CaCO_3 proceeds on the order of hours, the shape of the evolved CO_2 vs. time curve for the whole reaction should be determined in order to predict total CO_2 evolved using only measurements near the start of the reaction.

ACKNOWLEDGMENTS

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