The vesicular layer and carbonate collars of desert soils and pavements: formation, age and relation to climate change

Leslie D. McFadden a,*, Eric V. McDonald b, Stephen G. Wells b, Kirk Anderson c, Jay Quade d, Steven L. Forman e

a University of New Mexico, Albuquerque, NM 87131, USA
b Desert Research Institute, Reno, NV 89506, USA
c University of California at Riverside, Riverside, CA 92521, USA
d Desert Laboratory, Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA
e University of Illinois, Chicago, IL 60607, USA

Received 15 March 1996; revised 12 March 1997; accepted 9 November 1997

Abstract

The vesicular, fine-grained A horizon (Av) is the widespread, ubiquitous surficial horizon of desert soils in diverse landforms and parent materials of varying ages. Now known to form mostly through accumulation of eolian dust, recent studies show that dust accumulation and concomitant soil development are genetically linked to stone pavement formation. Changes in the magnitude of eolian activity and effective leaching related to Quaternary climatic changes are also hypothesized to have influenced the evolution of the Av horizon. Numerical modeling, geochronologic, and field/laboratory studies elucidate the nature of pedogenic processes controlling compositional evolution of Av, how the changing Av horizon increasingly influences soil infiltration and carbonate translocation and accumulation, and the control that clasts of the evolving pavement exert on pedogenic processes. Results of a model that determines soil bulk chemical composition based on mixing of estimated proportions of externally derived (eolian) material and parent materials imply that the evolution of the soil bulk composition is strongly influenced by Av horizon formation. The early development of a weakly to moderately developed Av horizon directly over gravelly parent material in late and middle Holocene soils moderately influences soil infiltration, but significant leaching of very soluble materials and some carbonate in dust are permitted. In older, Pleistocene soils, however, the texturally more mature Av and underlying, cumulic nongravelly horizons more strongly limit the rate and depth of leaching, and soil bulk composition therefore more closely approximates a simple mixture of dust and parent material. Other aspects of Av horizon development and its relations to the pavement are evaluated through studies of pavement clasts with coatings of soil carbonate, referred to as carbonate collars. Development of a numerical model that integrates soil hydrology, a CO₂ production–diffusion model, calcite kinetics and thermodynamic considerations, composition and thermal characteristics of pavement clasts and the textural and structural properties of the surface horizon provides the basis for testing a hypothesis of collar formation. Model results, combined with results of δ¹³C and δ¹⁸O analyses of collar carbonate, demonstrate how precipitation of calcite on pavement clasts and within the Av is favored at a depth much shallower than that indicated by the classic carbonate depth–climate relationship of Jenny and Leonard. Calculations of carbonate and water movement in soil from climatic data. Soil Science 96, 239–248]

* Corresponding author. Fax: +1 505 277 8843.

0169-555X/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0169-555X(97)00095-0
simulated by numerical models of carbonate accumulation. Simultaneous development of thick carbonate collars and the Av horizon requires the sustained pavement clast–Av horizon coupling for at least centuries to possibly millennia. New thermoluminescence ages also indicate that much of the Av horizon formed in the Holocene, and that it is certainly much younger than the older Pleistocene pavements. This supports the previously proposed hypothesis that increased dust flux during the Pleistocene-to-Holocene transition triggered and/or greatly accelerated Av horizon development. An understanding of the genesis of collars provides not just an understanding of how carbonate can accumulate in surface environments, but it also provides important clues into processes of pavement evolution and preservation of Av horizons during long glacial periods. The Av horizon is not merely an insignificant surficial zone of recent dust accretion; instead, its development profoundly influences the genesis of desert soils and pavements. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** desert pavements; vesicular soils; desert soils; climate change; soil model; calcic soils

### 1. Introduction

On many areally extensive landforms of desert regions, the most common surficial soil horizon is a vesicular layer (Fig. 1), also called the ‘Av’ horizon. The v modifier refers to its most obvious, distinguishing field property, well-developed commonly fine to large vesicular pores. Other common soil properties associated with vesicular horizons include a fine, loamy texture and strong, columnar structure with secondary, platy structure best expressed in the upper part of the Av horizon. The Av horizon occurs almost invariably below a desert stone pavement.

Several different models have been proposed for the formation of vesicular horizons and for the formation of desert pavements. In some early studies, soil researchers suggested that the Av horizon is due to chemical weathering favored by shallow leaching in arid, hot environments. Many researchers, noting the strong vertical sorting in many stony desert soils, concluded that the desert pavement formed by surficial deflation and/or sheetwash erosion of fines from initially gravelly deposits; they did not consider or recognize the development of the pavement to be related to that of the Av horizon (Cooke, 1970; McHargue, 1981; Ritter, 1986; Cooke et al., 1993; Williams and Zimbelman, 1994). Other researchers inferred, however, that the characteristically several-decimeter-thick, nearly stone-free argillic B horizons that underlay the pavement and vesicular crust resulted from cyclic shrink–swell cycles, frost action, growth of salt crystals, or expansion of entrapped soil air in the Av horizon. These processes presumably heave the coarser particles through the horizon to the soil surface causing pavement development (Springer, 1958; Jessup, 1960; Denny, 1965; Cooke, 1970; Mabbutt, 1977; Dan et al., 1982; Cooke et al., 1993). In contrast, Nettleton et al. (1987), on the basis of micromorphic fabric analysis, argued that pavements may have formed after the formation of argillic B horizons by extreme wind erosion. Virtually all researchers have concluded that the presence of the stone pavement, once formed, enhances entrainment of eolian dust, leading to or at least strongly accelerating formation of the vesicular layer and that the horizon does not form by shallow chemical weathering (Yaalon and Ganor, 1973; Gile, 1975; Peterson, 1977; McFadden et al., 1992).

These hypotheses of desert soil and pavement evolution, however, mutually conflict and are problematic in several respects. For example, requiring extensive deflation of an initially rough, gravelly surface sufficient to form a lag, but concomitant with dust entrainment below a ‘lag’ to form the Av horizon, is contradictory. These models are also inconsistent with a recent hypothesis of the origin of desert pavements. Wells et al. (1985) note that pavement clasts in volcanic soils of the Cima Volcanic Field (see Fig. 1) have progressively stronger, thicker desert varnish coatings, indicating the antiquity of the stone pavement. McFadden et al. (1987) showed that chemical alteration of stones in pavement differed from that in the subsurface, with the former displaying properties consistent with alteration in a subaerial environment and the latter exhibiting prop-

---

1 The lower case letter v formally stands for the presence of plinthite according to the Soil Taxonomy (Soil Survey Staff, 1975); however, v has been used in a substantial number of published studies of desert soils that possess strongly vesicular surficial horizons, and we therefore use the term in this paper.
properties reflecting subsurface alteration. These conclusions are consistent with recent chronologic studies of the stone pavement that not only show significant ages (e.g., greater than 40 to 50 ka) of stone pavements (Wells et al., 1995; Shepard et al., 1995), but also show that the pavement is isochronous with the underlying basaltic flow in which overlying soils have formed (Wells et al., 1995). Thus, a strongly developed argillic horizon with strong shrink–swell behavior is not required to heave the stones upward and generate a pavement. Instead, the pavement is born at the surface, and maintained as the underlying soil evolves (Wells et al., 1985; McFadden et al., 1986, 1987; Gerson and Amit, 1987).

