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Origin and significance of calcium carbonate in soils of southwestern Patagonia

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Abstract

A soil chronosequence spanning the last 0.76–1.0 Ma shows a progressive increase in calcium carbonates based on (1) thickness of the Bk +BCk horizons, (2) maximum carbonate stage, (3) profile accumulation of pedogenic carbonates, and (4) mass flux of Ca from a geochemical mass balance. We favor a dust origin of the carbonates because (1) the till parent materials contain low amounts of CaCO₃, (2) there is minimal evidence for weathering of Ca-bearing minerals in the soil, (3) the amount of CaCO₃ in the profile is far in excess of what could be released by weathering, (4) dust collected from the study area is enriched in CaCO₃, and (5) a source area for the carbonates was identified. Although there likely were changes in dust deposition rates during the Quaternary, our calculations suggest that the current deposition rate of 0.18 g CaCO₃ m⁻² yr⁻¹ is comparable to the long-term profile accumulation rate of 0.16 g CaCO₃ m⁻² yr⁻¹.²³⁰Th/U disequilibrium ages of carbonate pendants are consistent with cosmogenic surface-exposure ages indicating that this method has potential for dating other geomorphic surfaces in Patagonia. Cryogenic processes have affected many of the pedons, particularly during the last glacial maximum. © 2006 Elsevier B.V. All rights reserved.

Keywords: Dust; CaCO₃; Patagonia; Pedogenesis; Soil chronosequence

1. Introduction

There is considerable debate regarding the origin of CaCO₃ and petrocalcic horizons (calcretes) in semi-arid soils of Patagonia. [Trombotto \(1996\)](#page-11-0) points out the paucity of carbonate-rich sediments in Patagonia and argues that the Ca originates lithogenically, i.e., from soil weathering; in contrast, a second group [\(Vogt and del Valle,](#page-11-0) [1994; Zárate, 2003](#page-11-0)) proposed that the carbonates were deposited as dust from an expanded inner coastal shelf during Quaternary cold periods. Although we recognize that carbonate deposition rates have varied during the

⁎ Corresponding author. E-mail address: bockheim@wisc.edu (J.G. Bockheim). Quaternary, we will demonstrate that the carbonates are being deposited today as dust at rates that are consistent with profile quantities of $CaCO₃$.

Not only is dust important in pedogenesis, but also a Patagonian source of dust has been identified during glacial stages 2, 4 and 6 in Antarctic ice cores [\(Basile et al.,](#page-10-0) [1997; Delmonte et al., 2004a,b](#page-10-0)). Rare-earth elements and Sr–Nd isotopic data have been particularly useful in showing a Patagonian source for the dust [\(Smith et al.,](#page-11-0) [2003; Delmonte et al., 2004b](#page-11-0)).

Key hypotheses of this study are:

(1) carbonates in soils of the Lago Buenos Aires area originate from dust rather than from pedogenic weathering;

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- (2) the amount of carbonates in contemporary dust projected over the long-term generally is consistent with profile quantities of $CaCO₃$;
- (3) pedogenic carbonates are a key relative-age indicator in southern Patagonia; and
- (4) pedogenic carbonates offer promise for dating sediments in Patagonia.

2. Study area

The study was conducted along a 40-km transect from just west of the city of Perito Moreno to the Arroyo Telken lava flow (Fig. 1). Based on a decade of weather observations and longer regional records, the mean annual air temperature is 9 °C and the mean annual precipitation is 200 mm yr−¹ ([National Center for Atmospheric](#page-11-0) [Research, 2003\)](#page-11-0). Average summer (Dec.–Feb.) and winter (June–Aug.) temperatures are 14 °C and 3 °C, respectively. Approximately 75% of the annual precipitation falls from late fall through early spring (April to September). Summer winds are strong and persistently from the west; winter winds are weaker and more variable.

