

Mineralogical Distinctions of Carbonates in Desert Soils

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ABSTRACT

Soil carbonate-C is a large pool of C and, in desert environments, is the dominant type of C stored in soil. To more fully understand the global C cycle and the role of soil in C sequestration, it is important to recognize how C enters and leaves the carbonate pool, as well as identify the forms of carbonate that exist in the soil. In the Desert Project in southern New Mexico, soils formed in limestone and igneous (mostly quartz monzonite and some rhyolite) parent materials lie adjacent to each other, with climate, vegetation, topography, age, and, to a large extent, dust deposition constant across the soils of both parent materials. The purpose of this study was to determine if X-ray diffractometry (XRD) can mineralogically identify the size fraction in which pedogenic carbonate occurs and discern differences among (i) pedogenic carbonate formed in limestone parent material, (ii) pedogenic carbonate formed in igneous parent material, and (iii) soil carbonate in the form of detrital limestone. The diffractograms revealed that the size fractions in which pedogenic carbonate occurs in a dolostone residuum are fine sand, silt, and clay. X-ray diffraction could not discern differences in soil carbonate because calcite was the only carbonate mineral present in the samples of pedogenic carbonate formed in limestone parent material, pedogenic carbonate formed in igneous parent material and detrital limestone. Excepting the d-spacing associated with a minor peak, statistical analysis found no significant differences in d-spacings among the three types of soil carbonate. However, each of the three types of soil carbonate revealed significant differences in d-spacings relative to those of the calcite reference. While XRD mineralogically revealed the size distribution of pedogenic carbonate formed in a dolostone residuum, for the purpose of C sequestration, XRD was unable to distinguish the three soil carbonate types.

ATMOSPHERIC CO₂ has steadily increased since about 1850 and is currently increasing at a rate of 0.5% per year (Lal, 2002), stimulating investigations into the numerous reservoirs and fluxes within the global C cycle. Soil carbonate is the major form of soil inorganic C, which, with a global reservoir of approximately 940 Pg (Eswaran et al., 2000), is the third largest C reservoir, surpassed only by the soil organic C and ocean reservoirs. In humid environments, soil carbonate is subject to leaching, but when mean annual precipitation is limited to approximately 50 cm (Birkeland, 1999), at least a portion of soil carbonate accumulates in the soil profile. In this way, carbonate in desert soils may provide a sink for atmospheric C (Scharpenseel et al., 1999; Monger and Gallegos, 1999; Monger and Martinez-Rios, 2000).

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Pedology

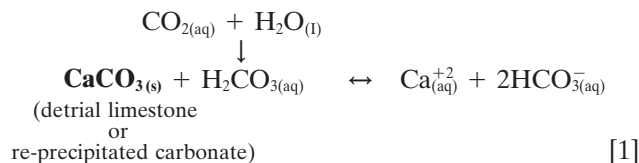
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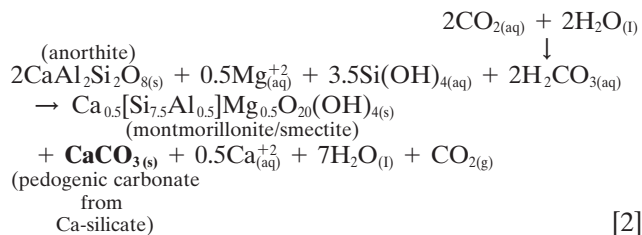
However, not all types of soil carbonate have the potential to sequester C from the atmosphere in a remediation timeframe of decades to centuries. For example, limestone detritus from the Permian Hueco Formation sequestered C over 240 million years ago (Kottlowski, 1975) and, for this reason, does not represent a sink for atmospheric C in a remediation timescale. On the other hand, delicate biotic features such as calcified fungal hyphae and root hairs found in Holocene soils of southern New Mexico may represent the process of C sequestration in a remediation timeframe (Kraimer, 2003). Further remediative evidence of carbonate pedogenesis was provided in a laboratory experiment when bacteria and fungi from a southern New Mexico soil precipitated carbonate crystals within a timespan of days to months (Monger et al., 1991a).

The ability of pedogenic carbonate to sequester atmospheric C depends on the source of Ca present during carbonate pedogenesis (Schlesinger, 1982). Pedogenic carbonate formed in desert soil of limestone alluvium, where the soil solution is generally alkaline, is described by Reaction 1 (Monger and Martinez-Rios, 2000).



During wet periods, atmospheric C introduced into the soil via root or microbial respiration combines with water to form carbonic acid which, in turn, dissolves the detrital limestone parent material to form two moles of bicarbonate ion. Upon desiccation, and subsequent re-precipitation of CaCO₃, the two moles of HCO₃⁻ generate one mole of reprecipitated CaCO₃ and one mole of CO₂, the latter ultimately being released back into the atmosphere. In this bidirectional process of dissolution and reprecipitation, no atmospheric C is newly garnered as soil carbonate.

Alternatively, pedogenic carbonate formed in igneous parent material can evolve as a weathering product (Bernier and Lasaga, 1989; Chadwick et al., 1994) via the incongruent dissolution of Ca-bearing silicates. For example, anorthite may follow Reaction 2 when weathered in the presence of a soil solution already containing magnesium ion and silicic acid (adapted from Sposito, 1989).



Abbreviations: XRD, X-ray diffractometry.

When root and microbial respiration generate two moles of CO_2 , one mole is sequestered in newly precipitated CaCO_3 and one mole may be released back into the atmosphere. However, as weathering proceeds, the products of Ca^{+2} , H_2O , and CO_2 may serve to sequester additional amounts of CaCO_3 . In this manner, pedogenic carbonate formed in igneous parent material may provide at least a partial sink subsequent to the photosynthetic harvesting of atmospheric C. Typical estimates of global C consumed during silicate weathering range from 6.0 to 6.6 Tmol yr^{-1} (Kump et al., 2000).