1.1. Av horizons: a product of Quaternary climate change?

If pavements are born at the surface and if pavements are as old as 0.5 m.y., how old are the underlying Av horizons? McFadden (1982) observed that soil properties, such as color, texture, chemical and mineralogical properties of Av horizons of middle Pleistocene to middle Holocene surfaces in the eastern Mojave Desert, are generally similar. In contrast, such properties in the underlying argillic and calcic horizons are highly variable, suggesting that all vesicular horizons in that area associated with geomorphic surfaces of varying ages might have formed largely in the Holocene. This was attributed (McFadden, 1982) to the influence of increased aridity and the accumulation of carbonates and salts at shallow depths, pedogenic properties that could subsequently inhibit deep translocation of clay and thereby result in concentration of eolian fines at the soil surface (McFadden, 1982). Subsequently, Wells et al. (1985) and McFadden et al. (1986) proposed that rates of soil development on surfaces of flows of the Cima area reflected times of active dust influx, driven by times of playa expansion, vegetation re-
duction, and dust movement. Thus, the Av horizon would form largely in the Holocene, reflecting the aridification following the latest Pleistocene to early Holocene climate change and desiccation of pluvial Lake Mojave. McFadden et al. (1986) also proposed that argillic horizon formation may partially reflect the coalescence of reddened, clay-rich interiors of the Av horizon. Chadwick and Davis (1990) also proposed times of accelerated soil development in some deserts of North America concurrent with interglacial periods due to increases in dust supply from playas and associated surfaces as extensive pluvial lakes disappeared. This process resulted in regional burial of landscapes of varying ages by latest Pleistocene to early Holocene loess in which soils have developed. Bull (1991) also proposed that this reflected the early Holocene increase in atmospheric dust flux.

In contrast to these conclusions regarding the age of the Av horizon, the properties of the Av horizon and the stone pavement are consistently and strongly correlated in increasingly older Holocene and Pleistocene soils, suggesting that the Av horizon and associated stone pavement are cogeneric over this long period of time (Gerson and Amit, 1987; McDonald, 1994; McDonald et al., 1998). This suggests that the vesicular horizon, or at least significant parts of it, of older Pleistocene soils may be substantially older than the Holocene. Reheis et al. (1995) show that there are compositional differences amongst the Av horizons of many Holocene and Pleistocene soils of California and Nevada. This may also suggest that the Av horizon formed partly before the Holocene.

Generally, virtually all studies show that the vesicular horizon is most typically associated with soils forming in a relatively hot and arid climate that favors sparse vegetation. As indicated above, development of such soils reflects the shallow depth of leaching, decreased permeability associated with dust accumulation in the upper part of the soil, and an increased influx of salt-rich dust. A large number of paleobotanical and other paleoclimatic studies demonstrate that the Late Pleistocene climate in the southwestern United States was effectively moister than Holocene climate. The Late Pleistocene climate probably favored formation of soils with characteristics quite different from those of Holocene soils (Gile and Grossman, 1979; Gile et al., 1981; McFadden, 1982, 1988; McFadden and Tinsley, 1985; Marion et al., 1985; Machette, 1985; McFadden et al., 1986, 1991a,b; Mayer et al., 1988; McDonald, 1994; McDonald and McFadden, 1994). Also, soils forming in the currently subhumid (xeric or ustic moisture regime, thermic to mesic temperature regime) areas within or adjacent to the Mojave, Sonoran, Chihuahuan, or Great Basin Deserts under a denser vegetation commonly lack Av horizons or evidence of ongoing pavement formation. These soils have largely nonvesicular Mollic or Ochric horizons. Thus, one might predict for areas subjected to a wetter climate during glacial periods the formation of Av horizons and pavements to be supplanted by accumulation of organic matter, development of granular soil structure in the A horizon, and net translocation of silt, clay, and carbonates below the A horizon. Also, finer-grained soils might well be preferred habitat for mammal activity, inducing bioturbation. It is unknown if and how Av horizons can be maintained through multiple glacial–interglacial cycles and what the associated surficial processes might be.

To address these fundamental questions regarding the interrelationships of the Av horizon and stone pavements and how they are affected by climate changes requires a clearer understanding of the factors controlling pedogenic processes operating in the uppermost part of desert soils, and the age of the Av horizon. To accomplish these goals a better understanding of the genesis of the Av horizon is necessary. The evolution of the Av horizon, as reflected by changes in its chemical and mineralogical composition, reflects the rates and magnitude of soil-water movement and chemical weathering in the horizon. Ultimately, two enigmatic characteristics of some Av and pavements must be explained by Av horizon-forming processes. The first characteristic is the accumulation of carbonate essentially at or very near the soil surface, a depth several centimeters to decimeters shallower than that predicted by (1) the classic mean annual precipitation–depth of accumulation relationship documented by Jenny and Leonard (1935) and later by Arkley (1963) and in numerous, subsequent studies, and (2) numerical models of calcic soil development (cf., McFadden et al., 1991a,b). The second feature is occasionally observed in pavements which Sena et al. (1994) informally called ‘carbonate collars’. Carbonate collars are truncated carbonate
coatings, that is, the coating occurs as a belt of carbonate, typically oriented parallel to the ground surface, but truncated both at the ground line and at a relatively shallow depth below it (Fig. 2). Collars are most prevalent on limestone pavement clasts, but they are also observed on noncalcareous pavement clasts (Fig. 2B–D). The presence of such collars in such materials has been noted in few studies other than that of Sena (e.g., Rundel and Gibson, 1996). Formation of the collar requires processes that somehow prevent or strongly limit the development of carbonate coatings on stone bottoms, despite the following observations. First, somehow, pedogenic processes favor carbonate accumulation in the region surrounding the stone bottoms, the Av horizon. Second, calcareous composition of coarse clasts typically favors even more rapid development of carbonate coatings compared to noncalcareous clasts, progressing during later stages to the formation of pendants. Third, the incorporation of calcareous dust in soils of desert regions of the western United States strongly influences virtually all aspects of calcic soil development. The association of most collars with limestone clasts suggests that the clast itself is the primary source of the carbonate, yet noncalcareous clasts with collars are occasionally observed in pavements lacking calcareous clasts. So any hypothesized process of collar formation must account for all of these features.

The spatial association of Av horizons and collars suggests that the origin of collars may be closely linked to that of the vesicular horizon and the uppermost, nongravelly transitional AB horizon. That is, the processes of vesicular horizon development should be linked to those controlling collar formation. Given the thickness of the collar and the most recently proposed model of pavement evolution, we surmise that formation of these collars requires long-term coupling of pavement clasts and the vesicular horizon. We test this hypothesis by first examining the nature and magnitude of pedogenic processes associated with soil infiltration and soil-water movement in the uppermost part of the soil as reflected in the changing chemical composition of the Av horizon. Secondly, we utilize these results, recent hydrological studies of the Av horizon, and a modified version of a numerical model of calcic soil development in a new numerical model of collar formation.

We also employ stable isotopic analyses of carbonate collars and new age estimates for Av horizons from optical dating studies to test the proposed hypothesis of collar and Av horizon formation. Finally, on the basis of the proposed hypothesis, we address some of the questions noted previously concerning the origins of soils and pavements and their relations to climatic changes in the Quaternary.

2. Properties of the vesicular horizon

2.1. Morphologic, textural, chemical and mineralogical characteristics

Numerous studies of soils with vesicular horizons have been conducted in the western United States. Many studies of desert soils in North America that include some attention to the attributes of the Av horizon have been conducted as part of soil chronosequence studies in the Mojave, Sonoran, Great Basin, and Chihuahuan Deserts (McFadden, 1982; McFadden et al., 1986, 1989; Reheis et al., 1989, 1995; Simpson, 1991; Ruzicka, 1994; Royek, 1991; McDonald, 1994; Treadwell, 1996). The following discussion of the horizon is based on data from approximately 160 soils described in these studies, as well as observations and results of numerous other studies.

As noted previously, the hallmark of the Av horizon is strong vesicularity (Fig. 3). The formation of disconnected, primarily ovoid vesicles and interconnected channels in the overlying Av horizon has been attributed to several causes (Springer, 1958; Miller, 1971; Evenari et al., 1974). Some researchers proposed they form by entrapment of air below infiltrating water that subsequently moves upward and escapes, leaving soil voids behind (Buol et al., 1989). Most soil scientists concur that their formation reflects soil-air expansion following infiltration events and that they can form very rapidly in very silty soils. The expansion, however, may also be favored by direct insolation and intense soil heating following soil wetting events, which greatly reduces soil shear strength. Thus, the zone of most recent vesicle formation may be in the uppermost few millimeters to centimeters of the Av horizon that is subject to very strong heating and little resistance to
expansion. Multiple generations of clay and fine-silt coatings on vesicular void walls in the interior of Av peds formed during wetting events (Fig. 3A) probably confer increased strength and help protect them from destruction during subsequent wetting-and-drying cycles. As the horizon thickness increases with time, however, previously formed vesicles become more deeply buried. The increasing weight of overlying, periodically saturated material may not only prevent vesicle formation, but, combined with the effects of episodic swelling and contraction, might also contribute to their deformation, flattening and eventual destruction. This may also favor the development of the fine, platy structure in these horizons (Springer, 1958; Allen, 1985; Anderson et al., 1994).