We collected data over a 20-month period using onset data loggers at two sites with the following results (1) the

mean annual air temperature from January 2004 to January 2005 was $8.0 \degree C$, (2) the mean annual soil temperature at 50 cm was 10° C, (3) the soil moisture content at 25 cm averaged $0.10 \text{ m}^3 \text{m}^{-3}$, and (4) the soil moisture regime appears to be xeric at elevations from ca. 500–700 m and aridic at elevations below 500 m [\(Fig. 2\)](#page-2-0).

The study area is part of the Southern Patagonian Steppe eco-region and contains shrub–steppe and grass–steppe vegetation types ([Soriano, 1983\)](#page-11-0); the amount of bare ground varies from 40–70%. Dominant plant species include coirón bunchgrass (Stipa humilis) and neneo (Mulinum spinosum), with occasional calafate (Berberis heterophylla) and molle (Schinus johnstonii) shrubs.

The Quaternary geomorphology of southern Argentina is comprised of spectacular sequences of glacial moraines and associated outwash terraces ([Clapperton,](#page-10-0) [1993](#page-10-0)). During ice ages, mountain glaciers expanded and coalesced to form the Patagonian Ice Cap. Outlet glaciers eroded deep valleys through the mountains and advanced out onto the flat plains east of the Andes at some locations. In the Lago Buenos Aires valley, glaciers advanced as far as 100 km from the mountain front. Dating of the glacial landforms is based on three

Fig. 1. Location of study area in the Lago Buenos Aires area.

Fig. 2. Weather data for the period January 1, 2003–Dec. 31, 2004, including air temperature, soil temperature at 50 cm, and soil moisture at 25 cm on (A) Fenix V (S46° 37′52.8″, W070°57′46.5″) and (B) Telken IV (S46°45′25.6″, W070°45′48.2″) moraines.

young basalt flows and about 100 cosmogenic-nuclide surface-exposure ages. Based on these ages, the chronology includes the Menucos drift (14.4 ka), Fenix I–V drifts (15.8–22.7 ka), Moreno I–III drifts (∼150 ka), Deseado I–III drift (∼350–760 ka), and Telken I–VI drifts (760–1016 ka) ([Singer et al., 2004; Kaplan et al.,](#page-11-0) [2004\)](#page-11-0).

A 1:2 million-scale soil map of Santa Cruz province shows Xerorthents on Menucos and Fenix surfaces and Haplargids on older surfaces ([INTA, 1995](#page-11-0)). However, our data show that all of the soils contain a mollic epipedon; therefore, we classify the soils as Haploxerolls and Calcixerolls, respectively ([Douglass and Bockheim,](#page-11-0) [2006\)](#page-11-0). Moreover, the clay enrichment in the Bk horizon of Telken soils does not reflect argilluviation. [Douglass](#page-11-0) [and Bockheim \(2006\)](#page-11-0) provided descriptions of the soils considered in this study.

3. Methods

3.1. Field

We sampled 34 pedons on or near moraine crests in locations that appeared to be stable and have representative vegetation cover and surface boulder frequency. Soils were excavated by hand and described according to [Schoeneberger and others \(2002\).](#page-11-0) Stages of carbonate morphology were identified using criteria of [Gile et al.](#page-11-0) [\(1966\)](#page-11-0) as modified by [Birkeland \(1999\)](#page-10-0). Percentages of coarse fragments were visually estimated in the exposed wall of the soil pit. Bulk samples were passed through a 2-mm sieve in the field. The fine-earth fraction was returned to the laboratory for characterization.

Bulk density was measured for 9 of the 34 soil profiles using the compliant cavity procedure (method 4A5, [Soil](#page-11-0) [Survey Staff, 1996](#page-11-0)) and corrections were applied for the>2 mm coarse-fragment content. Data from these profiles were used to generate an equation that was used to estimate bulk density for other soil horizons [\(Douglass](#page-11-0) [and Bockheim, 2006\)](#page-11-0). Three minimally disturbed, oriented samples were collected from the A2 and Bk horizons of Deseado II and Telken IV pedons in galvanized sheet-metal "Kubiena containers" measuring 6.0 cm× $20 \text{ cm} \times 5.0 \text{ cm}$ deep for preparation of thin sections.