Soil carbonate occurs in lithogenic and pedogenic forms. Lithogenic soil carbonate, such as detrital limestone, generally occurs as coarse fragments most conclusively identified by the presence of aquatic fossils. Conversely, pedogenic carbonate exhibits a variety of forms, from disseminated crystals in interstitial voids to massive laminar-capped petrocalcic horizons (West et al., 1988). Although pedogenic carbonate can occur as euhedral spars (Monger et al., 1991b; Monger and Adams, 1996), it more commonly precipitates in the silt- and clay-size fractions (Rostad and St. Arnaud, 1970; St. Arnaud and Herbillon, 1973; Sobecki and Wilding, 1983; West et al., 1988; Bui et al., 1990). This is especially apparent in pedogenic carbonate associated with biotic features of the rhizosphere, such as calcified roots, root hairs, fungal hyphae, and needle-fibers (Kraimer, 2003). Mineralogical distinctions among particle-size classes of carbonate formed in a dolostone environment would both clarify previous research and confirm the size fraction in which pedogenic carbonate primarily resides.

Since chemical diversity may influence the type of carbonate mineral that precipitates from solution (Hurlbut and Klein, 1977), mineralogical examination may provide a basis to identify soil carbonate that can remediate sequester atmospheric C. While it is plausible to expect mineralogical differences between pedogenic carbonate formed in igneous parent material (Reaction 2) and pedogenic carbonate formed in limestone parent material (Reaction 1), mineralogical distinctions may also exist between detrital limestone and each of the two pedogenic carbonates. Although various ions can affect the mineralogy during carbonate formation (Kitano, 1962; Taft, 1967; Folk, 1974), Mg is by far the most influential ion in carbonate mineralogy. Previous research concluded that only sparse amounts of Mg are required to drastically reduce the rate of calcite formation (Bischoff and Fyfe, 1968). St. Arnaud (1979) further observed a relationship between Mg-bearing calcites in pedogenic carbonate and the soluble $\text{Mg}^{+2}/\text{Ca}^{+2}$ ratios of the underlying or associated horizons. Others reported that pedogenic carbonate accumulates as Mg-substituted calcite when dolomite is present (Bui et al., 1990), as pedogenic dolomite (Capo et al., 2000), or as biogenic magnesian calcite crystals produced by the heterotrophic soil bacterium *Myxococcus xanthus* (González-Muñoz et al., 2000). However, in a long-term study by Sherman and Barak (2000), no evidence of dolomite precipitation from saturation was found at ambient conditions. Others found that pedogenic carbonate accumulates as calcite only (Rostad and St. Arnaud, 1970) and, among the three CaCO_3 poly-

morphs, calcite is the most thermodynamically stable at surface conditions (Marion et al., 1990). Although aragonite is commonly found in shells of aquatic organisms (Deere et al., 1966), the eventual recrystallization of aragonite to calcite is spontaneous at earth surface conditions (Winland, 1969). Vaterite also occurs in aquatic shells (Deere et al., 1966) and was recently identified as a biogenic precipitate of soil microorganisms in a Chihuahuan Desert Aridisol of New Mexico (Lindemann et al., 2002) but, in the presence of Ca-enriched distilled water, vaterite rapidly recrystallizes to calcite (Taft, 1967). In addition, small amounts of organic matter may interact with the crystal surface and influence crystal morphology (Chadwick et al., 1988) or suppress the growth of calcite crystals (Bui et al., 1990).

In an attempt to distinguish soil carbonate which can remediate sequester atmospheric C (Reaction 2) from soil carbonate which cannot (Reaction 1), the objectives of this study were to determine if XRD can (i) mineralogically identify the particle-size fraction in which pedogenic carbonate resides and (ii) detect mineralogical distinctions among pedogenic carbonate formed in limestone parent material, pedogenic carbonate formed in igneous parent material, and detrital limestone. This project is part of a larger investigation into the efficacy of different analytical techniques for the purpose of distinguishing the different types of soil carbonate. In addition to XRD, isotopic and micromorphological distinctions are also being examined.

MATERIALS AND METHODS

There were two parts to this research project. It was first necessary to determine in which particle-size fractions pedogenic carbonate generally dominates to validate the use of these size fractions in the second part of the project. To this end, the first part of the project investigated the particle-size distribution of pedogenic carbonate with respect to mineralogy. In this part of the project d-spacings were not statistically scrutinized, but were electronically compared with references for the sole purpose of mineralogical identification. The second part of the project examined the occurrence of mineralogical distinctions among the different types of soil carbonate and utilized the size fractions of pedogenic carbonate that were determined in the first part of the project. In this second part of the project, d-spacings were statistically examined to determine if differences exist among the three types of soil carbonate.

Research Setting, Design, and Sample Preparation

Part I. Particle-Size Distribution of Pedogenic Carbonate

To confirm the size fraction in which pedogenic carbonate primarily resides, three sample sites were selected in soil formed in dolostone residuum on Tortugas Mountain (King and Kelley, 1980) near Las Cruces, NM (Fig. 1). The distance between each of the sample sites ranged from approximately 200 m to 1 km. At each site a soil sample was collected from the horizon of predominant Stage I carbonate accumulation (Gile et al., 1966), air-dried, and sieved into the following particle-size fractions: soil clasts > 4.75 mm, coarse sand (1.00–0.50 mm), fine sand (0.25–0.106 mm), and silt and clay (<0.053 mm). Silt- and clay-size fractions were separated by sedimentation and centrifugation in deionized water (Jackson, 1969), except no Na-hexa-