Although this surficial horizon does have strong vesicularity and strongly developed structure as defining attributes, it is characterized by a relatively large range of variation in other soil properties. The thickness of the horizon may vary from less-than-a-centimeter to about 20 cm. The texture ranges from sandy-clay to silt- or sandy-loam, and often the horizon has the finest texture of all horizons in the soil, including subjacent argillic horizons, with the exception of some older Pleistocene soils. In general, the Av horizon with the finest texture in a chronosequence is observed in the older Holocene and Pleistocene soils. Usually only very small amounts of coarser sand and granules are present, which may be attributed primarily to particles produced by mechanical weathering and disintegration of pavement clasts, or to preservation of coarse material inherited from the soil parent material.

Soil pH of the Av horizon ranges from 7.0 to 8.9, although values most commonly range from 7.8 to 8.4. Electroconductivity (EC) values are typically low (0.1 to 0.5 mS/cm). Usually, soil EC increases with depth to maximum values in the lower horizons, indicating that most salts are leached deeply below the Av horizon. High values are observed rarely (2–4 mS/cm), reflecting the presence of soluble salts. In a few areas; efflorescent salts also are observed seasonally at the surface. Presumably, part of these surface salts reflect seasonal accumulation caused by capillary updraw of saline fluids from wetter horizons underlying a drier and finer-textured Av horizon. Given the extremely high solubility of such salts, the first rains should easily leach most of these salts to greater depths, so their presence in the Av horizon is possibly seasonal. Carbonate content ranges in soils from <0.1% to 30%, with the latter high percentages present in soils developed in limestone-rich parent materials. Pedogenic carbonate is present as disseminated carbonate in the ped interior, or as segregated coatings on the bottoms of peds. Carbonate is not uniformly distributed in the Av horizon. Often, the top and sides of the ped, sometimes lined by nonaggregated fine-soil material, effervesce little or not at all, whereas the interior is typically moderately to strongly effervescent. Anderson et al. (1994) have shown that these field properties are associated with carbonate contents that range from <0.2% on the exterior of the ped to as high as 12% in the ped interior.

The color of the Av horizon is typically very-pale brown (10YR 7/3), but is often redder (10YR 6/6 to 7.5YR 5/4) in the interior of the ped. The light color values are consistent with the low organic matter content of the horizon (0.1 to 0.2%). Fe$_2$O$_3$ (dithionite extractable iron oxides, including principally hematite, goethite, ferrihydrite) values range from 0.4 to 1.5%. The highest contents in a given area occur in the oldest soil in a chronosequence. Also, with the exception of soils with well-developed argillic horizons, the highest Fe$_2$O$_3$ content occurs in the vesicular horizon. Fe$_3$O$_4$O$_2$ (oxalate extractable iron oxides, consisting principally of ferrihydrite) contents are typically very low in vesicular horizons.

Fig. 2. Carbonate collars from various locations in the Mojave Desert, California. (A) Partly exposed collars (arrows) associated with limestone clasts on an early Holocene stone pavement on the piedmont of the Providence Mountains. (B) Collar on noncalcareous clast embedded in an Av horizon exposed in streamcut in late Holocene stone pavement associated with limestone-dominated piedmont deposits of the Providence Mountains. (C) Collar (arrow) on a basaltic clast excavated from a stone pavement on a flow surface of middle Pleistocene age in the Cima Volcanic Field. Lower part of clast is coated by thin, noncalcareous silt, clay and iron oxides. The exposed surfaces of clasts, such as the embedded clast on which the knife lies, are strongly varnished. (D) Remnant collar on a large basaltic boulder from the pavement of a middle Pleistocene volcanic flow. Knife is 8 cm long.
Fig. 2 (continued).
Fig. 3. Photomicrographs of the interior of an Av horizon of a soil formed on a middle Pleistocene volcanic flow in the Cima Volcanic Field. (A) Microlaminated, optically continuous clay pedofeature lines vesicular pore in matrix of nonoriented fine groundmass and abundant, quartz grains. Frame width 1.25 mm, plain light, 4× magnification. (B) Microlaminated, optically continuous clay pedofeature infills channel in a nonoriented matrix dominated by abundant quartz silt grains. Frame width 2.5 mm, plain light, 10× magnification.

ranging from 0.05% to 0.5%. Fe$_2$O$_3$o contents are uniformly very low (<0.1%) in soils forming in the most arid moisture regimes and hyperthermic soil temperature regimes. Fe$_2$O$_3$o/Fe$_2$O$_3$d ratios, a proxy for the degree of crystallinity of iron oxyhydroxides in soils, range from 0.07 to 0.5, but the ratio in most
soils ranges between 0.1 and 0.2. FeO/FexO4 ratios (the ferrous to ferric iron oxide ratio) has been measured for only a few vesicular horizons in soils on latest middle and latest Pleistocene basaltic flows in the Cima Volcanic Field (McFadden et al., 1986). The ratio in the Av horizon on the youngest flow is slightly lower (0.24) than in lower horizons (0.28, 0.35). In the soil on the older flow, the ratio of the Av is similar (0.21), but a few lower horizons had very low ratios (0.002), which was attributed to prolonged intense chemical weathering.

Most Av horizons have a thin (few mm to 5 cm) overlying layer with loose consistence and single-grain structure. This horizon, sometimes designated as an A horizon, has slightly coarser texture, slightly lower pH (from 0.1 to 1.0 pH units), and slightly to considerably lower carbonate and soluble salt content than the underlying Av horizon. On the basis of this evidence, McFadden et al. (1986) proposed that this horizon consists of the most recently accumulated eolian material that, through leaching, has been depleted of easily translocated clays, fine silt, carbonates and soluble salts. Although they are observed elsewhere in desert surfaces in the southwestern United States, biogenic crusts (cryptogamic crusts) have not been observed in soils with pavements and Av horizons.

Micromorphic observations of selected Av horizons demonstrate a complex pattern of soil constituents. Sorting of larger particles of the groundmass is poor to moderate (Fig. 3). Larger particles visible in Fig. 3 are quartz and form the predominant material of the coarse fraction of the groundmass, although occasionally other minerals such as feldspar or lithic fragments (basalt) are present. The finer fraction of the groundmass consists of very-fine silt, unoriented silicate clay, and micritic calcite. Clay is also present as often optically continuous, microlaminations. These features are often found in subhorizontal planar voids, but are also observed on walls of vesicular pores and vughs. Some clay exhibits a distinctly reddish hue, indicating that some cutans are ferriargillans. The organization of the coarse and fine material of the groundmass indicates a porphyric-related distribution. The clay mineralogy of the vesicular horizon is most commonly mixed, containing smectite, kaolinite, illite, mixed-layer clay minerals, quartz and rarely vermiculite and palygorskite (McFadden, 1982; McFadden et al., 1986; Reheis et al., 1995). Organic matter (other than live roots) is present only in trace amounts in Av horizons.

2.2. Origin and development: past and recent hypotheses

The presence of abundant quartz in an Av horizon capping soils developed on basalt flows in the Mojave Desert clearly demonstrates their eolian origin (Fig. 3). Distinct mineralogical and compositional similarity of Av horizons with dust from upwind sources in southern Nevada and California has been documented (Reheis et al., 1995). Dust may originate from various sources, including locally extensive playas and minimally vegetated geomorphic surfaces associated with loosely aggregated sediments. The finest dust may come from distant sources, whereas a large amount of the coarser dust may come from piedmonts in the region (Reheis and Kihl, 1995). Modern playas currently produce much of the soluble salts and carbonates in dust (Reheis and Kihl, 1995). The formation of playas following pluvial lake desiccation and regional aridification may have triggered an increase in dust accumulation and soil development during the Pleistocene-to-Holocene climate transition (Wells et al., 1985, 1987; Machette, 1985; McFadden et al., 1986; Chadwick and Davis, 1990; Reheis et al., 1989, 1995).