Stage I carbonate rinds (coatings) on coarse-gravel (7.5 cm diameter) clasts collected from Fenix, Moreno, and Deseado drifts were dated using the 230Th/U method and thermal ionization mass spectrometry at the Berkeley Geochronology Center [\(Sharp et al., 2003](#page-11-0)).

Six dust collectors were installed along a transect from LBA to Estancia Telken in January 2003 (locations shown in [Fig. 1\)](#page-1-0) to measure dust composition and deposition rates. We used plastic dishpans measuring 35 by 30 cm and 11 cm deep that contained a 2.5-cm depth of marbles. The dust traps were positioned 50–75 cm above the ground surface on rock cairns to reduce sampling the local saltating load. Samples were collected in January 2004

and October 2005. During the first year, we obtained a reliable sample for dust deposition rates from only one collector; five of six collectors yielded samples during the second sampling interval. We were unable to collect dust samples where wind or sheep had disturbed the collectors or where humans had removed them.

3.2. Laboratory

Soil samples were sent to the University of Missouri Soil Characterization Laboratory, where analyses were performed using methods established by the [Soil Survey](#page-11-0) [Staff \(1996\),](#page-11-0) including particle-size distribution with sand fractionation (method 3A), pH and electrical conductivity in distilled water (8Cla and 8I, respectively), NH₄OAcextractable bases (5B1), BaCl₂-triethanolamine-extractable acidity (6H1), cation-exchange capacity (CEC) by NH4OAc at pH 8.2 (5A2), and base saturation from summation. Total organic and inorganic carbon were measured with a Leco CNS-2000 analyzer. Samples from each horizon were homogenized and pulverized to pass a 100-mesh sieve. Two samples were analyzed for each

Fig. 3. Morphological features of carbonates in soils from the LBA area, including (A) stage I carbonate encrustations in a Menucos soil; (B) carbonate seams in alluvial fan materials of mid-Pleistocene age near Río Gallegos; (C) stage IV carbonates in Telken IV soil; and (D) stage V carbonates in soil in a Telken V soil.

horizon; an untreated sample was used to determine the total carbon content of the soil (i.e., organic carbon plus carbonate). The other sample was heated at 300 °C in a muffle furnace for 24 h to combust organic material and was then used to determine the carbonate content of the soil. Organic carbon was calculated as the difference between total carbon and carbonate content. Combustion temperatures inside the LECO are ∼1300 °C, high enough to oxidize all forms of carbonate. We were unable

to differentiate between calcite and other forms of carbonate, such as dolomite.

The following measurements were performed on dust samples: (1) organic C and $CaCO₃$ using the methods described for soils and (2) total elemental analysis as described in the following section.

Nine of the thirty-four pedons described in [Douglass](#page-11-0) [and Bockheim \(2006\)](#page-11-0) were selected for detailed chemical analysis. These pedons displayed representative soil

Fig. 4. Relation between time of exposure and (A) thickness of the Bk +BCk horizon and carbonate morphology stage; (B) profile quantities of carbonates; and (C) transport function of carbonates from a geochemical mass balance.

morphology for their moraine groups and were sampled to un-weathered parent material in most cases. Elemental composition was measured on the fine-earth $(\leq 2$ mm) fraction, the silt + clay fraction $($ < 50 μ m), and the medi $um + fine$ sand fraction (0.50–0.10 mm). The latter two fractions typically represent $\sim 65\%$ of the fine-earth fraction. Samples were ground in a micro ball mill and sent to Activation Laboratories Ltd. (Ancaster, Ontario) for measurement of major-oxide and trace-element concentrations by inductively coupled plasma emission spectrometry following fusion with lithium metaborate/ tetraborate. Elements analyzed include Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P, Ba, Sr, Y, Sc, Zr, Be, and V, as well as loss on ignition.

