UC Irvine

UC Irvine Previously Published Works

Title

Isotopic approach to soil carbonate dynamics and implications for paleoclimatic interpretations

Permalink

<https://escholarship.org/uc/item/8b42z95n>

Journal

Quaternary Research, 42(1)

ISSN

0033-5894

Authors

Pendall, EG
Harden, JW
Trumbore, SE
et al.

Publication Date

1994

DOI

10.1006/qres.1994.1054

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Isotopic Approach to Soil Carbonate Dynamics and Implications for Paleoclimatic Interpretations

ELISE G. PENDALL¹ AND JENNIFER W. HARDEN

U.S. Geological Survey, 345 Middlefield Road, MS 975, Menlo Park, California 94025

SUE E. TRUMBORE

Department of Geosciences, University of California, Irvine, California 92717-3100

AND

OLIVER A. CHADWICK

Jet Propulsion Laboratory, 4800 Oak Grove Drive, MS 183-501, Pasadena, California 91109

Received June 22, 1993

The radiocarbon content and stable isotope composition of soil carbonate are best described by a dynamic system in which isotopic reequilibration occurs as a result of recurrent dissolution and reprecipitation. Depth of water penetration into the soil profile, as well as soil age, determines the degree of carbonate isotope reequilibration. We measured $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and radiocarbon content of gravel rinds and fine (<2 mm) carbonate in soils of 3 different ages (1000, 3800, and 6300 ^{14}C yr B.P.) to assess the degree to which they record and preserve a climatic signal. In soils developing in deposits independently dated at 3800 and 6300 radiocarbon yr B.P., carbonate radiocarbon content above 40 cm depth suggests continual dissolution and reprecipitation, presumably due to frequent wetting events. Between 40 and 90 cm depth, fine carbonate is dissolved and precipitated as rinds that are not redissolved subsequently. Below 90 cm depth in these soils, radiocarbon content indicates that inherited, fine carbonate undergoes little dissolution and reprecipitation. In the 3800- and 6300-yr-old soils, $\delta^{13}\text{C}$ in rind and fine carbonate follows a decreasing trend with depth, apparently in equilibrium with modern soil gas, as predicted by a diffusive model for soil CO_2 . $\delta^{18}\text{O}$ also decreases with depth due to greater evaporative enrichment above 50 cm depth. In contrast, carbonate isotopes in a 1000-yr-old deposit do not reflect modern conditions even in surficial horizons; this soil has not undergone significant pedogenesis. There appears to be a lag of at least 1000 but less than 3800 yr before carbonate inherited with parent material is modified by ambient climatic conditions. Although small amounts of carbonate are inherited with the parent material, the rate of pedogenic carbonate accumulation indicates that Ca is derived primarily from eolian and rainfall sources. A model describing carbonate input and radiocarbon decay suggests that fine carbonate below 90 cm is mostly detrital (inherited) and that carbonate rinds have been forming pedogenically at a constant rate since alluvial fans were deposited. ©1994 University of Washington.

¹ To whom correspondence should be addressed at the Department of Geosciences, University of Arizona, Tucson, Arizona 85721.

INTRODUCTION

Horizons enriched with calcium carbonate are a prominent feature of many arid- and semiarid-zone soils. The accumulation of pedogenic carbonate in response to climatic variables was studied by early workers such as Jenny (1941) and Arkley (1963). More recently, models have been constructed to relate the depth of carbonate accumulation to climatological data (McFadden and Tinsley, 1985; Mayer *et al.*, 1988; Machette, 1985; Marion *et al.*, 1985). Stable isotopes of C and O in paleosol carbonate are used to estimate paleoenvironmental parameters, such as temperature, effective moisture, and atmospheric CO_2 concentration, during carbonate formation (e.g., Cerling, 1991; Quade *et al.*, 1989a; Mack *et al.*, 1991). These interpretations require that sampled carbonate form pedogenically, not undergo subsequent reprecipitation, and be formed during a relatively homogeneous climate. Unfortunately, several studies (particularly in relict paleosols) suggest that dissolution and reprecipitation processes occur readily in soil environments (Salomons and Mook, 1976; Gile and Grossman, 1979; Amundson *et al.*, 1989).

Inconsistencies reported in several studies between radiocarbon ages of pedogenic carbonates and deposit ages suggest the dynamic nature of carbonate in the soil environment. In soils developed on limestone alluvium in southern Nevada, Sowers *et al.* (1988) obtained radiocarbon ages from carbonate rinds that were generally older than the best-estimate surface age based on geomorphologic properties; they attributed this to incorporation of detrital limestone. Gile and Grossman (1979) obtained older radiocarbon ages for Pleistocene than for Holocene pedogenic carbonate, but most of the Pleistocene samples appeared to "have undergone exchange with environmental C-14 after emplacement" (p. 197) and were appreciably younger than geomorphic age estimates.

Callen *et al.* (1983) also found that radiocarbon ages of pedogenic carbonate were younger than the surface age and inconsistent with depth in the profile and even within individual horizons. Williams and Polach (1971) found that carbonate precipitated in semiarid to arid climates (<500 mm precipitation) was likely to be "too old," while in subhumid climates (~500 mm precipitation), carbonate appeared to have undergone reprecipitation and was "too young," a finding supported by Damon *et al.* (1963).

During formation of pedogenic carbonate, its stable isotope composition is determined by the isotopic values of soil CO₂ (for C) and soil water (for O). Ideally, in a soil of homogeneous porosity, organic matter distribution, and isotope composition, carbonate $\delta^{13}\text{C}$ values should change gradually with depth, reflecting the diffusion gradient of ^{13}C -depleted, plant-derived soil CO₂ out of the profile and the mixing of ^{13}C -enriched, atmospheric CO₂ down into the profile (Cerling, 1984). This model assumes that the carbonate system (soil CO_{2(g)}, carbonate, and soil solution) is in isotopic equilibrium (i.e., sufficient time exists for complete isotopic exchange of carbon and oxygen between all components), which implies that ^{14}C is also in isotopic equilibrium within the system. Few studies of carbonate in modern (Holocene) soils have been performed to evaluate this model, but generally the isotopic pattern with depth is found to follow the predicted model (Quade *et al.*, 1989b; Amundson *et al.*, 1989; Pendall and Amundson, 1990).

In this study, we examine stable and radiogenic isotopes of C and stable isotopes of O in carbonate sampled from gravel coatings and soil matrix in three Holocene soils from a semiarid region in Nevada. By comparing isotopic measurements with modeled stable isotope profiles and radiocarbon ages, we assess the nature of soil carbonate with respect to its origin (detrital, dust, or pedogenic) and dynamic nature (closed or open to atmospheric CO₂) over time.