The net accumulation of eolian dust immediately beneath the stone pavement is attributed to effectiveness of the pavement to trap dust. Although some dust accumulation occurs by wet deposition, Wells et al. (1985) proposed that the deposition of dust was attributable to the roughness of geomorphic surfaces that caused local air-flow turbulence, flow separation, and deposition of eolian grains. The lack of topographically rough surfaces on dunes or fine-grained flood plain deposits partially explains the lack of or presence of only weakly developed Av horizons in soils formed in these deposits. Variables such as stone size, flattening, and cover density strongly determine whether or not dust deposition occurs by complexly affecting air flow structure immediately above a gravelly surface (Goosens, 1995). Consequently, the spatial patterns and abso-
lute rates of dust incorporation on surfaces may vary significantly. Gerson and Amit (1987) proposed, for example, that as the accumulation of dust progressively filled available pore space in the upper part of the soil, the efficiency of dust entrapment of the increasingly smoother desert pavement would diminish. Research in the Cima Volcanic Field shows, however, that despite diminished trapping efficiency, when regional dust influx increases significantly, rates of accretionary B horizon accelerate significantly as shown by burial of relict Av and Bt horizons by up to several decimeters of sediment (Wells et al., 1985; McFadden et al., 1986).

Analysis of the total chemical composition of soils can also be used to evaluate factors influencing the genesis of soil horizons and to determine general patterns of leaching and chemical weathering (Birkeland, 1984). McDonald (1994) concluded, utilizing molar ratio analysis based on major elements + trace element concentrations (calculated as oxide contents), that dust was the major source of silt and clay in soils on piedmonts of the Providence Mountains. The highest concentrations of the major oxides, Al_2O_3, TiO_2, and FeO, and also other less abundant elements (e.g., MnO, P_2O_5 and many trace elements such as ZrO_2) occur in surface and near-surface horizons. He also noted significant changes in the ratio of Zr/Cr and TiO_2/MnO and noticeable decreases in the variation of relative proportions of these elements in the Av horizons relative to those in the soil parent material. McDonald attributes these trends to the addition of dust to these soils, because they cannot be accounted for by the minimal chemical weathering exhibited by these desert soils. Similar studies elsewhere in southern California and Nevada, supplemented by analysis of modern dust as well as statistical analysis, demonstrate the strong imprint of dust on soil accumulation, particularly in the Av horizon (Reheis et al., 1995).

A quantitative evaluation of the net losses or gains of certain elements during soil formation may be achieved by comparison of concentration of a given element or group of elements in a weathered material to that of chemically conservative elements (i.e., Al, Ti, Zr). The strategy usually entails calculation of molar ratios, such as the base–alumina or base–titania ratios (Birkeland, 1984). In soils strongly influenced by dust accumulation, however, this strategy is unrealistic, because as chemical weathering progresses, conservative elements commonly present in minerals in dust simultaneously accumulate in the soil. Development of a constitutive mass-balance model (Brimhall and Dietrich, 1987; Brimhall et al., 1988; Chadwick et al., 1990) has partially addressed this problem. In soils with an initially homogeneous parent material composition, the origins of some essentially insoluble minerals (e.g., zircon in dust, ZrO_2, or in parent material, ZrO_2) can be identified through microscopic examination. These data, along with measured soil bulk density and mineral density data, enable determination of changes in soil volume (strain) with progressive soil development. Ultimately, this permits determination of the proportion of mass that has been derived from external sources.

The variable, inhomogeneous composition of alluvial fan materials, however, means that the original content of a component such as ZrO_2 is likely to vary with depth. McFadden et al. (1991a,b) attempted to overcome this problem by estimating changes in strain differently. The late Quaternary gravelly fan deposits of the Soda Mountains in the eastern Mojave Desert, the subject of several studies (Wells et al., 1987; Reheis et al., 1989; McFadden et al., 1989) are poorly sorted, as expected. Yet, a detailed, statistical analysis of the grain-size distribution of the sand fractions of different units showed that sorting of this fraction, particularly the coarsest sand fraction, is very similar (McFadden, 1991). On the basis of the assumption that the content of such coarse sediment is approximately conserved during soil development, these data can be used to estimate the amount of volume change (strain), if: (1) the particle size component is not changed significantly through eolian additions, and (2) if mechanical weathering of pavement clasts produces only small amounts of material in this size range. Particle-size analysis of Av horizons of the Cima Volcanic Field basalt flows shows that additions of exogenous coarse sand are either nil or extremely small. Mechanical weathering does produce some coarse sand-sized material, but examination of numerous soils in the Silver Lake area show that most of such material remains on the soil surface and that very little of it is incorporated below the thin A horizon. Thin-section observations of soils in the Cima area and chemical
and mineralogical analysis of the Av and lower horizons (McFadden et al., 1986) also show that accumulation of sand-size materials from mechanical weathering is minimal.

The study of McFadden (1991) indicated that Av horizons of mid-Holocene surfaces contain about 71% eolian material, whereas the Av horizon of a Late Pleistocene soil has 85%. The average composi-

Fig. 4. Plots showing model residual values for major elements and selected trace elements determined on the basis of admixtures of estimated proportions of initial soil parent material and incorporated eolian material for two soils on the piedmont of the Soda Mountains, Mojave Desert, California. Model assumptions described in text. Bars, from left to right within each bin, represent the residual values for each oxide component in the uppermost horizon (Avk) through progressively lower soil horizons. (A) Residual values for mid-Holocene soil. (B) Residual values for Late Pleistocene soils.
...tion of dust in this region has been determined in the area of the Soda Mountains and Cima Volcanic Field (Reheis et al., 1995) (modified by McFadden to include carbonates and soluble salts, components measured separately by Reheis). These data permit calculation of the bulk chemical composition of a given horizon by mixing appropriate proportions of soil parent material and inferred dust constituents. Comparisons of ‘synthetic’ compositions using this procedure and soil horizon compositions for middle Holocene and Late Pleistocene soils determined from laboratory analysis are shown in Fig. 4. This figure shows that the smallest model residual values are associated with SiO₂ and Al₂O₃, the two components that comprise the majority (65 to 85%) of the material in the parent material and dust and that are largely conserved during chemical soil weathering (especially Al₂O₃) in this climate. This suggests the general validity of the model, as do the general similarities in component gain-loss patterns observed in both soils.

Other features, however, are attributable to pedogenic alteration subsequent to incorporation of dust. For example, the very slight apparent enrichment of Fe₂O₃ + FeO possibly reflects chemical oxidation of FeO in dust to iron oxyhydroxides, as is indicated also by redder colors of the interior of this horizon noted previously. The apparently large losses of NaO and moderate losses of K₂O are attributable to leaching of these very soluble bases from the upper part of the soil relatively soon after their initial incorporation, resulting in salt accumulation in the lower parts of the soil. The small net losses of CaO and MgO implied by the model are consistent with the observed accumulation of carbonate in lower horizons, but also accommodates spatially segregated accumulation of pedogenic carbonate characteristic of Av horizons noted by McFadden et al. (1986) and Anderson et al. (1994). The origin of the apparently large P₂O₅ net gain is not as clear; it could reflect much larger-than-present contents of phosphates, a component of playa sediments of this region (Reheis and Kihl, 1995), in eolian dust during earlier parts of the Holocene. In the Late Pleistocene soil, ZrO₂ is apparently significantly depleted, but no such trend is observed in the Holocene soil. As loss of this component through chemical weathering is highly unlikely, perhaps dust incorporated during the latest Pleistocene and early Holocene contained less ZrO₂ than it does now. Interpretations of trends associated with trace-element components are problematical, as even small variations in their initial values in the parent material with depth would generate residuals unrelated to either weathering or temporal changes in dust composition. Nevertheless, the systematic changes in component values with soil depth is not suggestive of a parent material variation-induced residual.