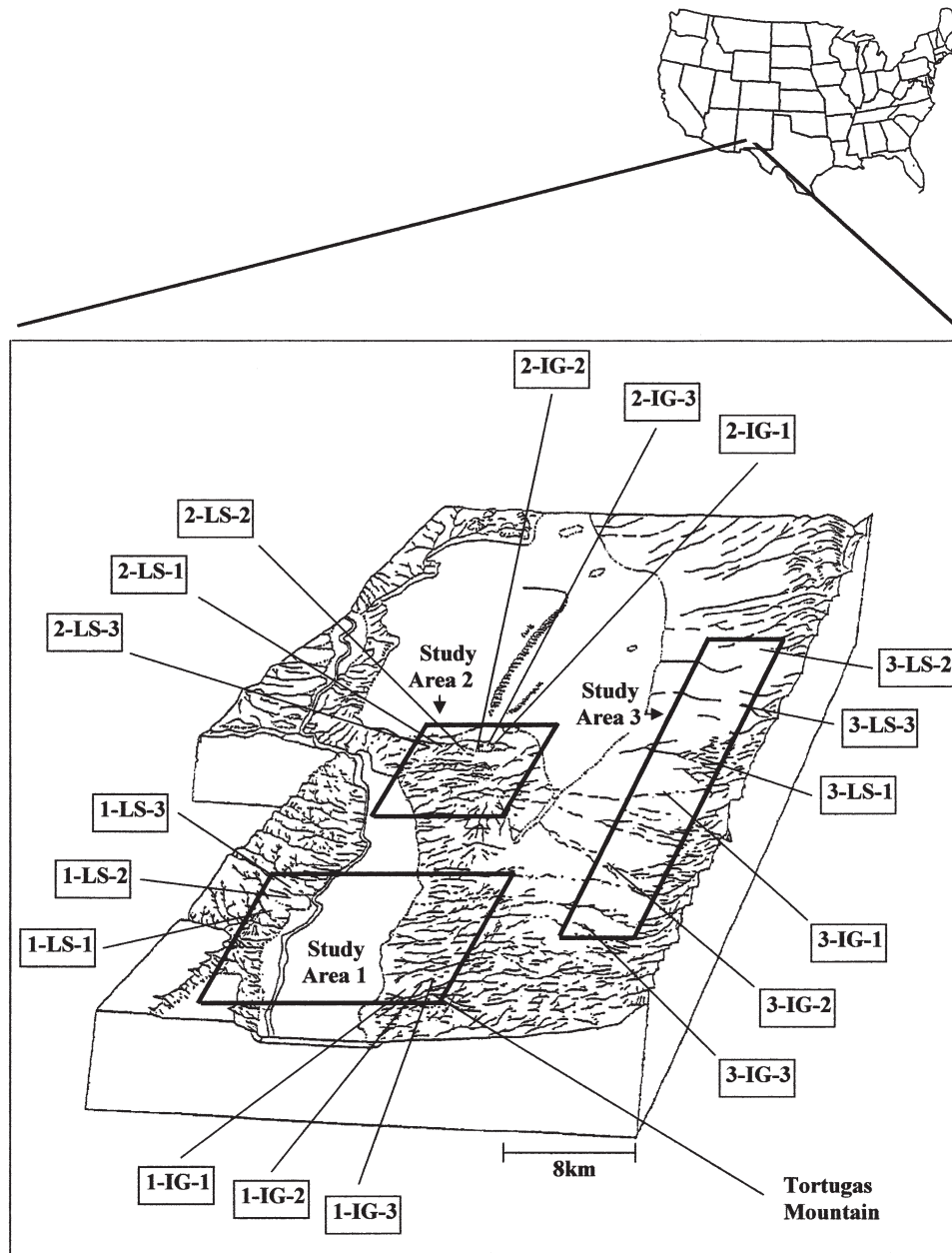


Fig. 1. Block diagram of the research project and location of each limestone (LS) and igneous (IG) sample site in Study Areas 1, 2, and 3 (adapted from Gile et al., 1981) where Study Area 1 is a fan terrace, Study Area 2 is a pediment, and Study Area 3 is a fan piedmont. Tortugas Mountain is the site of the dolostone study.

metaphosphate was used as a dispersing agent. Silt- and clay-size fractions were confirmed using petrographic microscopy. Surface clasts > 4.75 mm were also collected at each site and treated with 10% (w/w) HCl for about 2 to 3 min to remove surficial pedogenic carbonate. Each sample of surface clasts, soil clasts, coarse sand, and fine sand was ground with mortar and pestle until grittiness was no longer evident. Clay-size fractions were not ground.

Part II. Mineralogical Distinctions within Soil Carbonate

This study was conducted in the northern Chihuahuan Desert within the boundaries of the USDA-SCS Desert Soil-Geomorphology Project (Gile and Grossman, 1979; Gile et al., 1981; Gile et al., 1995) near Las Cruces, NM (Fig. 1). To mineralogically distinguish the three types of soil carbonate, the

research comprised three study areas that provided a basis for blocking and represented landforms typical of the region: Study Area 1 is a fan terrace, Study Area 2 is a pediment, and Study Area 3 is a fan piedmont. Within each study area, three soil samples were collected from soil formed in igneous parent material and three soil samples were collected from soil formed in limestone parent material. The igneous parent material was dominated by quartz monzonite containing k-feldspar, albite, and anorthite; rhyolite was also present at the igneous sites of Study Area 1 (Gile and Grossman, 1979; Seager, 1981). The distance between each limestone sample site ranged from approximately 30 to 100 m, 1 to 2.5 km, and 0.75 to 1.5 km, for Study Areas 1, 2, and 3, respectively. The distance between each igneous sample site ranged from approximately 300 to 400 m, 75 to 150 m, and 175 m to 10 km,