METHODS

Pebbles and fine (<2 mm) soil were collected from soils developed on three Holocene fans at Fish Lake Valley, Nevada (Fig. 1). Bulk soils were sieved to remove the >2-mm fraction and ground to <200 mesh before measurement of disseminated carbonate (referred to as "fine carbonate"). In the laboratory, pebbles were cleaned, and outer, powdery carbonate was removed from pebble bottoms by brushing with a stiff brush and discarded. Inner, indurated rinds, in contact with the pebble bottoms, were scraped off and ground to pass a 200-mesh sieve (referred to as "rind carbonate").

Radiocarbon analyses of soil carbonate were carried out by accelerator mass spectrometry at Lawrence Livermore National Laboratory. Carbonates were reacted *in*

vacuo with orthophosphoric acid. CO₂ released was cryogenically purified and reduced to a graphite AMS target using methods described in Vogel *et al.* (1984). Independent age estimates of charcoal contained in deposits were determined by conventional radiocarbon techniques using proportional gas counters and by AMS (Slate, 1991).

Carbonate C and O stable isotope ratios were measured on a Finnigan MAT 251 gas source mass spectrometer at the U.S. Geological Survey, Menlo Park, after reaction in 100% H₃PO₄ and CO₂ separation. Stable isotope ratios are reported with respect to a standard; $\delta\text{‰} = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}] \times 1000$; C standard is Pee Dee Belemnite (PDB) (Craig, 1957); O standard is standard mean ocean water (SMOW) (Craig, 1961).

Total carbonate mass in the <2 mm (fine) and >2 mm (rind) fractions was determined by multiplying carbonate content (%) by wt% of fines or gravel and by whole-soil bulk density. Carbonate content was determined by coulometric titration of samples acidified in 2 M HClO₄. The liberated CO₂ was scrubbed in H₂O₂ and AgClO₄ columns and then combined with monoethanolamine, which converts it to a strong acid that is titrated coulometrically (Brandt *et al.*, 1990). Profiles sampled in 1989 (Table 2) had rind carbonate removed from pebbles and combined with the fine fraction before carbonate analysis. Weight% of gravels was determined by sieving representative volumetric samples (2- to 3-kg samples taken with care to obtain all coarse and fine particles). The <2 mm fraction was ground to <100 mesh, and gravels (with attached carbonate rinds) were chipped and then ground to <100 mesh. The youngest soil had no pedogenic rinds, and thus, only fine carbonate was determined. Bulk density was determined by the clod method (Blake and Hart, 1986), correcting for gravel volume assuming a measured average gravel density of 2.56 g cm⁻³. We obtained whole-soil bulk density values ranging from 1.4 to 1.9 g cm⁻³ and averaging about 1.6 g cm⁻³; these are comparable to values measured in stony soils by Andraski (1990).

PEDOGENIC SETTING

The soils have developed in gravelly debris flows of the Trail Canyon alluvial fans, originating in the White Mountains of Nevada and California (Fig. 1). Rhyolite dominates the lithology of Holocene deposits and limestone is absent from the study area drainages. However, some carbonate is present in parent material alluvium, presumably derived from eroded older soils. We refer to this carbonate as "detrital." With the exception of one finer-textured horizon, gravel contents range from 20 to nearly 90% by weight; the alluvial matrix is generally sandy loam. The sediments are composed of debris flow "packets," which consist of a somewhat less gravelly layer overlain by a very gravelly layer. Soil horizon boundaries

FIG. 1. Surficial geologic map of Trail Canyon area of Fish Lake Valley showing location of soil profiles. Modified from Slate (1991) on base map compiled from USGS 7.5-min topographic quadrangles Davis Mountain, NV-CA, and Volcanic Hills West, NV. Elevations shown in feet; 1 m = 3.281 ft. Inset shows general location.

strongly correlate with boundaries of these depositional units.

Soil ages are independently constrained by radiocarbon-dated charcoal and by tephra interbedded in the debris flows and a buried A horizon dated by thermoluminescence (Slate, 1991). The youngest soil is developed in late alluvium of Marble Creek and is constrained to <1100 ^{14}C yr B.P. (1090 ± 50 yr B.P. (TO-1668)) by charcoal buried at 2 m depth, exposed in the same streamcut less than 1 km from profile FLV-7a (referred to as the "late Marble Creek" or "1000-yr-old" soil) (Tables 1 and 2). The next oldest soil is developed in early alluvium of

Marble Creek, with an age of 3800 yr, constrained by tephra and charcoal buried at 90 cm depth in profile FLV-6a (A. Sarna-Wojcicki, written communication, 1991) (referred to as the "early Marble Creek" or "3800-yr-old" soil) (Tables 1 and 2). The oldest soil is developed in alluvium of Leidy Creek, dated to 6300 yr by charcoal buried at 1 m depth in profile FLV-5c (6260 ± 100 yr B.P. (QL-4369)) and with a limiting age of a buried A horizon (depth 133–150 cm, profile FLV-5b) (Tables 1 and 2) dated by thermoluminescence to 11,000 yr B.P. (Slate, 1991) (referred to as the "Leidy Creek" or "6300-yr-old" soil).

The climate of the study area is semiarid and warm (mean annual precipitation, 17 cm; mean annual temperature, 15°C) and dominated by desert scrub (mainly *Sarcobatus bayleyi*, *Artemisia spinescens*, and *Atriplex confertifolia*, with $>60\%$ bare ground). The Leidy Creek soil may have experienced somewhat warmer and/or drier conditions during the middle Holocene (ca. 5000–7000 ^{14}C yr B.P.; Spaulding, 1991) relative to the present.

The three soils exhibit different morphologies, reflected in the amount of dust and carbonate accumulation and development of desert pavement. These features were used in field mapping alluvial fans of different ages (Slate, 1991). Holocene soils older than 1000 yr have loamy to sandy Av horizons up to 18 cm thick into which dust has infiltrated (Table 1). A well-developed desert pavement has formed on surfaces older than 3800 yr. B horizon development includes slight clay or silt accumulation in soils older than 1000 yr, presumably formed as dust is worked down into the soils, but carbonate accumulation is the predominant pedogenic feature (Table 1). The 1000-yr-old soil has disseminated (<2 mm) carbonate, but has not yet formed pedogenic rinds. The 3800- and 6300-yr-old soils have indurated, 2- to 4-mm-thick rinds beneath pebbles (Stage I to II, Gile *et al.*, 1966) as well as fine carbonate.