Statistical analysis of measured horizon values for the highly soluble constituent, Na, and model-simulated values for the mid-Holocene soil show that they are inversely correlated (y = -0.28x + 2.52; r² = 0.98), whereas in the Late Pleistocene soil these values are positively correlated (y = 3.10x - 13.86; r² = 0.90). This complete reversal of the correlation can be attributed to conversion of soils from very permeable gravels to a much less permeable, silt- and clay-rich soil as eolian materials are incorporated in these soils (McFadden, 1991). The former character favors very deep leaching of soluble constituents while the latter favors a shallower depth of leaching. These results show that although the chemical composition of the Av horizon does not reflect significant pedogenic modification, temporal trends in its compositional change are neither simple or monotonic.

This general approach can be used to evaluate total composition of Av horizons from other areas. On the basis of results of the study of McFadden et al. (1991a,b), concentrations of SiO₂ in dust, soil parent material and the Av horizon can be used to estimate the relative fractions of dust and original parent material in a given horizon where:

\[ X_{pm} = \frac{\left( \text{SiO}_2 h - \text{SiO}_2 d \right)}{\left( \text{SiO}_2 pm - \text{SiO}_2 d \right)} \]

\[ X_{pm} = \text{fraction SiO}_2, \text{ parent material (fraction SiO}_2, \text{ dust} = 1 - X_{pm} \); \text{ SiO}_2 h = \text{SiO}_2 \% \text{ in horizon}; \text{ SiO}_2 pm = \text{SiO}_2 \% \text{ in parent material}; \text{ SiO}_2 d = \text{SiO}_2 \% \text{ in dust.} \]

This approach, applied to Av horizons of soils of the piedmont and volcanic flows in the Cima area, reveals trends similar to those exhibited by the soils of Soda Mts. piedmont (Table 1). For example, there is a higher proportion of dust in Av horizons of older soils as compared to that in the Av horizons of younger soils. Comparison of the synthetic SiO₂ value and the measured value for the Av horizon of a...
Table 1
Compositional data for Av horizons, soil parent materials, model residual values and estimated net gains or losses of elements (see text for discussion of results)

<table>
<thead>
<tr>
<th>Element</th>
<th>Regional dust</th>
<th>CV-11</th>
<th>CV-6 Avk</th>
<th>CV-6 Avk</th>
<th>Model</th>
<th>Net gain/loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>53.57</td>
<td>71.14</td>
<td>58.81</td>
<td>61.5</td>
<td></td>
<td>0.24</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.15</td>
<td>13.05</td>
<td>15.76</td>
<td>16.48</td>
<td>12.56</td>
<td>0.24</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.7</td>
<td>1.82</td>
<td>5.64</td>
<td>5.9</td>
<td>3.4</td>
<td>0.27</td>
</tr>
<tr>
<td>MgO</td>
<td>3.39</td>
<td>0.87</td>
<td>2.93</td>
<td>3.06</td>
<td>2.25</td>
<td>0.27</td>
</tr>
<tr>
<td>CaO</td>
<td>8.98</td>
<td>2.07</td>
<td>3.47</td>
<td>3.63</td>
<td>5.86</td>
<td>-0.61</td>
</tr>
<tr>
<td>Na₂O</td>
<td>10.6</td>
<td>3.21</td>
<td>2.67</td>
<td>2.79</td>
<td>7.26</td>
<td>-1.6</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.85</td>
<td>3.95</td>
<td>3.43</td>
<td>3.59</td>
<td>4.99</td>
<td>-0.39</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.6</td>
<td>0.31</td>
<td>0.807</td>
<td>0.84</td>
<td>0.47</td>
<td>0.45</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>0.03</td>
<td>0.1</td>
<td>0.1</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.055</td>
<td>0.01</td>
<td>0.0282</td>
<td>0.03</td>
<td>0.04</td>
<td>-0.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>CV-13, Avk</th>
<th>CV13, Avk</th>
<th>model</th>
<th>net gain/loss</th>
<th>CS-S-2, Avk</th>
<th>CS-S-2 vs. Dust</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>61.14</td>
<td>63.85</td>
<td></td>
<td></td>
<td>54.42</td>
<td>0.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.26</td>
<td>14.89</td>
<td>12.68</td>
<td>0.15</td>
<td>14.77</td>
<td>0.18</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.24</td>
<td>4.423</td>
<td>3.02</td>
<td>0.32</td>
<td>6.14</td>
<td>0.23</td>
</tr>
<tr>
<td>MgO</td>
<td>2.07</td>
<td>2.16</td>
<td>1.92</td>
<td>0.11</td>
<td>3.64</td>
<td>0.07</td>
</tr>
<tr>
<td>CaO</td>
<td>3.86</td>
<td>4.03</td>
<td>4.94</td>
<td>-0.22</td>
<td>6.04</td>
<td>-0.49</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.72</td>
<td>2.84</td>
<td>6.28</td>
<td>-1.201</td>
<td>2.54</td>
<td>-3.17</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.49</td>
<td>3.65</td>
<td>4.74</td>
<td>-0.3</td>
<td>3.06</td>
<td>-0.91</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.55</td>
<td>0.57</td>
<td>0.43</td>
<td>0.25</td>
<td>1.02</td>
<td>0.41</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.064</td>
<td>0.05</td>
<td>0.14</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>-0.41</td>
<td>0.03</td>
<td>-1.19</td>
</tr>
</tbody>
</table>

1Lowest, least pedogenically modified horizon of soil occurring on late Holocene fan surface in area of Cima Volcanic Field, approximating the parent material composition.
2Horizon from soil on Late Pleistocene alluvial fan surface in area of Cima Volcanic Field. Estimated dust fraction: 54.9%; alluvial parent material: 45.1%.
3Model-determined value based on mixing equation and dust and parent material fractions estimated from silica content (see text for explanation).
4Residual value determined from ratio of model-calculated value and measured value of horizon.
5Horizon from soil on latest Pleistocene to early Holocene fan surface in area of Cima Volcanic Field; estimated dust fraction: 41.5%; estimated alluvial parent material fraction: 58.5%.
6Horizon in soil in eolian mantle atop middle Pleistocene flow in the Cima Volcanic Field.
7Ratio of measured constituent value in Avk horizon and constituent value in regional dust.

soil present in an eolian mantle on a middle Pleistocene (560 ka) flow in the Cima Volcanic Field indicates a very small residual value, 1.56%. This implies that the fraction of the horizon consisting of dust exceeds 90%. Synthetic vs. measured values of ZrO₂ from soils from the flow surface and the fan surface, however, yield residuals that imply net ZrO₂ loss. This was not observed in the analysis of the Soda Mountains study (see Fig. 4). This is not attributable to chemical weathering, and dust composition data (Reheis et al., 1995) indicate that the ZrO₂ content in the dust in both areas is similar. This indicates that the parent material content of ZrO₂ may vary significantly, unsurprising given the diverse rocktypes in the source area in the Cima region.

The elemental analysis studies generally support the conclusion of Reheis et al. (1995) that the chemical and clay mineralogic composition of the Av horizon is very similar to the composition of dust. Elemental analysis shows that the composition, however, has been significantly modified by processes of leaching of relatively soluble components with concomitant concentration of chemically insoluble components. As noted above, factors such as changing dust composition and variable parent material com-
position complicate interpretation of the model results. Reheis and Kihl (1995), for example, documented changes in dust composition in the southwest United States even over time periods of a few years. In addition, as suggested previously, at least some chemical alteration of the Av occurs with increase in its age. Also, as described previously, the redness in the interior of Av horizon peds suggests that ferric oxyhydroxides (e.g., hematite) have formed by oxidation of ferrous iron in the soil, a conclusion also consistent with the generally very low Feo/Fe t ratios in this horizon (McFadden et al., 1986). Rapid conversion of ferrihydrite to hematite should be favored by the seasonally high soil temperatures, low soil humidity, and the oxidation of soil organic matter (Schwertmann and Taylor, 1989). The, FeO/Fe t ratios of Cima soils demonstrated alteration of large amounts of ferrous iron oxides in dust to ferric oxides (McFadden et al., 1986). Reheis et al. (1995) also attribute certain contrasts between the clay mineralogy of Av and subjacent B horizons and that of modern dust to chemical weathering. In addition, in the soil chronosequences of the Whipple Mountains (McFadden, 1982) and Cima Volcanic Field (McFadden et al., 1986), the X-ray peaks of many phyllosilicate minerals are much lower than those associated with quartz. This is unexpected, considering the high clay content as well as stickiness and plasticity of the horizon, wet consistence attributes typically associated with a large quantity of expansible clay. Also, Av horizon peds slake in water and thin-section observations do not reveal obvious evidence of pedogenic (opaline) silica. These data suggest that a significant amount of the clay in the Av horizon could be authigenic, but largely ‘amorphous’ (short-range order), partly expansible (2 : 1) clay. This possibility, the iron oxide data, and the elemental analyses show that Av horizon formation does not simply entail accumulation of dust, but that its formation is characterized by at least some chemical alteration of accumulated dust.