for Study Areas 1, 2, and 3, respectively. All soil samples were collected from the horizon of maximum carbonate expression, exhibiting Stage I carbonate morphology (Gile et al., 1966), in Holocene soils of the Organ or Fillmore geomorphic surfaces. To ensure the collection of pedogenic carbonate as determined in Part I of this project, all soil samples were sieved to pass 0.053 mm. Detrital limestone >4.75 mm was also collected from the surface of each limestone site within each study area and treated with 10% (w/w) HCl for about 2 to 3 min to remove surficial pedogenic carbonate. Each soil sample and detrital limestone sample was ground with mortar and pestle until grittiness was no longer evident. To ensure that grinding did not appreciably affect d-spacing, the <0.053 -mm size fraction of soil formed in limestone parent material and soil formed in igneous parent material were each ground for 2 and 4 min. The estimate of standard deviation as a routine assessment of precision (Snedecor and Cochran, 1980; Allmaras and Kempthorne, 2002) for the most prominent carbonate peak (104) was 0.009646 and 0.000085 for soil formed in limestone parent material (3-LS-2) and soil formed in igneous parent material (1-IG-3), respectively. Middle Holocene age among sample sites was confirmed by charcoal radiocarbon dates in Study Areas 1 and 3 (Gile et al., 1981) and inferred by the Stage I carbonates of the pediment soils at Study Area 2. All sample sites occur within an arid to semi-arid climate that has remained relatively constant since the modern climate was established approximately 5000 yr ago (Van Devender, 1990; Monger, 2003), inferring a reasonably consistent influ-

ence of climate on the rates of chemical, physical, and biological processes across the landscape (Brady and Weil, 2004). As evidence of the consistent influence by climate on the soil environment, Monger and Lynn (1996) found similar clay mineral contents of kaolinite and mica in soils of this age across the landscape of this project. Hence, the soils at all 18 sample sites developed in environments of similar age, biota, topography, and climate, with the two parent materials serving as treatments.

Mineralogical Analysis

During the course of the research project, a new XRD was acquired. This provided the opportunity to strengthen the experiment by comparing results from both manual and electronic measurements. In both studies, each sample was prepared for XRD analysis as a random powder mount. Manual measurements were made from strip charts of a Rigaku Geigerflex (Tokyo, Japan), denoted XRD #1, using $\text{CuK}\alpha$ radiation of $\lambda = 1.54178 \text{ \AA}$ at 40 kV, 25 mA, and 1000 counts min^{-1} at a $2\theta/\theta$ scale; reference calcite d-spacings occur at 3.8551, 3.0359, 2.8440, 2.4949, 2.2848, and 2.0946 \AA (Graf, 1961). Electronic measurements were made with a Rigaku Miniflex (Tokyo, Japan), denoted XRD #2, using $\text{CuK}\alpha$ radiation of $\lambda = 1.54178 \text{ \AA}$ at 30 kV, 15 mA, and 1000 counts min^{-1} at a $2\theta/\theta$ scale where calcite #47–1743, dolomite #36–0426, and quartz #46–1045 references were used for identification and the centroid algorithm was used for pattern processing (JADE,

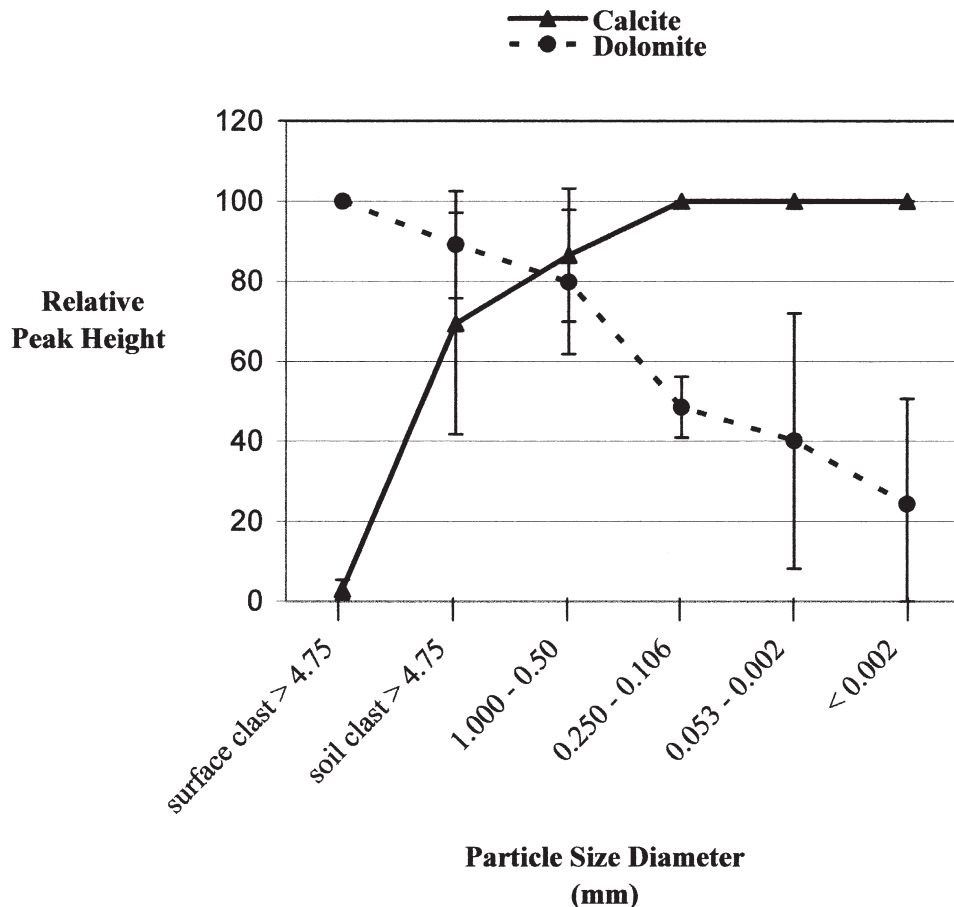


Fig. 2. Peak height with respect to the dominant (Peak 104) calcite or dolomite in Tortugas Mountain samples of surface clast (>4.75 mm), soil clast (>4.75 mm), coarse sand (1.000–0.50 mm), fine sand (0.25–0.106 mm), silt (0.053–0.002 mm), and clay (<0.002 mm) using calcite and dolomite references (JADE, 1993–2002). Standard error of the mean is depicted by error bars ($n = 3$). Absence of visible error bars reflects the absence of variability.