Fine (<2 mm) carbonate is distributed somewhat irreg-

TABLE 1
Properties of Trail Canyon Soils

Horizon	Depth (cm)	Carbonate stage	Structure	Texture
Late alluvium of Marble Creek; age, 1000 yr; 1646 m elev.				
A	0–4	Disseminated	Fine platy	Sandy loam
C1 to C6	4–98	0 to disseminated	Fine blocky and single grained	Sandy loam
Early alluvium of Marble Creek; age, 3800 yr; 1657 m elev.				
A1, A2, Av	0–18	0 to disseminated	Med. blocky	Loam
Bk1 to Bk3	18–68	I, under clasts	Blocky	Sandy loam
BC	68–98	I, under clasts	Single grained	Coarse sandy loam
Alluvium of Leidy Creek; age, 6300 yr; 1669 m elev.				
A, Av	0–16	0 to disseminated	Fine blocky	Loam
Bk1 to Bk4	16–133	I to II, under clasts	Fine blocky	Sandy loam to loamy sand
Ab or Bb	133–150	0	Fine blocky	Loam

TABLE 2
Carbonate and Radiocarbon Data for Soils at Fish Lake Valley

Horizon	Depth (cm)	Gravel (wt %)	CaCO ₃	CaCO ₃	CaCO ₃	Age (¹⁴ C yr B.P.)	
			fines + rind (%)	fines (%)	rind (%)	Fines	Rind
Soil profile FLV-5B developed in alluvium of Leidy Creek, Sampled March 1991							
	0-4	33		0.02	NP		
	4-16	25		0.37	NP	2050 (130, CAMS-1819)	
	16-38	58		0.18	0.24	2620 (90, CAMS-1195)	2920 (90, CAMS-1194)
	38-52	83		0.05	0.42		2770 (180, CAMS-856)
	52-77	63		0.09	0.08		
	77-88	86		0.46	0.11	6920 (200, CAMS-1197)	3440 (100, CAMS-1196)
	88-114	30		0.51	3.13	8620 (90, CAMS-1820)	
Soil profile FLV-5C developed in alluvium of Leidy Creek, Sampled March 1991							
Av1	0-6	25		0.05	0.36		
Av2	6-13	20		0.01	0.28	630 (90, CAMS-1821)	
2Btj	13-25	44		0.01	0.02		
3Btjk	25-40	73		0.04	0.05		
4Bk1	40-55	66		0.35	0.16		
5Bk2	55-70	87		0.51	0.23		
6BCk	70-95	75		0.34	0.16		
7CB	95-110	3		0.28	0.04		
8C	110-135	76		0.33	0.07	10603 (100, CAMS-1822)	
9Bb	135-150	88		0.21	0.02		
Soil profile FLV-5b developed in alluvium of Leidy Creek, Sampled April 1989							
A	0-4	52		0.04	NA		
Av	4-16	22		0.65	NA		
Bk1	16-32	51		0.26	NA		
Bk2	32-52	83		0.13	NA		
	52-77	76		0.48	NA		
2Bk3	77-87	66		0.69	NA		
	87-109	9		0.51	NA		
2Bk4	109-133	71		0.44	NA		
3Avb?Btb	133-150	43		0.17	NA		
Soil profile FLV-5c developed in alluvium of Leidy Creek, Sampled April 1989							
Av1	0-8	34	1.5				
Av2	8-10	23	2.42				
2Btj	10-25	38	0.25				
3Btjk	24-40	70	0.17				
4Bk1	40-55	58	0.42				
5Bk2	55-70	80	0.5				
6BCk	70-95	65	0.25				
7CB	95-110	39	0.33				
8C	110-120	65	0.33				
9Bb	120-135	81	0.17				
Soil profile FLV-6A developed in early alluvium of Marble Creek, Sampled March 1991							
A	0-2	41		0.02	NA		
Av	2-8	29		0.42	NA		
Btk	8-20	46		1	NA		
Bk1	20-50	63		0.97	NA		
2Bk2	50-65	54		1.2	NA		
2Bk3	65-80	73		0.38	NA		
3Bkz4	80-110	66		0.2	NA		
3Bz	110-120	69		0.15	NA		
Soil profile FLV-6D developed in early alluvium of Marble Creek, Sampled March 1991							
	0-7	34		0.06	0.28		
	7-14	33		0.33	0.48	1360 (110, CAMS-1823)	
	14-34	75		0.65	0.28	830 (100, CAMS-1199)	220 (90, CAMS-1198)
	34-50	41		0.24	0.06		
	50-68	76		0.49	0.59	3620 (200, CAMS-1201)	2640 (400, CAMS-1200)
	68-98	58		0.06	0.12	2220 (100, CAMS-1824)	

TABLE 2—Continued

Horizon	Depth (cm)	Gravel (wt %)	CaCO ₃ fines + rind (%)	CaCO ₃ fines (%)	CaCO ₃ rind (%)	Age (¹⁴ C yr B.P.)	
						Fines	Rind
Soil profile FLV-6b developed in early alluvium of Marble Creek, Sampled April 1989							
A	0–13	35	0				
Bwk	13–24	64	2.5				
Btk	24–35	45	0.67				
Bkq	35–44	30	0.33				
2Bk	44–59	57	0.42				
3Bz	59–94	44	0				
4Bwzjb	94–104	27	0				
5BC	104–135	70	0				
Soil profile FLV-6a developed in early alluvium of Marble Creek, Sampled April 1989							
Av	0–10	35	0.5				
Bw	10–19	45	0.25				
Bt	19–29	62	1				
Bk1	29–42	46	0.67				
2Bk2	42–52	76	1.25				
3Bz	52–89	42	0				
4Bwb	89–107	41	0				
5BC	107–137	77	0				
Soil profile FLV-7B developed in late alluvium of Marble Creek, Sampled March 1991							
A	0–4	29		0.2	NP		
2C1	4–15	66		0.11	NP	4650 (100, CAMS-1825)	
3C2	15–25	29		0.11	NP		
4C3	25–50	40		0.1	NP		
5C4	50–63	68		0.23	NP	3580 (100, CAMS-1826)	
6C5	63–78	76		0.27	NP		
	78–90	33		0.61	NP	11050 (100, CAMS-1827)	
Soil profile FLV-7b developed in late alluvium of Marble Creek, Sampled April 1989							
A	0–4	40		0	NP		
2C1	4–20	45		0.33	NP		
3C2	20–50	42		0.25	NP		
4C3	50–63	69		0	NP		
5C4	63–78	44		0.17	NP		
6C5	78–90	79		0.33	NP		
Soil profile FLV-7a developed in late alluvium of Marble Creek, Sampled April 1989							
Av	0–3	28		0.04	NP		
A	3–13	42		0.06	NP		
C1	13–25	34		0.05	NP		
C2	25–50	43		0.1	NP		
C3	50–70	71		0.24	NP		
C4	70–85	45		0.24	NP		