The observed chemical alteration of the Av horizon may reflect partly its decreasing permeability and the concomitant development of conditions that enable enhanced chemical weathering. Anderson et al. (1994) hypothesize that as clay accumulates in the horizon, its matric potential becomes increasingly negative, which in turn favors movement of water into the ped interior during sustained wetting events. Development of fine platy structure, which to some extent presumably reflects vertical expansion and contraction cycles, also facilitates movement of water, dispersed clays, and solutes into the ped interior. Compositional analysis, however, shows that the most soluble constituents in recently incorporated dust and at least some calcium carbonate are translocated to greater depths where soluble salt contents noticeably increase. This in turn reflects the presence of cracks in the Av horizon that when open favor rapid and deep flow through the horizon.

The Av horizon is a dynamic soil horizon, characterized by processes that favor simultaneous processes of accretionary, cumulic growth below a desert pavement and pedogenic modification. Carbonate accumulation may be transient in parts of the horizon but more permanent in other parts (McFadden et al., 1986; Anderson et al., 1994). Such patterns of morphologic and compositional change show that the Av horizon is not a conventional A horizon. Evidently, its evolution is intimately and interdependently linked to complexly evolving soil hydrology: as the Av horizon develops, it increasingly influences soil infiltration rates, depths of soil-water movement, and thus, rates and processes of carbonate translocation and accumulation for the entire soil.

3. Carbonate collars

3.1. General characteristics

Carbonate collars occur rarely in pavements of the Cima Volcanic Field associated with flows older than 0.5 m.y. They are relatively abundant in pavements associated with alluvial fans of various ages formed on limestone-rich alluvium, such as in the Providence Mountains, California, the Los Pinos Mountains, New Mexico and the Spring Range, Nevada. The only previous study of collars is a field study of surficial deposits of the Providence Mountains piedmont (Sena et al., 1994). They observed that the thickness of collars ranged from typically < 1 mm on late Holocene surfaces to as much as 6 mm on a latest Pleistocene surface. The width of the collar ranged from < 1 cm to 13 cm on certain larger clasts. On the basis of statistical analysis of a
selection of tilted collars of soils from three surfaces, they concluded, given a slight preference in tilting direction from the oldest surface, that some non-random geomorphic process, such as soil creep might be influencing pavement evolution.

Thin sections of carbonate collars from pavements associated with fans and terraces of the Providence Mountains and the Los Pinos Mts. (Fig. 5) show that much of the carbonate is microlaminated. Lamination may be due to differences in crystal size and morphology within individual laminae (Chadwick et al., 1989). Coarser grains enclosed in the laminated carbonate represent part of the parent material matrix that became engulfed as the growing coating expanded.

3.2. Collar characteristics and processes of formation

Features observed in Fig. 5 closely resemble those typically observed in coatings of pedogenic carbonate in calcic horizons of gravelly soils (Bullock et al., 1985; Allen, 1985; Chadwick et al., 1989). The lamination is indicative of slow, layer-by-layer carbonate accretion over time. Sena et al. (1994) suggested that these collars could form through the upward, capillary-flow driven translocation of carbonate from lower, carbonate-rich horizons into the Av horizon. Carbonate would be subsequently transported through this horizon laterally, accommodated by thin platy structure and pore potential differences.

The pavements associated with soils that lack parent materials with relatively large proportions of carbonate-rich lithologies, however, only very rarely exhibit such collars, even though the Av horizon usually contains significant amounts of carbonate. This demonstrates that Av horizon carbonate is not the major source of collar carbonate; if it was, virtually all clasts in pavements would have collars. Also, certain features of limestone clasts with these collars demonstrate that the primary source of much of the carbonate is dissolution of the clast itself. First, the clast surfaces exhibit strongly developed microkarstic features (e.g., solution channels, pits, positive relief associated with cherty or dolomitic layers). These features do not macroscopically resemble the surface pits and micro-grooves produced by algae and endolithic lichen on limestone surfaces described by Danin et al. (1982) that may be caused by secretion of organic acids. Also, some recent studies indicate that the magnitude of chemical weathering attributable to lichen-assisted weathering relative to that associated with abiotic processes (i.e., dissolution by rainwater) may be much less than previously thought (cf., Berner, 1992). Studies of limestone-dominated fan deposits of the Providence Mountains, California (McDonald, 1994; McDonald and McFadden, 1994; McDonald et al., 1998) show that the average size of the limestone clasts in the pavement greatly decreases with increasing age. This is explained at least partly by chemical weathering, because features reflecting pronounced shattering of clasts by salts, as described for example by Amit et al. (1993) or by McFadden et al. (1989) are not observed in these soils or pavements. Also, salt accumulation in the surficial horizons of these soils in areas where the collars have been observed is minimal (McFadden et al., 1986; McDonald, 1994). Finally, in some cases the collar thickens closer to the soil surface and locally progrades several millimeters out onto the surface of interclast areas. Such features point to the clast as the ultimate source of collar carbonate, and not the Av horizon or underlying pedogenic carbonate-rich horizon. Thus, the rare collars on clasts in pavements that lack limestone clasts imply the former presence of a carbonate coating on the clast. The presence of such clasts

Fig. 5. Photomicrographs of carbonate collars. (A) Microlaminated carbonate collar associated with limestone clast from pavement of Late Pleistocene surface in the Los Pinos Mountains, New Mexico. Frame length 1 mm; 10× magnification, crossed nichols. Arrow indicates contact of limestone and collar. (B) Carbonate collar exhibiting largely massive fabric with few areas of weak microlamination associated with sandstone clast from pavement of Late Pleistocene surface in the Los Pinos Mountains, New Mexico. Frame width 0.5 mm; 20× magnification; crossed nichols. (C) Multiple generations of strongly microlaminated ‘pendent’ associated with collar formed on limestone clast from a pavement on an early Holocene fan unit on the piedmont of the Providence Mountains, California. Frame width 1.4 mm; 100× magnification, plain light. (D) Strongly microlaminated collar formed on igneous clast from a pavement on an early Holocene fan unit on the piedmont of the Providence Mountains, California. Note incorporation of matrix in lower part of collar. Frame width 7.0 mm; 2× magnification, plain light.
could be due to bioturbation or reworking of clasts with carbonate coatings from older calcic soils. 

On the basis of (a) the observed characteristics of collars, and (b) the compositional evolution of Av horizons and their genetic relation to the pavement, a general model for the accumulation of pedogenic carbonate on clasts and in Av horizons is proposed (Fig. 6):

1. Rainfall onto, dissolution of, and runoff from relatively impermeable carbonate-rich clasts in the pavement provide the major source of dissolved calcium in infiltrating soil water.

2. Much infiltration initially occurs at the contact between clast and surface soil horizon, and consequently, much infiltration is concentrated at the rock–soil matrix contact.

3. Interaction of the percolating soil water and with an increasingly higher soil CO$_2$ maintains a soil solution undersaturated with respect to calcium carbonate, which enables continued, slow dissolution of calcite from the rock surface.

4. As a rainfall event proceeds, increasingly slower infiltration rates enable surface water accumulation with progressively higher dissolved carbonate concentrations.

5. Ultimately, the strongly negative matric potential of the Av horizon drives soil water with significant amounts of dissolved calcite from the rock–soil matrix.
contact to the interior or the base of the Av horizon, where carbonate can accumulate.