1993–2002). The study investigating the particle-size distribution of pedogenic carbonate formed in dolostone residuum relied on electronic measurements (XRD #2) only and required no comparison of d-spacings other than that which was necessary for mineralogical identification by the JADE (1993–2002) electronic library. The study of mineralogical distinctions within soil carbonate utilized both manual (XRD #1) and electronic (XRD #2) measurements and provided the basis for comparisons of d-spacings among the different types of soil carbonate.

RESULTS AND DISCUSSION

Part I. Particle-Size Distribution of Pedogenic Carbonate

In the Tortugas Mountain samples, where the parent material is dolostone residuum, the relative height with respect to the most prominent calcite or dolomite peak (104) in the Hexagonal-rhombohedral crystal system was measured. Using the data of Peak 104, Fig. 2 shows a comparison of the mean relative concentrations of calcite and dolomite with respect to particle size. The data revealed an inverse relationship between dolomite and calcite. That is, the relative concentration of calcite increased with decreasing particle size, while the relative concentration of dolomite increased with increasing par-

ticle size. These results concur with previous research which found that, in a dolomitic parent material, pedogenic carbonate accumulates as calcite in clay and fine silt-size fractions (Rostad and St. Arnaud, 1970), with the occurrence of calcite increasing with decreasing particle size while dolomite increased with increasing particle size (Fuller et al., 1999). Additional findings detected no evidence of dolomite precipitation from supersaturation under ambient conditions (Sherman and Barak, 2000). Our study found that pedogenic carbonate formed in dolostone residuum dominated in the fine sand, and, to a progressively greater extent, silt and clay particle-size fractions as calcite.

Part II. Mineralogical Distinctions within Soil Carbonate

Representative samples of the three types of soil carbonate are shown in Fig. 3. The set of X-ray diffractograms illustrates the six peaks generated between 20 and 47°2 θ for minerals of the Hexagonal-rhombohedral crystal system (Tables 1 and 2). Each vertical line in Fig. 3 corresponds to the angle of diffraction (°2 θ) of the calcite reference (JADE, 1993–2002). Although a comparison of the three diffractograms revealed that all peaks exhibited a slight up-angle shift with respect to

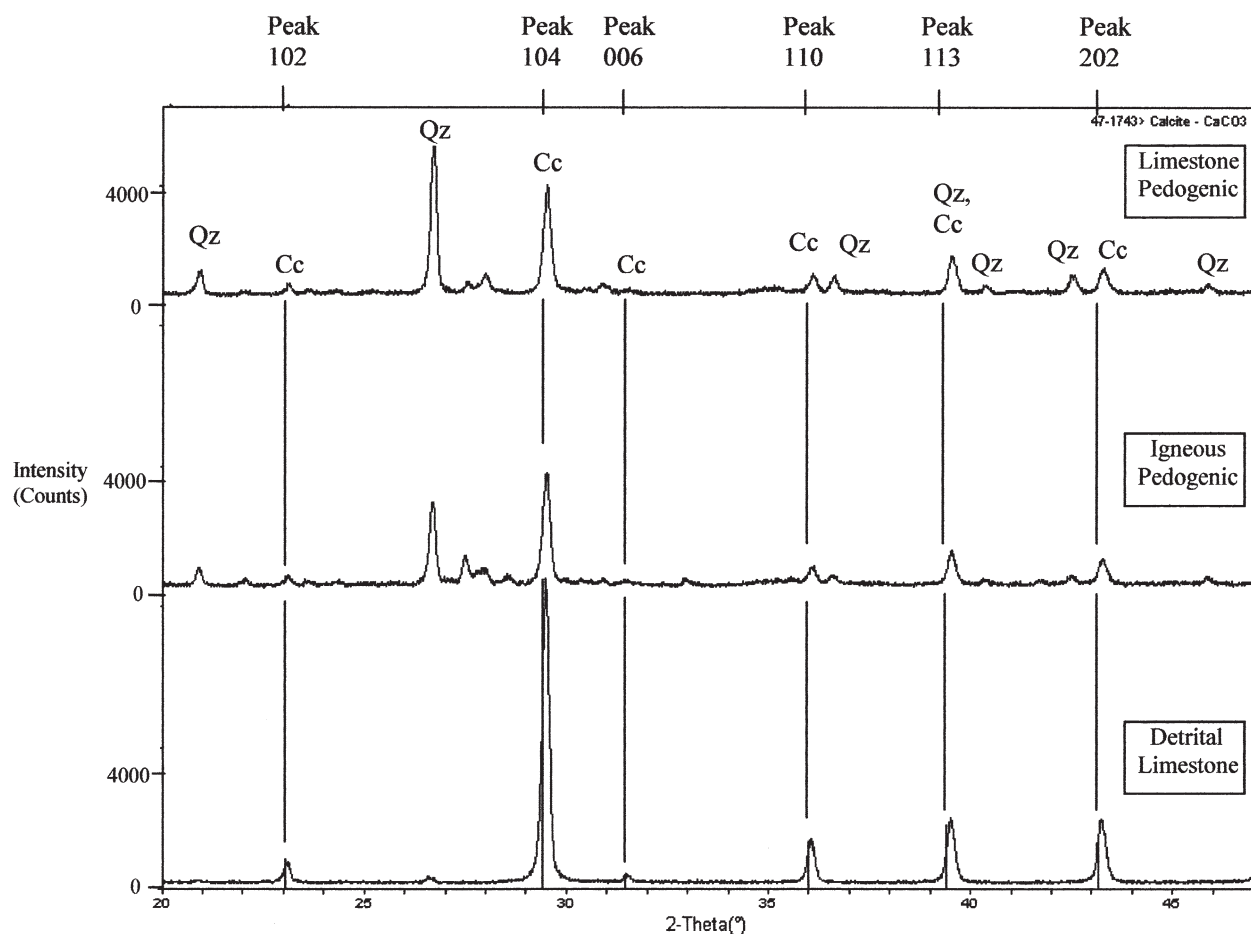


Fig. 3. Representative X-ray diffractograms of pedogenic carbonate formed in limestone parent material (3-LS-2), pedogenic carbonate formed in igneous parent material (2-IG-1), and detrital limestone (1-LS-3) with calcite reference lines provided, calcite hkl peaks identified, and calcite (Cc) and quartz (Qz) peaks labeled (JADE, 1993–2002).