Thin sections were prepared using the techniques of [FitzPatrick \(1993\).](#page-11-0) Samples were impregnated with epoxy resin under a vacuum and cured for a minimum of 24 h; oriented sections were cut with a diamond saw and cemented onto glass microscope slides. The slides were ground and polished to a thickness of 30 μm and examined under natural and polarized light with a polarizing microscope.

3.3. Calculations and statistics

Profile quantities of $CaCO₃$ were determined by multiplying the percent by mass of the constituent by the bulk density and the thickness of the horizon, with a correction for the percentage of coarse fragments in the soil; horizon values were summed to determine the profile quantity [\(Bockheim et al., 2000\)](#page-10-0). The percent by mass of the constituent in the parent material was subtracted from the horizon value to account for the original starting composition. Profile quantities of carbonates were regressed against time of exposure using two mathematical models, a logarithmic model $(y = A + \ln B)$ and a reservoir model that consists of a linear input function and a loss function that is dependent on the concentration of the constituent (i.e. a zero-order input function and first-order loss) [\(Douglass and Bockheim, 2006\)](#page-11-0).

We calculated long-term accumulation rates (LTA) of carbonates as the total amount of carbonate accumulation divided by the age of the soil ([Schlesinger, 1990;](#page-11-0) [Bockheim et al., 2000\)](#page-11-0). This analysis assumes that the accumulation rate of the constituent in the soil is constant.

Geochemical mass balances were used to calculate the gain and loss of elements, as well as the translocation of elements within selected pedons [\(Brimhall and](#page-10-0) [Dietrich, 1987](#page-10-0)). The method is based on the principle of conservation of mass and the ability to determine the volumetric change of the soil during the weathering process. Uncertainties of the method for soils in the LBA

area are described in detail in [Douglass and Bockheim](#page-11-0) [\(2006\).](#page-11-0)

The statistical significance of trends in the data was tested using analysis of variance (ANOVA) and Fisher's test of least probabilities using a MINITAB software package ([MINITAB, Inc., 2000](#page-11-0)).

4. Results

There was a progressive increase in carbonate stage with time of exposure, including from youngest to oldest: Menucos, stage I; Fenix stage I–II; Moreno and Deseado stage III; and Telken, stage III+ $-V$ [\(Figs. 3 and 4A](#page-3-0)). Similarly, the thickness of the $Bk + BCk$ horizons increased with soil age [\(Fig. 4](#page-4-0)A); however, the differences were not statistically significant. Profile accumulation of carbonates increased sharply with age in Fenix to Deseado soils but appeared to equilibrate in Telken soils, particularly in the case of the reservoir model [\(Fig. 4](#page-4-0)B). Transport functions calculated from geochemical mass balance

Fig. 5. Thin sections showing (A) minimal weathering of plagioclase grains in the Bk2 horizon of a soil on Deseado drift (cross polar; 0.6 mm across) and (B) carbonate nodules (encased in white) in the Bk horizon of a soil on Telken drift (plain light, 2.4 mm across).

Table 1

Key properties of soils in the Lagos Buenos Aires area, southern Patagonia

(continued on next page)

Physical and chemical properties of representative soils from the Lago Buenos Aires area, southern Patagonia.

Table 2 Deposition rate and composition of dust from the Lagos Buenos Aires area

| Location | Deposition rate $(g m^{-2} yr^{-1})$ | | Organic C $(\%)$ | Carbonate $(\%)$ |
|------------------------|---|------|---------------------|---------------------|
| | | | | |
| | Fenix Va | | 3.3 | |
| Fenix Vb | | 21.4 | | |
| Moreno | | | 3.7 | 4.9 |
| Deseado | | | 1.6 | 1.4 |
| Telken IVa | 27.1 | 7.4 | 3.4 | 4.4 |
| Telken IV _b | | 4.2 | - | |
| Telken VI | - | 3.5 | 5.9 | 5.4 |
| Average | 27.1 | 8.0 | 3.7 | 4.0 |

Amount and composition of dust samples from the LBA area.

illustrate the progressive accumulation of $CaCO₃$ in Bk and BCk horizons ([Fig. 4](#page-4-0)C).