(6) Relatively rapid surface evaporation rates in the upper few centimeters and at the stone and soil surface caused by seasonally high temperatures, and the presence of a relatively permeable surface layer strongly favor carbonate precipitation preferentially on stable surfaces of larger pavement clasts firmly anchored in the Av horizon.

3.3. A numerical model of collar development

Compartment-based modeling, following procedures developed by Kline (1973) and Frissel and Reiniger (1974), has been used in studies of calcic soil development (Rogers, 1980; McFadden, 1982; McFadden and Tinsley, 1985; Mayer et al., 1988; McFadden et al., 1991a,b). This type of model enables integration of several factors that influence calcic soils (e.g., carbonate solubility, soil-water balance, carbonate dust influx). Modeling entails subdivision of the profile into a vertical sequence of compartments of arbitrary dimensions; each compartment is characterized by an initial texture, bulk density, composition, available water-holding capacity, and \( p_{CO_2} \). A series of equations simulates an evolving carbonate depth function (McFadden, 1982; McFadden and Tinsley, 1985). Such models required several simplifying assumptions. For example, infiltration was assumed to occur by downward, saturated flow (piston flow) and the impacts of the dissolution of the parent material carbonates were ignored. The simulated carbonate depth functions, nevertheless, closely resemble those in soils observed over a range of relatively arid environments (McFadden, 1982; McFadden and Tinsley, 1985). Computer simulations based on this model (Mayer et al., 1988) were developed later to help investigate the climatic sensitivity of calcic soil development. Modeling results emphasized the critical control of dust influx magnitude, soil-water movement and \( p_{CO_2} \) on carbonate movement and depths of accumulation in calcic soils (McFadden et al., 1991a,b).

In order to numerically model the process of carbonate-collar evolution described above, certain aspects of calcic soil development must be more explicitly considered. Simulating collar development requires quantification of the rate of dissolution of surface limestone clasts to specify, in turn, the composition of water immediately prior to infiltration. It also requires the determination of the changing dissolution rate and solubility of calcite as water descends through the uppermost 5 cm of the soil. To accomplish this, a different approach from that used in previous models designed to address calcic soil development over long periods of time (e.g., hundreds to thousands of years) is required. The model must also consider changing soil-water infiltration rates at the spatial and temporal scales associated with the formation of carbonate collars. The basic design of this model (computations were conducted using Microsoft Excel, version 5.0) is summarized below:

(1) The determination of the calcite saturation ratio, \( C/C^* \), (also known as the calcite saturation index \( IAP/keq \), calcite) is made immediately prior to initial infiltration by presuming rainfall impacts minimally permeable rock, and begins to flow down the clast surface towards the soil surface after a period of several minutes. A rainfall rate is specified. Calcite dissolution is immediately initiated. The solubility of calcite is derived from the following equation, after Drever (1991):

\[
m^{Ca^{2+}} = \frac{\left( p_{CO_2} K_i K_{calc} K_{CO_2} \right)}{4 K_2 \gamma Ca^{2+} + \gamma HCO_3^-}
\]

where \( K_{calc} \) is the calcite solubility product and \( K_i, K_2 \) and \( K_{CO_2} \) are dissociation constants in the carbonate system and \( \gamma Ca^{2+} \) and \( \gamma HCO_3^- \) are the activity coefficients of \( Ca^{2+} \) and \( HCO_3^- \). Eq. (1) is appropriate only if other solutes are not present or can be considered negligible (i.e., the charge balance relationship, \( 2mCa^{2+} = mHCO_3^- \), is valid for the system) and only if dissolution occurs in a chemically open system, relative to \( CO_{2(g)} \). In the subaerial environment, these conditions are generally satisfied and the partial pressure of carbon dioxide (\( p_{CO_2} \)) is specified as its average atmospheric value (10^{-3.5 atm}). In the subsurface environment, the solubility of calcite was also calculated according to Eq. (1) for the following reasons:

(a) At a pH \( \geq 7.9 \) and values of \( p_{CO_2} \), at or near atmospheric, \( Ca^{2+} \) concentration is controlled by calcite and not gypsum (Sposito, 1989).

(b) Only very low values of \( SO_{4^{2-}} \) are observed in Av horizons (McFadden, unpublished data), and
gypsum is not visible in field settings or in thin sections. (c) Numerical calculations of solubility of gypsum show that this mineral and other more soluble Ca-bearing salts would be rapidly dissolved and leached by very small volumes of rainfall, favoring subsequent calcite dissolution in a system that more closely approaches the CaCO$_3$–H$_2$O–CO$_2$ system (McFadden et al., 1990). We have also tested the simplified charge balance assumption noted above through an analysis of a analogous water using a modified version of the model WATEQ (Truesdell and Jones, 1974), taking into account the presence of other ions, an ionic strength appropriate for the Av, and speciation. Results demonstrate the error introduced given the assumption is negligible.

These assumptions are even more appropriate at zones of strong throughflow and leaching, such as at the rock–soil boundaries, but less appropriate in the interior of the Av horizons where EC values may be elevated. Ionic strength, which is used to calculate the values of activity coefficients for Ca$^{2+}$ and HCO$_3^-$ through the Debye–Huckel relationship, was estimated from the equation, $I = EC \times 0.013$ (Griffin and Jurinak, 1973). However, given the results of WATEQ calculations, the approach used is deemed valid. Subaerial rock temperatures and Av horizon temperatures based on climatic data sets of McDonald (1994) were used in the model, and data from Drever (1991) was used to specify values of temperature-dependent dissociation constants.

(2) In most environments, calcite dissolution rates are surface-controlled rather than diffusion-controlled (Reddy and Nancollas, 1971; Plummer and Wigley, 1976). In open system weathering environments, the dissolution rate is defined ultimately by the rate-limiting conversion of dissolved carbon dioxide (CO$_2$) to H$_2$CO$_3$. At very low solution-volume to surface-area ratios, H$_2$CO$_3$ is rapidly depleted by virtue of fast, surface-controlled calcite dissolution rates. The reaction rate defined for these circumstances is:

$$R = (V/F)K_{CO_2}p_{CO_2}$$

(2)

where $K_{CO_2}$ is reaction coefficient, $V$ is solution volume, and $F$ is surface area. Only at very low $V/F$ values associated with very low infiltration rates should this dissolution rate limit carbonate dissolution and movement in most soils (McFadden, 1982). For most geomorphic circumstances, a commonly used rate equation used to determine dissolution rates in the CO$_2$–CaCO$_3$–H$_2$O system is (after Palmer, 1991):

$$dC/dt = (A'k'/V)(1 - C/CU's)^n \text{ mg}/\text{l} \cdot \text{s}$$

(3) where $A' =$ surface area of rock in contact with water (cm$^2$), $V =$ water volume (cm$^3$), $k' =$ reaction coefficient (mg-cm/l-s), and $n =$ reaction order; $C =$ moles of calcite in solution; $C^* =$ solubility of calcite. Values of $n$ and $k'$ vary with saturation ratio, temperature, and $p_{CO_2}$. In the model, $A'/V = 4$ for the subaerial water–rock contact is assumed, $A'/V = 30$ for the subsurface water–rock contact; and $A'/V = 1000$ is assumed for the Av horizon.

(3) After determination of the $C/C^*$ of water immediately prior to infiltration, downward infiltration of soil water is given at a specified, average rate (mm/s).