Table 1. Data manually measured from the strip chart of XRD #1. XRD d-spacings with means (Å) for each hkl calcite peak of each type of soil carbonate at limestone (LS) and igneous (IG) sites and variability of \pm one standard deviation (Std Dev). Calcite reference values are also provided.

	Peak 102	Peak 104	Peak 006	Peak 110	Peak 113	Peak 202
Limestone Pedogenic						
1-LS-1	3.83	3.02	2.83	2.48	2.27	2.08
1-LS-2	3.84	3.02	2.83	2.49	2.28	2.09
1-LS-3	3.85	3.03	2.84	2.49	2.28	2.09
2-LS-1	3.83	3.01	2.83	2.48	2.27	2.08
2-LS-2	3.83	3.02	2.83	2.48	2.28	2.09
2-LS-3	3.82	3.01	2.83	2.48	2.27	2.08
3-LS-1	3.83	3.02	2.83	2.48	2.27	2.09
3-LS-2	3.83	3.02	2.82	2.48	2.27	2.08
3-LS-3	3.84	3.03	2.84	2.49	2.28	2.09
Mean	3.83	3.02	2.83	2.48	2.27	2.09
Std Dev	0.01	0.01	0.01	0.00	0.01	0.01
Igneous Pedogenic						
1-IG-1	3.83	3.02	2.84	2.49	2.28	2.08
1-IG-2	3.84	3.02	2.83	2.48	2.28	2.09
1-IG-3	3.83	3.02	2.83	2.48	2.27	2.08
2-IG-1	3.83	3.02	2.83	2.48	2.28	2.08
2-IG-2	3.85	3.03	2.84	2.49	2.28	2.09
2-IG-3	3.86	3.03	2.84	2.49	2.29	2.09
3-IG-1	3.84	3.02	2.83	2.48	2.28	2.09
3-IG-2	3.86	3.04	2.84	2.49	2.28	2.09
3-IG-3	3.85	3.03	2.84	2.49	2.28	2.09
Mean	3.84	3.03	2.84	2.49	2.28	2.09
Std Dev	0.01	0.01	0.01	0.01	0.00	0.01
Detrital Limestone[†]						
#1	3.84	3.02	2.83	2.49	2.28	2.09
#2	3.83	3.02	2.83	2.48	2.28	2.09
#3	3.82	3.01	2.83	2.48	2.27	2.08
Mean	3.83	3.02	2.83	2.48	2.28	2.09
Std Dev	0.01	0.01	0.00	0.01	0.01	0.01
Calcite reference values						
JADE #47–1743 (1993–2002)	3.8548	3.0355	2.8435	2.4948	2.2846	2.0944
Graf (1961)	3.8551	3.0359	2.8440	2.4949	2.2848	2.0946
Berry and Thompson (1962)	3.857	3.037	2.844	2.497	2.286	2.096

[†] Detrital limestone is a surface clast containing fossils from the 1-LS-3 sample site. Three chips were removed from a single clast and ground separately.

the calcite reference lines, none of the shifts was great enough to indicate the presence of any other carbonate mineral but calcite. This supports previous research in that pedogenic carbonate accumulates as calcite (Rostad and St. Arnaud, 1970) and, more specific to this study, soil of the northern Chihuahuan Desert is supersaturated with respect to calcite (Marion et al., 1990).

Graphic display of the data from XRD #1 and #2 is shown as Fig. 4. To better evaluate the comparisons of the three types of soil carbonate and the significance of up-angle peak shifts relative to the calcite reference lines, analysis of variance was applied to the data (Table 2) from XRD #2 using the general linear model (GLM) procedure (SAS, 1999). *P*-values for each comparison of d-spacings associated with each hkl peak are provided in Table 3. No significant difference in d-spacings was detected at any peak when pedogenic carbonate formed in igneous parent material was compared with detrital limestone. Only a minor peak (110) generated a significant difference in d-spacing when pedogenic carbonate formed in limestone parent material was compared with detrital limestone and, again, when pedogenic carbonate formed in limestone parent material was compared with pedogenic carbonate formed in igneous parent material. The lack of distinctions is attributed to the ranges of d-spacings (denoted as high and low values in Table 2) that exhibit considerable overlap among the three types of soil carbonate. However, aerosolic additions may have

diluted further distinctions between the two types of pedogenic carbonate. An 11-yr study of dust trap collections during the windiest months of the year revealed CaCO_3 concentrations that ranged from 0.019 to 0.085 $\text{g m}^{-2} \text{yr}^{-1}$ in this region (Gile and Grossman, 1979).