There appears to be minimal chemical weathering of soils in southern Patagonia. Thin sections show fresh plagioclase feldspar grains ([Fig. 5](#page-5-0)A). Geochemical massbalance shows minimal weathering of aluminosilicate

Table 3 Total elemental analysis of dust and the surface A horizon of soils in the Lagos Buenos Aires area

minerals [\(Douglass, 2005](#page-11-0)) but substantial input of $CaCO₃$ [\(Fig. 4](#page-4-0)C). Microfabric analysis verifies field evidence that the carbonates are pedogenic, including the presence of CaCO3 nodules ([Fig. 5B](#page-5-0)). Older surfaces showed clas-sical forms of stage III +and IV carbonates [\(Gile et al.,](#page-11-0) [1966; Rabenhorst and Wilding, 1986; Monger et al.,](#page-11-0) [1991\)](#page-11-0), including a whitish cast for >90% of the horizon [\(Fig. 3D](#page-3-0)), cappings on columns and prisms, a weak platy structure, laminations [\(Fig. 3](#page-3-0)C), and $>20\%$ CaCO₃ content [\(Table 1](#page-6-0)).

Three different layers of carbonate rinds from a clast from Deseado outwash yielded 239 U $-^{230}$ Th ages of 224, 209, and 24 ka (Sharp, personal communication).

5. Discussion

Our data support a dust origin of carbonates in soils of the LBA area. The parent materials generally contain low amounts of $CaCO₃$ [\(Table 1](#page-6-0)). There is minimal evidence for weathering of Ca-bearing minerals in soils, based on examination of thin sections ([Fig. 5](#page-5-0)A) and geochemical mass-balance ([Fig. 4](#page-4-0)C). Dust is enriched (∼4%) in

Chemistry of dust and soil parent materials from the LBA area.

 $CaCO₃$ ([Table 2](#page-8-0)). The Tertiary Santa Cruz Formation, a highly weathered Paleozoic marble unit in the Andean Cordillera, and carbonate-rich lacustrine sediments along the shores of LBA, were identified as likely sources for the carbonates. These interpretations are consistent with those in other semi-arid regions, including the Silver Lake playa in southeastern California ([Reheis et al., 1989\)](#page-11-0) and Kyle Canyon, Nevada [\(Reheis et al., 1992\)](#page-11-0).

Excluding the extreme values of 27.1 and 21.4 g m ⁻² yr−¹ , our data suggest an average deposition rate of $0.18 \text{ g m}^{-2} \text{yr}^{-1}$ of CaCO₃ in dust [\(Table 2\)](#page-8-0). Long-term accumulation rates (LTA) of $CaCO₃$ in soils of the LBA area are 0.32, 0.14, 0.14, and 0.042 g m⁻² yr⁻¹ on Fenix, Moreno, Deseado, and Telken drifts, respectively. The mean LTA value of 0.16 is comparable to the measured short-term dust deposition rate of 0.18 g m⁻²yr⁻¹ of CaCO₃.

We compared the total elemental composition of dust that is from the surface A horizon of soils from the LBA

area. Compared with the topsoil, dust was enriched in Si, Al, K, and Sr and depleted in P and Na [\(Table 3](#page-8-0)). Our data are comparable to values reported for dust and topsoils in Patagonia by [Gaiero et al. \(2003\)](#page-11-0). These data suggest that the dust originates from wind-eroded topsoil that is enriched in organic C [\(Table 2](#page-8-0)) and the weathered sediments mentioned previously that are enriched in CaCO₃.