Note. Fine + rind data determined by scraping carbonate from clasts into the fine fraction. NA or blank, not analyzed; NP, not present. Numbers in parentheses under Age are error and lab number, respectively. Upper- and lowercase letters in soil profile name indicate replicate profiles sampled at different times.

ularly with depth, particularly in the late Marble Creek soil (1000 yr old), partially due to the layering of debris flows (Table 2). Soils on the early Marble Creek fan (3800 yr) show a distinct increase of rind and fine carbonate at about 30 to 50 cm depth. Soils developing on the Leidy Creek fan (6300 yr) also have somewhat variable carbonate profiles, with increases in fine carbonate above 20 cm depth and in both rind and fine carbonate at about 100 cm depth (e.g., profile FLV-5B, Table 2). The distinct increase at about 100 cm possibly represents the maximum leaching depth or a buried horizon. Morphological characteristics and total carbonate content for the 3800- and

6300-yr-old soils are similar, but the 1000-yr-old soil is distinctly less well developed.

RESULTS

Carbonate Accumulation Rates

Accumulation rates of soil carbonate vary over the western United States possibly due to differences in dust sources, precipitation, and lithology, such as the local abundance of limestone. Carbonate accumulating in these soils is considered pedogenic when there is evidence for dissolution and reprecipitation (e.g., carbonate

occurs as pebble coatings, or stable isotopes are in equilibrium with soil CO_2 and H_2O). We cannot discount the possibility of fine carbonate accumulating without undergoing pedogenesis, e.g., as dust which infiltrates downward mechanically. However, silt-sized particles of calcite or gypsum in infiltrated dust are likely to dissolve and come into equilibrium with soil CO_2 and H_2O , supplying Ca but not significant C or O to pedogenic carbonate. There is <0.6% carbonate present in parent material (referred to as "detrital"; e.g., C horizons in profile FLV-7a, Table 2), which we consider to be eroded from older soils since limestone is absent from the watershed. We measured the mass of total carbonate in the three Holocene soils in order to compare carbonate accumulation rates to rates in other regions and to locally measured dust fluxes. Carbonate accumulation from calcareous dust or limestone sources does not represent a net sink of atmospheric CO_2 , whereas silicate weathering consumes CO_2 (Schlesinger, 1982). Although the climate in western Nevada is not conducive to rapid weathering, soils at Fish Lake Valley contain abundant tephra, which potentially is easily weathered.

Total soil carbonate inventories [(% CaCO_3 by weight in fines * whole soil bulk density * % fines * horizon thickness) plus (% CaCO_3 by weight in rinds * whole soil bulk density * % gravel * horizon thickness), summed for all horizons in each profile] give an accumulation rate of $0.5 \pm 0.2 \text{ g m}^{-2} \text{ yr}^{-1} \text{ CaCO}_3$ (Fig. 2), calculated by the Switzer method (Switzer *et al.*, 1988). Our method of measurement includes pedogenic, dust, and detrital carbonate. The gross accumulation rate of soil carbonate

measured at Fish Lake Valley is lower than rates measured in dust traps in New Mexico ($2 \text{ to } 4 \text{ g m}^{-2} \text{ yr}^{-1} \text{ CaCO}_3$, Gile and Grossman, 1979) and on Holocene surfaces in the Las Cruces area ($1 \text{ to } 10 \text{ g m}^{-2} \text{ yr}^{-1} \text{ CaCO}_3$, Machette, 1985). Our measured carbonate accumulation rate is also lower than estimates by Chadwick and Davis (1990) of $1 \text{ to } 10 \text{ g m}^{-2} \text{ yr}^{-1}$ for the Lahontan Basin, northern Nevada. However, their estimates were strongly influenced by proximity to large playas. Estimated carbonate accumulation rates near Silver Lake playa, 300 km south of Fish Lake Valley, appear consistent with our measured rate (Reheis *et al.*, 1989; Harden *et al.*, 1991).

Integrated wet and dry atmospheric deposition, measured with dust collectors at three sites within 100 km of soil locations, contains enough Ca^{2+} as calcite to precipitate $1.3 \pm 0.6 \text{ g m}^{-2} \text{ yr}^{-1} \text{ CaCO}_3$, and an additional Ca^{2+} input from gypsum equivalent to about $0.15 \pm 0.12 \text{ g m}^{-2} \text{ yr}^{-1} \text{ CaCO}_3$ (M. Reheis, unpublished data, Traps T-37, T-41, T-42). Thus, we calculate a potential atmospheric input rate in the range of $0.7 \text{ to } 2.2 \text{ g m}^{-2} \text{ yr}^{-1}$ as CaCO_3 . This is slightly higher than the range of $0.3 \text{ to } 0.7 \text{ g m}^{-2} \text{ yr}^{-1}$ for carbonate accumulation based on our mass measurements (Fig. 2). Atmospheric sources Ca^{2+} are more than enough to account for the mass of carbonate accumulated in our soils.

Total soil carbonate content for replicate profiles on each surface has standard deviations ranging from 3 to 52% of the mean. Data variability could be due to variation in dust flux rates over the Holocene, detrital carbonate content, erosional history, differences in particle size distribution and water holding capacity, and other factors that cause natural variability in soils. Because the profiles are located within 4 km of one another at similar elevations, we believe that dust deposition probably has been spatially uniform at a given time at these sites.

^{14}C Isotopic Exchange

Radiocarbon content of fine and rind carbonate was analyzed to assess the degree of isotopic exchange with modern CO_2 in these soils. Holocene soils contain carbonate that is isotopically both "older" and "younger" than independent age estimates of the deposits (Table 2).

The fine carbonate fraction in soils on the Leidy Creek fan (6300 yr) shows a regular increase in radiocarbon age with increasing profile depth. A similar trend was noted in an early report on radiocarbon content of calcic soils (Damon *et al.*, 1963). Below 77 cm depth, carbonate accumulating as rinds beneath pebbles is younger than fine carbonate of the same horizon, opposite to what was expected. Above 77 cm, rind and fine carbonate have similar radiocarbon ages. The fine-fraction carbonate is consistently younger toward the surface and may dissolve preferentially relative to the rind carbonate.