It is notable that the variability of all six d-spacings at the limestone sites is much larger than that at the igneous sites. Variability of pedogenic carbonate at the limestone sites may reflect the influence of both biotic (i.e., precipitation on root hairs and fungal hyphae) and abiotic (i.e., dissolution and reprecipitation) processes, while the biotic process may dominate at the igneous sites where variability is much smaller. That is, pedogenic carbonate formed in limestone parent material is derived from biotic precipitation in which root and microbial respiration provide the source of CO_2 , abiotic reprecipitation of solubilized detrital limestone, and the reprecipitation of solubilized pedogenic carbonate formed biotically and abiotically. On the other hand, pedogenic carbonate formed in igneous parent material is derived from the biotic precipitation of CaCO_3 (Kraimer, 2003) and its subsequent dissolution and reprecipitation. While both types of pedogenic carbonate in this study were undeniably calcite, the biotic process of precipitation and the abiotic process of reprecipitation may impart distinctions on the d-spacings during crystallization. In this way, the variability of pedogenic carbonate formed in limestone parent material may reflect the diverse in-

Table 2. Data electronically measured from XRD #2. XRD d-spacings with means (Å) for each hkl calcite peak of each type of soil carbonate at limestone (LS) and igneous (IG) sites with high and low values in underline and variability of \pm one standard deviation (Std Dev). Calcite reference values are also provided.

	Peak 102	Peak 104	Peak 006	Peak 110	Peak 113	Peak 202
Limestone Pedogenic						
1-LS-1	3.8498	3.0275	2.8457	2.4882	2.2799	2.0914
1-LS-2	<u>3.8312</u>	<u>3.0170</u>	<u>2.8340</u>	<u>2.4832</u>	<u>2.2746</u>	<u>2.0882</u>
1-LS-3	3.8418	3.0263	2.8434	2.4874	2.2800	2.0924
2-LS-1	3.8531	3.0281	2.8338	2.4906	2.2817	2.0928
2-LS-2	<u>3.8506</u>	3.0284	2.8371	<u>2.4909</u>	2.2797	<u>2.0930</u>
2-LS-3	3.8397	3.0224	2.8491	2.4857	2.2921	2.0902
3-LS-1	3.8436	3.0259	<u>2.8352</u>	2.4879	2.2791	2.0897
3-LS-2	3.8438	3.0247	2.8361	2.4872	2.2782	2.0901
3-LS-3	3.8476	3.0287	2.8406	2.4890	2.2804	2.0921
Mean	3.8446	3.0254	2.8394	2.4878	2.2806	2.0911
Std Dev	0.0067	0.0038	0.0055	0.0024	0.0047	0.0016
Igneous Pedogenic						
1-IG-1	3.8428	3.0279	2.8392	2.4907	2.2803	2.0915
1-IG-2	<u>3.8449</u>	<u>3.0254</u>	2.8404	<u>2.4867</u>	2.2792	2.0897
1-IG-3	3.8575	3.0301	2.8468	2.4903	2.2805	2.0906
2-IG-1	<u>3.8457</u>	3.0264	<u>2.8362</u>	2.4864	2.2790	2.0906
2-IG-2	3.8483	3.0281	2.8402	2.4899	2.2796	2.0920
2-IG-3	3.8457	3.0292	2.8404	2.4894	2.2795	2.0918
3-IG-1	†	3.0254	2.8388	†	2.2798	2.0906
3-IG-2	3.8478	3.0260	2.8455	2.4890	2.2789	2.0900
3-IG-3	3.8448	3.0278	2.8388	2.4888	2.2780	2.0916
Mean	3.8472	3.0274	2.8407	2.4889	2.2794	2.0909
Std Dev	0.0045	0.0017	0.0034	0.0016	0.0008	0.0008
Detrital Limestone						
1-LS-1	3.8474	3.0284	2.8400	2.4907	2.2807	2.0923
1-LS-2	3.8537	3.0303	2.8395	2.4920	2.2815	2.0923
1-LS-3	3.8483	3.0263	2.8386	2.4895	2.2807	2.0911
2-LS-1	3.8337	3.0183	2.8304	2.4849	2.2750	2.0875
2-LS-2	<u>3.8538</u>	3.0297	<u>2.8389</u>	2.4910	2.2815	2.0933
2-LS-3	3.8536	3.0332	2.8427	2.4932	2.2829	2.0936
3-LS-1	3.8455	3.0268	2.8342	2.4877	2.2787	2.0901
3-LS-2	<u>3.8576</u>	3.0319	2.8448	2.4922	2.2815	2.0944
3-LS-3	<u>3.8505</u>	3.0279	2.8393	2.4897	2.2796	2.0914
Mean	3.8492	3.0281	2.8387	2.4901	2.2802	2.0918
Std Dev	0.0071	0.0043	0.0043	0.0026	0.0023	0.0021
Calcite reference values						
JADE #47–1743 (1993–2002)	3.8548	3.0355	2.8435	2.4948	2.2846	2.0944
Graf (1961)	3.8551	3.0359	2.8440	2.4949	2.2848	2.0946
Berry and Thompson (1962)	3.857	3.037	2.844	2.497	2.286	2.096

† Too little carbonate present for detection.

fluence of formation processes that are less pronounced during the genesis of pedogenic carbonate formed in igneous parent material.

Based on thin section analysis (data not shown), the high variability of detrital limestone (Table 2) may indicate the presence of pedogenic carbonate within the porous limestone, which was not completely removed with acid pretreatment. No significant difference ($p = 0.9313$) was detected with respect to the landform blocking factor. The d-spacings calculated from measurements on strip charts (XRD #1) were not statistically compared because these visual estimates could not be reliably resolved beyond two significant figures (Table 1).

Comparison of d-spacings for each of the three types of soil carbonate to those of the calcite references revealed a pronounced trend (Fig. 4) in data derived both manually (XRD #1) and electronically (XRD #2). For each peak within each type of soil carbonate, the mean d-spacing is less than the corresponding mean d-spacing of the calcite references (Tables 1 and 2), giving rise to the consistent up-angle shift of the soil carbonates relative to the calcite reference lines (Fig. 4). For the electronically derived data (XRD #2), statistical examination (Table 3) produced a significant difference in d-spacing

at nearly every peak between each of the three types of soil carbonate and the calcite reference (JADE, 1993–2002). At all six peaks, pedogenic carbonate formed in igneous parent material and detrital limestone were significantly different from the calcite reference. A significant difference was also detected in five peaks when pedogenic carbonate formed in limestone parent material was compared with the calcite reference; only Peak 006 produced no significant difference.