[Péwé \(1959\)](#page-11-0) differentiated between sand- and icewedge casts. Sand-wedge casts tend to be thin, vertically foliated, and devoid of coarse fragments (Fig. 6B); in contrast, ice-wedge casts are broader, lack vertical foliation, and contain coarse fragments (Fig. 6D). Both are common in Moreno, Deseado, and Telken drifts. These cryogenic features appear to result from a periglacial climate, primarily during the last glacial maximum (LGM). In some cases cryogenesis has disrupted the calcrete layer (Fig. 6A). Fossil sand wedges generally are found only in dry climates such as Antarctica with continuous

Fig. 6. Effect of relict cryogenesis in selected soils of southern Patagonia: (A) a fossil sand or ice wedge on Telken IV drift showing infilling of the petrocalcic horizon with A horizon material; (B) a fossil sand wedge in outwash of mid-Pleistocene age near Río Gallegos showing the classical narrow form and vertically foliated structure; (C) cryoturbation in Sierra de los Frailes drift of mid-Pleistocene age near Río Gallegos; and (D) icewedge casts in multiple drifts near Río Gallegos.

permafrost and mean annual air temperature colder than −8 °C [\(Péwé, 1959](#page-11-0)).

The existence of fossil sand wedges in southern Patagonia implies that the climate during the LGM may have been drier than the current 100–200 mm yr^{-1} of precipitation and colder by as much as 16 °C. [Trombotto](#page-11-0) [\(2002\)](#page-11-0) proposed a similar change in temperature from fossil ice wedges in North Patagonia. However, other studies suggest that the mean annual air temperature was ∼6 °C cooler than modern at the height of the LGM in the Southern Hemisphere and perhaps a little drier at the LBA latitude, including glacier models ([Hulton et al.,](#page-11-0) [2002\)](#page-11-0), fossil pollen records [\(Moreno et al., 2001\)](#page-11-0) and ocean-core geochemistry ([Lamy et al., 2004\)](#page-11-0). Cryogenic features have reported throughout Patagonia, the Falkland Islands, and the Antarctic Peninsula [\(Vogt and del](#page-11-0) [Valle, 1994; Trombotto, 1996, 2002](#page-11-0)).

The results of this study have important implications regarding the origin and timing of dust incorporated in Antarctic ice cores. Diekmann et al. (2000) suggested that the spikes in dust at Vostok and Dome C originated from the Patagonian outwash plains during glacial stages 2, 4, and 6. Stages 2 and 6 correspond to Fenix and Moreno drifts, but no terrestrial record of stage 4 has been iden-tified at LBA. [Vogt and del Valle \(1994\)](#page-11-0) suggest that much of the calcareous dust in Patagonia was deposited during glacial cycles when sea level was lowered by 100–120 m and the continental shelf was widened by 400 to 1000 km. Our dust trap measurements suggest that carbonate deposition continues in the modern environment.

6. Conclusions

Carbonates in soils of LBA originate from dust rather than from pedogenic weathering in that (1) the till parent materials contain low amounts of $CaCO₃$, (2) there is minimal evidence for weathering of Ca-bearing minerals in the soil, (3) the amount of $CaCO₃$ in the profile is far in excess of what could be released by weathering, (4) dust collected from the study area is enriched in $CaCO₃$ (~4%), and (5) a source area for the carbonates was identified northwest of the study near Lago General Carraras.

Our data suggest a current deposition rate of 0.18 g m⁻²yr⁻¹ of CaCO₃. The mean LTA calculated from soil profiles is 0.16 $g \text{ m}^{-2} \text{yr}^{-1}$ of CaCO₃. Therefore, the profile quantities of $CaCO₃$ can be explained by contribution of carbonates in aeolian dust.

Pedogenic carbonates are important as a relative-age indicator in that the following properties increase with age of exposure: (1) thickness of the Bk+BCk horizons, (2) maximum carbonate stage, (3) profile accumulation of pedogenic carbonates, and (4) mass flux of Ca from a geochemical mass balance.

Finally, pedogenic carbonates offer a promise for dating of sediments in Patagonia. Stage I carbonate pendants on a coarse-gravel clast from Deseado outwash were dated at 224 kv from 230Th-U and thermal ionization mass spectrometry, which is consistent with dates obtained from cosmogenic dating.

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