FIG. 2. Mass of carbonate versus age of soil and alluvium for soils at Trail Canyon. Calculated as carbonate in <2 mm or >2 mm size fraction $\times$ wt% size fraction $\times$ total bulk density $\times$ horizon thickness (cm) summed through the profile. Individual profile data calculated from Table 2 (carbonate in g cm^{-2}): 7a (0.09), 7b (0.16), 7B (0.26), 6a (0.26), 6b (0.30), 6A (0.50), 6D (0.43), 5B (0.81), 5b (0.46), 5c (0.41) with no rind carbonate, 5C (0.36). Line, slope, and intercept were calculated by the Switzer method (Switzer *et al.*, 1988). Accumulation rate of $0.00005 \pm 0.00002 \text{ g cm}^{-2} \text{ yr}^{-1}$ is equivalent to $0.5 \pm 0.2 \text{ g m}^{-2} \text{ yr}^{-1}$.

Carbonate radiocarbon ages measured for the early Marble Creek fan are comparable to or younger than its charcoal and tephra-controlled age of 3800 yr B.P. (Table 2). Radiocarbon ages increase slightly with depth, presumably due to decreased wetting events lower in the profile. As with Leidy Creek soils, rind carbonate is somewhat younger than fine carbonate in the horizons measured.

Soils developing on the late Marble Creek fan (1000 yr) contain only fine carbonate; rinds have not yet formed. Apparent ages of fine carbonate between 10 and 100 cm depth are much older than geomorphic age estimates and charcoal buried at 2 m depth and must reflect detrital carbonate reworked from older soils. No limestone exists in the watershed, but we cannot discount the presence of limestone-derived eolian inputs.

Carbonate Stable Isotope Composition

Stable C isotope ratios in fine and rind carbonate of both Leidy Creek and early Marble Creek deposits become depleted with depth (Fig. 3). $\delta^{13}\text{C}$ (PDB) of carbonate is in equilibrium with atmospheric CO_2 of -6.5‰ near the soil surface and decreases with depth due to an increasing proportion of plant-respired CO_2 depleted in ^{13}C . This trend suggests that the entire C isotopic system is in equilibrium with soil CO_2 , as predicted by a diffusion model (Cerling, 1984; Cerling *et al.*, 1989). Fine and rind carbonate appear to be in equilibrium with model input values for soil CO_2 of $\delta^{13}\text{C} = -17\text{‰}$ and soil organic matter of -21‰ at a modeled respiration rate of $0.25 \text{ mmole m}^{-2} \text{ hr}^{-1}$ and 50% porosity² (solid line in Fig. 3). Soil organic C in the fine fraction had $\delta^{13}\text{C}$ ranging from -18 to -23‰ in these soils (Pendall *et al.*, 1991, and unpublished data), which corresponds to soil CO_2 $\delta^{13}\text{C}$ of -14 to -19‰ . Measured parameters will necessarily be more variable than model parameters; especially difficult to model is the variability of soil organic matter $\delta^{13}\text{C}$ with depth. The model is relatively insensitive to differences in porosity in the range likely to be found in our soils (40 to 60%). The respiration rate is comparable to that obtained by Quade *et al.* (1989b) at a similar elevation in southern Nevada.

Fine carbonate in late Marble Creek soils lacks a definable trend of $\delta^{13}\text{C}$ with depth and has not reequilibrated with modern soil CO_2 (Fig. 3). It is also much more depleted than other Holocene soil carbonate or any older, upslope soil (minimum Pleistocene carbonate $\delta^{13}\text{C} = \sim -5.5\text{‰}$; data not shown). Fine carbonate in late Marble Creek soils apparently has not undergone signif-

icant recrystallization, which is consistent with radiocarbon results.

In Leidy Creek and early Marble Creek soils, $\delta^{18}\text{O}$ (SMOW) values of carbonate in rinds and in the fine fraction decrease with depth (Fig. 4). Below 100 cm depth, $\delta^{18}\text{O}$ in these soils ranges from 17 to 22‰. This is slightly more enriched than carbonate would be if it precipitated in equilibrium with estimated local meteoric water $\delta^{18}\text{O}$. Precipitation data from the region indicate that carbonate equilibrated with meteoric water should have $\delta^{18}\text{O}$ of 12 to 17‰ (C. Kendall, pers. commun., 1991; data corrected for elevation at 15°C). Between 100 cm and the surface, there is about 10‰ enrichment compared with deeper values, with $\delta^{18}\text{O}$ increasing to greater than 30‰. We attribute this enrichment to evaporation of soil water, which causes lighter isotopes to be removed from the soil as vapor, while heavier isotopes remain; the effect is greatest near the surface.

The $\delta^{18}\text{O}$ values of carbonate in the late Marble Creek soil do not decrease with depth, implying no apparent evaporative enrichment (Fig. 4). However, fine carbonate $\delta^{18}\text{O}$ values generally fall within the expected range of carbonate precipitated from modern meteoric water (12 to 17‰). Although we cannot rule out the possibility that equilibrium between oxygen in water and carbonate has been attained (e.g., above 40 cm depth, Fig. 4), the random depth pattern, as well as evidence from C isotopes, makes this possibility unlikely.

DISCUSSION

Dissolution and reprecipitation of pedogenic carbonate in soils has been shown to be an equilibrium process following the reaction

where CO_2 is derived from plant and microbial respiration mixed with some proportion of atmospheric CO_2 in an open system (Cerling, 1984; Amundson *et al.*, 1989; Quade *et al.*, 1989b). Some suggest that the bicarbonate produced by this reaction is influenced by isotopic composition of parent material or preexisting detrital carbonate (e.g., Salomons and Mook, 1976; Schlesinger *et al.*, 1989); however, others have shown that limestone does not contribute substantially to the carbon isotope signature of pedogenic carbonate (Quade *et al.*, 1989b). Soil CO_2 , even at low respiration rates in desert soils, apparently is the primary contributor to $\delta^{13}\text{C}$ (and presumably ^{14}C) of pedogenic carbonate; this is the basis of recent paleoclimatic reconstructions using these techniques (e.g., Mack *et al.*, 1991; Quade *et al.*, 1989b; Wang and Zheng, 1989; Cerling *et al.*, 1988). Pedogenic carbonate thus acquires C from soil gas and Ca from weathering of dust or detrital minerals. It is not always possible to de-

² We did not measure the porosity of these skeletal soils, which is dependent on rock mass and volume, fine particle density, and organic matter content (Childs and Flint, 1990), all of which vary greatly in our soils.

FIG. 3. (A) $\delta^{13}\text{C}$ in fine carbonate of late Marble Creek soil, relative to PDB standard. (B) $\delta^{13}\text{C}$ in fine and rind carbonate of early Marble Creek and Leidy Creek soils relative to PDB standard; line shows model fit from Cerling (1984) of $\delta^{13}\text{C}$ of soil carbonate using respiration rate of $0.25 \text{ mmole m}^{-2} \text{ hr}^{-1}$, soil-respired CO_2 $\delta^{13}\text{C}$ of -21‰ , at 50% porosity and 15°C . Ages correspond to profiles 7b (1000 yr old), 6A and 6D (3800 yr old), and 5b, 5B, and 5C (6300 yr old), described in Table 2.

termine petrographically whether carbonate in soil is pedogenic, detrital, or a mixture; if it is pedogenic, it is not possible to determine whether it has undergone reequilibration since the time of deposition without radiocarbon analysis.