Although pedogenic carbonate formed in limestone parent material and pedogenic carbonate formed in igneous parent material were likely formed in different chemical environments and influenced by different proportions of biotic and abiotic precipitation, this study found no robust mineralogical distinctions between the two types of pedogenic carbonate. Detrital limestone, lacking any exposure to pedogenesis, also provided no basis for distinctions among the soil carbonates. All soil carbonate was calcite. With respect to C sequestration, XRD was unable to detect distinctions between soil carbonate which can remediatively sequester atmospheric C (Reaction 2) and soil carbonate which cannot (Reaction 1).

Table 3. Statistical analysis of electronic measurements by XRD #2 generated *p*-values for the comparisons of d-spacings for each hkl peak of pedogenic carbonate formed in limestone (LS) parent material ($n = 9$), pedogenic carbonate formed in igneous (IG) parent material ($n = 9$), detrital LS ($n = 9$), and the calcite reference (JADE, 1993–2002).

	Peak 102	Peak 104	Peak 006	Peak 110	Peak 113	Peak 202
IG Pedogenic vs. Detrital LS	0.5401	0.6931	0.3660	0.4148	0.5820	0.2887
LS Pedogenic vs. Detrital LS	0.1449	0.0625	0.7368	0.0061*	0.7855	0.3922
LS Pedogenic vs. IG Pedogenic	0.3973	0.1144	0.5834	0.0329*	0.4472	0.7830
IG Pedogenic vs. Calcite Ref.	0.0020*	<0.0001*	0.0370*	<0.0001*	<0.0001*	<0.0001*
LS Pedogenic vs. Calcite Ref.	0.0018*	<0.0001*	0.0594	<0.0001*	0.0361*	0.0003*
Detrital LS vs. Calcite Ref.	0.0457*	0.0009*	0.0097*	0.0006*	0.0005*	0.0054*

* Statistically significant difference at $\alpha = 0.05$.

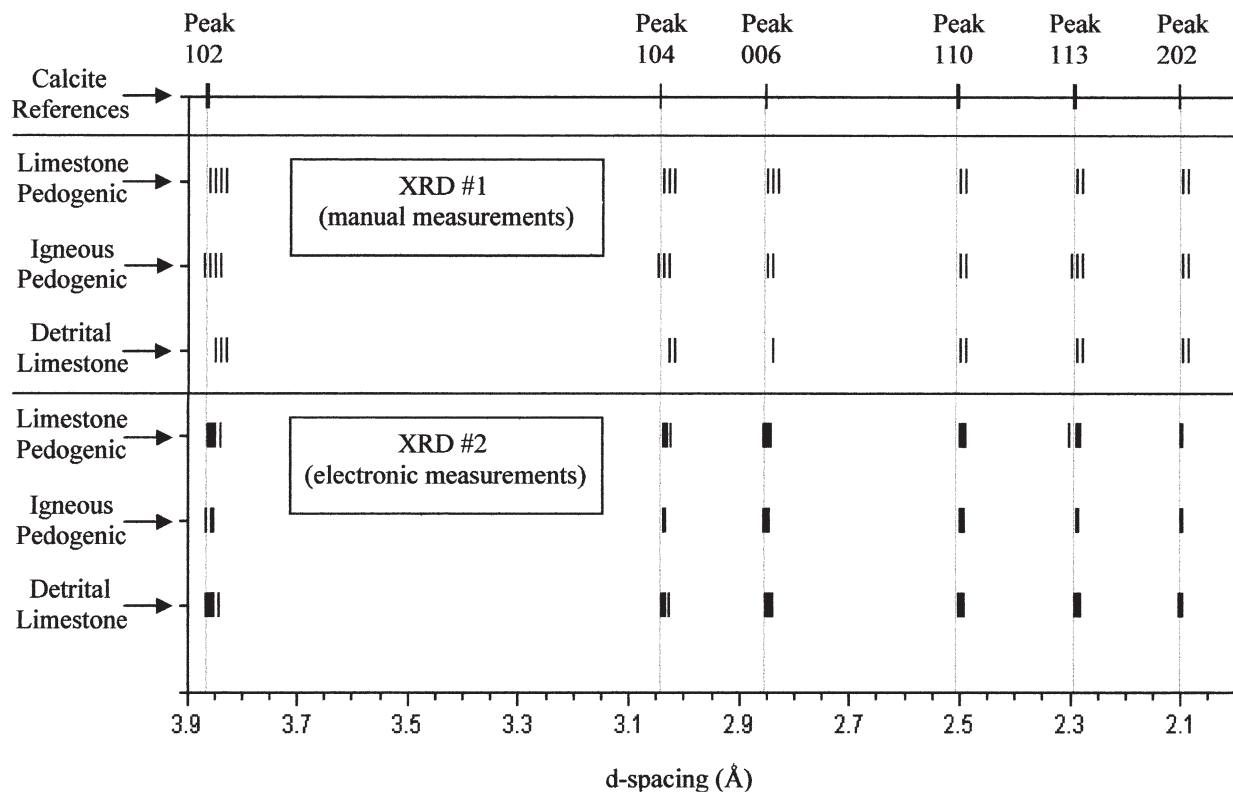


Fig. 4. X-ray diffraction data derived manually (XRD #1) and electronically (XRD #2) for pedogenic carbonate formed in limestone parent material ($n = 9$), pedogenic carbonate formed in igneous parent material ($n = 9$), and detrital limestone ($n = 3$ for XRD #1; $n = 9$ for XRD #2). Calcite reference lines are also included (Graf, 1961; Berry and Thompson, 1962; Jade, 1993–2002).

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