In Holocene soils that have experienced relatively uniform climate conditions and dust deposition rates, carbonate "ages" can be compared to ages predicted from

two simple models. These models are meant to be end-members of a continuum of possibilities. As one end-member, we assume that carbonate accumulating due to dust is immediately "reset" to modern ^{14}C content upon leaching down into the profile (probably starting as "dead" carbonate before rewetting), accumulates at a constant rate, and after deposition undergoes only radioactive decay (no further reequilibration). In this "dust

FIG. 4. (A) $\delta^{18}\text{O}$ in carbonate of late Marble Creek soil, relative to SMOW standard. (B) $\delta^{18}\text{O}$ in carbonate of early Marble Creek and Leidy Creek soils, relative to SMOW standard. Symbols are the same as in Figure 3.

model," we used 10-yr time steps, incrementally adding modern carbonate to the existing pool (starting with none in the soil), not allowing the existing carbonate to reequilibrate. "Modern" carbonate has the ^{14}C content of 1950 CO_2 (the spike of atmospheric ^{14}C produced by nuclear bomb testing can be detected in soil organic matter, but not yet in carbonate). The mass of carbonate added does not affect the age, as long as the input rate is constant. The dust model assumes pedogenic reequilibration of all incoming carbonate as soon as it is added, but not after. The other end-member model ("detrital model") considers a nonaccumulating, nonpedogenic system: detrital carbonate in alluvium can be completely reset to modern at the time of fan deposition and decay radioactively to the present, or it can start out with an "age" of 10,000 yr at the time of fan deposition (based on the deepest C horizon in the late Marble Creek soil) and decay radioactively until the present. Neither model takes into consideration decreasing $^{14}\text{CO}_2$ concentrations with increasing depth in soil, due to the presence of an increasing proportion of old organic matter, as suggested by a recently developed model (Wang *et al.*, 1994).

According to the dust model, carbonate accumulating in the 1000-, 3800-, and 6300-yr-old soils would have ^{14}C "ages" of 490, 1820, and 2940 yr B.P., respectively. Only carbonate that has the dust-model age or younger can be considered primarily pedogenic, since it requires equilibration with soil CO_2 . Measured ages that are younger than modeled ages reflect more dissolution and reprecipitation than would be due to accumulation alone. Ages

older than the dust-model ages reflect the presence of some proportion of detrital (or nonequilibrated dust) carbonate.

Both fine and rind carbonate above 40 cm depth in early Marble Creek and Leidy Creek soils appear to have reequilibrated more frequently than predicted by the dust model (Fig. 5). At these shallow depths, input of new carbonate apparently cannot "keep up" with reequilibration due to wetting events. Between about 40 and 90 cm depth in these soils, rind carbonate ages are quite close to the dust model ages. Consistency with the dust model suggests that at these depths, as pedogenic carbonate precipitates, it reequilibrates with contemporaneous soil CO_2 but does not dissolve and reprecipitate once it has formed. Therefore, rind samples from these depths may reflect the average pedogenic conditions over the lifetime of the soil. Below 90 cm, fine carbonate has experienced fewer wetting events and retains inherited isotopic values.

If detrital carbonate is reset to modern ^{14}C content at the time of debris flow deposition, the detrital model predicts ages that correspond to the independent ages. If the detrital carbonate in alluvium were not reset, but instead had an initial radiocarbon age of 10,000 yr, the ages would be 11,000, 13,800, and 16,300 yr B.P. for the 1000-, 3800-, and 6300-yr-old soils, respectively. Dates on fine carbonate below 90 cm in the Leidy Creek soil fall in between the predicted ages of 16,300 and 6300 yr B.P., suggesting that it was older than modern at the time of deposition and has partially reequilibrated since then. Carbonate ra-

FIG. 5. Radiocarbon content vs depth for (A) late Marble Creek, (B) early Marble Creek, and (C) Leidy Creek soils. Dashed line represents "dust model" for atmospheric deposition of modern C in 10-yr time increments, with radiocarbon decay but no reequilibration. Symbols are the same as in Figure 3; open symbols, rind; closed symbols, fine.

diocarbon "dates" that are equivalent to the deposit (charcoal) age may be due to complete resetting at the time of deposition with no further additions or reequilibration, but we consider this unlikely. Radiocarbon data in the late Marble Creek soil especially argue against resetting at deposition; obviously this soil (and by analogy the others as well) has inherited older detrital carbonate (Fig. 5). We cannot rule out the possibility that dust infiltrates as colloidal material, without dissolving, but we believe that the presence of reworked soil carbonate from higher on the fans is a more likely source of detrital material and therefore of old radiocarbon dates. A weakly developed, buried soil is present on the Leidy Creek fan below about 130 cm; our radiocarbon and stable isotope data are from the deposit above this buried soil, and thus were not influenced by greater effective moisture during the late Pleistocene. The magnitude of the increase in age with depth in the Leidy Creek soil is too great to be explained by a contribution of CO_2 from old organic matter (Wang *et al.*, 1994).

At Fish Lake Valley, rinds generally contain more modern C than fine carbonate, implying that water may flow preferentially around pebbles, causing carbonate to precipitate as pendants as it evaporates. Carbonate may dissolve preferentially in the fine fraction but reprecipitate as rinds, in which calcite nuclei are concentrated. Rinds probably have lower dissolution rates than disseminated carbonate (Chadwick *et al.*, 1987). Other workers have found pebble coatings to be much older than carbonate in the fine fraction (Gile and Grossman, 1979; Schlesinger, 1985). In these cases, fine carbonate appears to equilibrate with modern CO_2 while accumulating, rather than inheriting, detrital isotopic values, and sampled rinds may include a wide range of ages of pedogenic carbonate.

Radiocarbon analyses of pedogenic carbonate are rarely done in conjunction with stable isotope studies; however, knowledge of the radiocarbon age aids paleoclimatic interpretation from stable isotope data. In soils at Fish Lake Valley, rinds accumulate pedogenically without subsequent dissolution between 40 and 90 cm depth. Although the rinds represent a range of ages, C and O stable isotopes suggest that vegetation contributing to soil CO_2 , and rainfall patterns contributing to soil H_2O , have been relatively constant since middle Holocene time. Analysis of very thin increments of rinds from this depth may produce a more detailed record of Holocene climate variability.

Radiocarbon ages show that fine carbonate in these soils may have precipitated pedogenically or that it may be more similar to detrital carbonate. Interpretation of stable isotope composition of fine carbonate is difficult because of the range of ages it may represent and because it may not be related to soil-forming conditions. The apparent equilibrium with modern CO_2 of stable C isotopes

in fine and rind carbonate at all depths in the Leidy and early Marble Creek soils, illustrated by Cerling's (1984) model, may be coincidental (old, detrital carbonate below 90 cm depth happens to have $\delta^{13}\text{C}$ values similar to those of pedogenic carbonate) or may indicate that pedogenic conditions have been similar throughout the Holocene.

At Fish Lake Valley, radiocarbon ages of inner rind carbonate of Pleistocene soils (surface units 1 to 4, Fig. 1) demonstrate that the pedogenic carbonate of these soils is much younger than the deposits in which the soils are forming. For example, in a 50,000-yr-old soil (surface unit 4, Fig. 1), the massively cemented calcic/duric horizon (37–63 cm depth) contains approximately 75% modern carbon (Pendall *et al.*, 1991). In these relict soils, wetting events have reequilibrated pedogenic carbonate more quickly than new carbonate can accumulate. Additionally, organic C extracted from rinds is much younger than, and thus not in isotopic equilibrium with, the carbonate in which it was presumed to be "occluded," in soils of three different ages (Pendall *et al.*, 1991). Pleistocene pedogenic carbonate at Fish Lake Valley is clearly dissolving and exchanging isotopically with modern soil CO_2 and is apparently unsuitable for dating or stable isotope paleoenvironmental interpretation.

CONCLUSIONS

Radiocarbon analysis of soil carbonate helps elucidate processes of carbonate formation and aids in interpreting paleoclimate from stable isotope composition. However, evidence from these soils shows that pedogenic carbonate is too dynamic (too open for exchange with atmospheric CO_2) to be reliable in dating deposit ages. Radiocarbon and stable carbon isotope values show that soil carbonate is actively exchanging with modern CO_2 in the upper 40 cm of a 3800- and a 6300-yr-old soil. Between 40 and 90 cm, pedogenic rind carbonate appears to be accumulating but not redissolving. In these soils, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between 40 and 90 cm probably represent average middle to late Holocene environmental conditions. Soil CO_2 and meteoric water isotope ratios may have been relatively constant throughout the period of pedogenesis for these soils. Radiocarbon ages older than deposit ages in horizons below 90 cm suggest the presence of detrital carbonate that has undergone little dissolution and reprecipitation, although stable C isotopes appear to be in equilibrium with modern soil CO_2 .

Old radiocarbon ages of carbonate in a 1000-yr-old soil show that it takes up to 3800 yr before a pedogenic signal is found in these soils and that detrital carbonate is present in the parent material. Pleistocene soils exposed at the surface in our study area do not retain a Pleistocene paleoclimatic signature or radiocarbon ages, suggesting that continual accumulation and exchange processes, especially at shallower depths, may cause inaccurate inter-

pretation of paleoclimatic signals from carbonate isotope composition of relict soils.

Carbonate accumulation rates at Fish Lake Valley are comparable to or lower than rates measured at other locations in the southwestern United States. Dust trap measurements indicate that the modern dust input is more than sufficient to provide the total mass of carbonate measured in the soils. Net atmospheric C consumption rates due to silicate weathering must be very low, since carbonate in dust accounts for most of the carbonate accumulating in these soils.

ACKNOWLEDGMENTS

We thank Janet Slate, Alan Gillespie, and Marith Reheis, who contributed their great understanding of the soil-geomorphic relationships at Fish Lake Valley; Cindy Preen and Doug White for expert instruction in vacuum line operation; Carol Kendall for data on $\delta^{18}\text{O}$ of precipitation and soil organic C analyses; Dan Scherer and Paul Lamothe for laboratory assistance; and Jay Quade, Janet Sowers, William Schlesinger, Thure Cerling, and two anonymous reviewers for helpful suggestions on an earlier version of this paper. This work was supported by the U.S. Geological Survey Program on Global Change and by NASA Land Processes Branch.

REFERENCES

- Amundson, R. G., Chadwick, O. A., Sowers, J. M., and Doner, H. E. (1989). The stable isotope chemistry of pedogenic carbonates at Kyle Canyon, Nevada. *Soil Science Society of America Journal* 53, 201–210.
- Andraski, B. J. (1990). Rubber-balloon and drive-core sampling for determining bulk density of an alluvial desert soil. *Soil Science Society of America Abstracts* 1990.
- Arkley, R. J. (1963). Calculation of carbonate and water movement in soil from climatic data. *Soil Science* 96, 239–248.
- Blake, G. R., and Harte, K. H. (1986). Bulk density. In "Methods of Soil Analysis" (A. Klute, Ed.), Part 1. Am. Soc. of Agronomy, Madison, WI.
- Brandt, E., Aruscavage, P., and Papp, C. (1990). Determination of carbonate carbon in geologic materials by coulometric titration. In "Quality Assurance Manual for the Branch of Geochemistry" (B. F. Arbogast, Ed.), pp. 68–72. U.S. Geological Survey Open-File Report 90-668.
- Callen, R. A., Wasson, R. J., and Gillespie, R. (1983). Reliability of radiocarbon dating of pedogenic carbonate in the Australian arid zone. *Sedimentary Geology* 35, 1–14.
- Cerling, T. E. (1984). The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth and Planetary Science Letters* 71, 229–240.
- Cerling, T. E. (1991). Carbon dioxide in the atmosphere: Evidence from Cenozoic and Mesozoic paleosols. *American Journal of Science* 291, 377–400.
- Cerling, T. E., Bowman, J. R., and O'Neil, J. R. (1988). An isotopic study of a fluvial-lacustrine sequence: The Plio-Pleistocene Koobi Fora sequence, East Africa. *Palaeogeography, Palaeoclimatology, Palaeoecology* 63, 335–356.
- Cerling, T. E., Quade, J., Wang, Y. R., and Bowman, J. R. (1989). Carbon isotopes in soils and palaeosols as ecology and palaeoecology indicators. *Nature* 341, 138–139.
- Chadwick, O. A., and Davis, J. O. (1990). Soil-forming intervals caused by eolian sediment pulses in the Lahontan basin, northwestern Nevada. *Geology* 18, 243–246.
- Chadwick, O. A., Hendricks, D. M., and Nettleton, W. D. (1987). Silica in duric soils. I. A depositional model. *Soil Science Society of America Journal* 51, 975–981.
- Childs, S. W., and Flint, A. L. (1990). Physical properties of forest soils containing rock fragments. In "Sustained Productivity of Forest Soils" (S. Gessel, Ed.) Proceedings of the North American Forest Soils Conference 7th, Edmonton, Alberta. University of British Columbia, Faculty of Forestry Publishers, Vancouver.
- Craig, H. (1957). Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. *Geochimica et Cosmochimica Acta* 12, 133–149.
- Craig, H. (1961). Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* 133, 1833.
- Damon, P. E., Long, A., and Sigalove, J. J. (1963). Arizona radiocarbon dates, IV. *Radiocarbon* 5, 283–301.
- Gile, L. H., and Grossman, R. B. (1979). "The Desert Project Soil Monograph." U.S. Department of Agriculture Soil Conservation Service, Washington, DC.
- Gile, L. H., Peterson, F. F., and Grossman, R. B. (1966). Morphological and genetic sequences of carbonate accumulation in desert soils. *Soil Science* 101, 347–360.
- Harden, J. W., Taylor, W. E., Hill, C., Mark, R. K., McFadden, L. D., Reheis, M. C., Sowers, J. M., and Wells, S. G. (1991). Rates of soil development from four soil chronosequences in the southern Great Basin. *Quaternary Research* 35, 353–399.
- Jenny, H. (1941). "Factors of Soil Formation." McGraw-Hill, New York.
- Machette, M. N. (1985). Calcic soils of the southwestern United States. In "Soils and Quaternary Geomorphology of the Southwestern United States" (D. L. Weide, Ed.), pp. 1–22. Geological Society of America Special Paper 203.
- Mack, G. H., Cole, D. R., Giordano, T. H., Schaal, W. C., and Barcellos, J. H. (1991). Paleoclimatic controls on stable oxygen and carbon isotopes in caliche of the Abo Formation (Permian), south-central New Mexico, U.S.A. *Journal of Sedimentary Petrology* 61, 458–472.
- Marion, G. M., Schlesinger, W. H., and Fonteyn, P. J. (1985). Caldepe: A regional model for soil CaCO_3 (Caliche) deposition in southwestern deserts. *Soil Science* 139, 468–479.
- Mayer, L., McFadden, L. D., and Harden, J. W. (1988). The distribution of calcium carbonate in desert soils: A model. *Geology* 16, 303–306.
- McFadden, L. D., and Tinsley, J. C. (1985). Rate and depth of pedogenic-carbonate accumulation in soils: Formulation and testing of a compartment model. In "Soils and Quaternary Geomorphology of the Southwestern United States" (D. L. Weide, Ed.), pp. 23–41. Geological Society of America Special Paper 203.
- Pendall, E., and Amundson, R. (1990). The stable isotope chemistry of pedogenic carbonate in an alluvial soil from the Punjab, Pakistan. *Soil Science* 149, 199–211.
- Pendall, E., Harden, J. W., and Trumbore, S. (1991). Pedogenic isotopic indicators of climate and carbon cycling in Fish Lake Valley, Nevada. In "Friends of the Pleistocene Guidebook for Fieldtrip to Fish Lake Valley, California-Nevada" (M. C. Reheis, Ed.) U.S. Geological Survey Open File Report 91-290.
- Quade, J., Cerling, T. E., and Bowman, J. R. (1989a). Development of Asian monsoon revealed by marked ecological shift during the latest Miocene in northern Pakistan. *Nature* 342, 163–166.
- Quade, J., Cerling, T. E., and Bowman, J. R. (1989b). Systematic variations in the carbon and oxygen isotopic composition of pedogenic carbonate along elevation transects in the southern Great Basin, United States. *Geological Society of America Bulletin* 101, 464–475.

- Reheis, M. C., Harden, J. W., McFadden, L. D., and Shroba, R. R. (1989). Development rates of late Quaternary soils, Silver Lake Playa, California. *Soil Science Society of America Journal* 54, 1127–1140.
- Salomons, W., and Mook, W. G. (1976). Isotope geochemistry of carbonate dissolution and reprecipitation in soils. *Soil Science* 122, 15–24.
- Schlesinger, W. H. (1982). Carbon storage in the caliche of arid soils: A case study from Arizona. *Soil Science* 133, 247–255.
- Schlesinger, W. H. (1985). The formation of caliche in soils of the Mojave Desert, California. *Geochimica et Cosmochimica Acta* 49, 57–66.
- Schlesinger, W. H., Marion, G. M., and Fonteyn, P. J. (1989). Stable isotope ratios and the dynamics of caliche in desert soils. In "Stable Isotopes in Ecological Research" (P. W. Rundel, J. R. Ehleringer, and K. A. Nagy, Eds.), pp. 309–317. Springer-Verlag, New York.
- Slate, J. L. (1991). Quaternary stratigraphy, geomorphology, and geochronology of alluvial fans, Fish Lake Valley. Univ. of Colorado Ph.D. dissertation.
- Sowers, J. M., Szabo, B., Jull, T., Ku, T. L., Reheis, M. C., Chadwick, O. A., Robinson, S. W., and Amundson, R. G. (1988). Age data for Kyle Canyon soils and deposits. In "This Extended Land, Geological Journeys in the Southern Basin and Range: Field Trip Guidebook, Geological Society of America Cordilleran Section" (D. L. Weide and M. L. Faber, Ed.), pp. 141–142.
- Spaulding, W. G. (1991). A Middle Holocene vegetation record from the Mojave Desert of North America and its paleoclimatic significance. *Quaternary Research* 35, 427–437.
- Switzer, P. S., Harden, J. W., and Mark, R. K. (1988). A statistical method for estimating rates of soil development and ages of geologic deposits: A design for soil-chronosequence studies. *Mathematical Geology* 20, 49–61.
- Vogel, J. S., Southon, J. R., Nelson, D. E., and Brown, T. A. (1984). Performance of catalytically condensed carbon for use in AMS. In "International Conference on Accelerator Mass Spectrometry, 3rd Proc. Nuclear Instruments and Methods v. B5" (W. Wolfli, Ed.), pp. 284–293.
- Wang, Y. R., Amundson, R., and Trumbore, S. (1994). A model for soil CO₂ and its implications for using ¹⁴C to date pedogenic carbonate. *Geochimica et Cosmochimica Acta* 58, 393–399.
- Wang, Y. R., and Zheng, S.-H. (1989). Paleosol nodules as Pleistocene paleoclimatic indicators, Louchuan, P. R. China. *Palaeogeography, Palaeoclimatology, Palaeoecology* 76, 39–44.
- Williams, G. E., and Polach, H. A. (1971). Radiocarbon dating of arid-zone calcareous paleosols. *Geological Society of America Bulletin* 82, 3069–3086.