(4) Although several factors, such as soil moisture content, daily evaportranspiration rates and soil temperature and texture variation with depth, influence soil CO$_2$ concentrations over short-time intervals (Kiefer and Amey, 1992), generally accurate estimates of seasonal ranges in the concentration of soil CO$_2$ to depth are derived assuming mass transport of CO$_2$ by gas diffusion (cf., Cerling, 1984, Solomon and Cerling, 1987; Cerling et al., 1989). The following diffusion-reaction equation, essentially Fick’s second law for a one-dimensional case, is used in the model:

$$\frac{\partial C^*_s}{\partial t} = D^*_s \left( \frac{\partial^2 C^*_s}{\partial z^2} \right) + \phi^*_r (z)$$

(4) where $C^*_s$ is the concentration of CO$_2$ in the soil (moles/cm$^3$); $t =$ time (s), $D^*_s$ is the diffusion coefficient for CO$_2$ in the soil (cm$^2$/s), $z =$ depth in the soil (cm); and $\phi^*_r (z)$ is the production rate of CO$_2$ as a function of depth (moles cm$^{-2}$ s$^{-1}$). At steady state, where $\frac{\partial C^*_s}{\partial t} = 0 = D^*_s \frac{\partial^2 C^*_s}{\partial z^2} + \phi^*_r$, the general solution to this equation is:

$$C^*_s (z) = \phi^*_r / D^*_s (Lz - z^2/2) + C^*_0$$

(5) where $C^*_0$ is the concentration of CO$_2$ in the atmosphere (ppm) and $L$ is the depth to the lower, no-flux boundary (in this study, $L = 100$ cm). This solution is appropriate for a simple production function, that is, production of CO$_2$ is constant to the lower, no-flux boundary. A simple production func-
tion is assumed because specific CO$_2$ respiration as a function of depth, and thus there is no basis to presume that some more complex, exponential function is appropriate. Also, in this study, $D_i^* = D_{ai} \cdot \epsilon \cdot \rho$, where $\epsilon$ = free air porosity in the soil, and $\rho$ = tortuosity. For circumstances appropriate to this study, $D_{ai} = 0.14$, $\epsilon = 0.4$, and $\rho = 0.5$. Values of the soil respiration rate and soil production rates used in modeling in this study were based on an average production rate estimated on the basis of analysis of isotopic carbon concentrations in pedogenic carbonate from gravel coatings in soils from the Providence Mountains piedmont (Wang et al., 1996). These soils have formed in middle to early Holocene alluvial deposits (McDonald, 1994; McDonald and McFadden, 1994) and the production rate probably reflects the average rate for periods of the year when the majority of carbonate precipitates. This production rate is consistent with that associated with other calcic soils forming in arid regions elsewhere in the southwest United States (Cerling, 1984).

(5) In order to calculate the potential mass of calcite that can be dissolved in the subsurface rock–soil contact area with depth requires specification of an infiltration rate. Steady-state infiltration rates in Av horizons measured by McDonald (1994) were used (see discussion in following subsection) on this study. Combining Eqs. (1), (2) and (4) with an infiltration rate enables determination of the mass of calcite dissolved in a specified time interval for an associated depth interval at the calculated value of $dC/dt$. The change in this value was calculated using an iterative procedure for intervals of 0.1, 1.0, 10.0 and 60 s. The results of this procedure showed that $dC/dt$ and resulting $C/C^*$ values calculated using an iteration step of 0.1 s converged with those using 10-s steps over a small depth range. Thus, subsequent modelling was conducted using the 10-s iteration steps (which equals depth intervals of approximately 0.006 cm) over a depth range of 5 cm for all months in the year.

(6) Precipitation and climate data used in the model were based on data from McDonald (1994), to determine, for example, an average number of monthly rainfall events. These data, and soil-water modeling results (described below), show that virtually no infiltration occurs below a relatively shallow depth in the hot months of June, July, August, and September, when only 3.6% of the annual average total of 235 mm precipitation falls. McDonald’s research also shows that as much as 30% of all rainfall is evaporated in the upper few cm of the soil. So, during these hottest months, all dissolved calcite from subaerial dissolution is precipitated in the collar or in the interior of the AV horizon.

(7) Available water-holding capacity data for Av horizons from McFadden (1982) (values range from 0.20 ml/cm$^3$ to 0.30 ml/cm$^3$) were used to calculate the mass of carbonate derived by evaporation of the soil matrix.

Results of numerically simulated changes in $P_{CO_2}$, solubility, and $dC/dt$ for selected months are shown in Fig. 7.

3.4. Weathering of subaerially exposed calcareous pavement clasts

Many factors potentially influence the rate, magnitude and processes of dissolution of the surfaces of calcite-rich boulders. At the beginning of a precipitation event, rain drops partly wet rock surfaces and the fraction of this moisture that infiltrates depends partly on rock permeability and rock temperature. Secondary impacts associated with rainsplash will also contribute to wetting the rock surface. The differing trajectories and velocities of raindrops striking variably oriented rock surfaces influence the character of rainsplash and the time required to fully saturate rock surfaces and initiate runoff from surface rocks. Simple laboratory simulations of rainfall on limestone boulders, for example, suggest that sustained surface runoff may occur only after tens of seconds to minutes of ‘moderate’ rainfall. Thus, many brief rainfall events may cause little or no net dissolution. Nevertheless, stone surfaces are essentially impermeable relative to the soil matrix, and during rainfall events that last for tens of minutes to hours, it is certain that a large percentage of falling rain that impacts rock surfaces ultimately runs off these surfaces and contributes a substantial part of the infiltrating soil water. We have developed a simple model to determine the rate of dissolution of calcite and change in the value of $C/C^*$ of the initially infiltrating solution during such sustained soil wetting events (summarized below).
Fig. 7. (A) Soil $P_{CO_2}$ as a function of soil depth in an arid, hot climate. Depth function calculated using soil CO$_2$ production-diffusion model, assuming average soil respiration, porosity, and tortuosity as described in text. (B) Solubility of calcite as function of soil depth, given $P_{CO_2}$ shown in (A), average January temperature of 15°C over the 0–5 cm depth range. Other relevant parameters, assumptions used to calculate calcite solubility discussed in text. (C) Dissolution rate ($dC/dt$) of calcite over the 0–5 cm depth range. Soil temperature is 15°C; $P_{CO_2}$ as in 7a; other model parameters described in text.
Calcite solubility and dissolution rates are temperature-dependent, but the actual reaction temperature must change relatively quickly during the initial wetting. This is due to the initially different and variable rock surface and rainwater temperatures. During a rainfall event, a steady-state temperature is presumably attained that reflects some value intermediate between the two initially different temperatures. In the model, we assume the temperature to be approximated by the average monthly air temperature, shown in numerous studies to be within a few degrees centigrade of the mean monthly soil temperature (Soil Survey Staff, 1975). The atmospheric $p_{CO_2}$ value is specified.

(2) $A/V = 10$.

(3) The rainfall rate is 10 mm/h (a value observed in many rainfall events in desert regions, although rates may be much higher during brief, intense rainstorms) and maintained for the duration (several minutes to an hour) of the rainfall event. The mass of carbonate lost monthly is approximated as the area under curves shown in Fig. 8.

Results of the simulation of subaerial dissolution given these assumptions indicate that rate of dissolution, as shown by changes in $C/C^*$, are initially rapid, but slow systematically with time (Fig. 8). A transition from fast, approximately second-order kinetics, to slower, fourth-order kinetics occurs between 200 and 700 s after rainfall begins and after 15 to 30 min (i.e., after 2.5 to 5 mm of rainfall), $C/C^*$ slowly approaches an approximately steady state value of 0.8. Calculations also show that unless a substantially higher rainfall rate occurs, the pattern of dissolution-rate change is not strongly influenced by rainfall rate. Simulation results indicate that the annual rate of denudation of calcite is 2.6 $\mu$m/yr.

Many field observations (e.g., vein relief, maximum channel depth, flattening of upper surface compared to lower surface of rock) and estimated rates of denudation of limestone bedrock in desert regions (1 $\mu$m to 10 $\mu$m/yr) of Israel (Gerson, 1975) indicate that this rate is possible. Complete dissolution of 0.5-mm-thick pedogenic coatings on basaltic boulders excavated from bouldery calcic soils by prehis-
Fig. 8. (A) Numerically simulated change in the carbonate saturation ratio ($C/C^*$) with time during a rainfall event. Reaction order changes (2.2 to 4) at $C/C^* = 0.7$. Model assumptions and other parameters described in text. (B) Numerically simulated change in the rate of calcite dissolution ($dC_{\text{calcite}}/dt$) during a rainfall event in January (average temperature during event $= 15^\circ\text{C}$) and in May (average temperature during event $= 35^\circ\text{C}$) Net dissolution for each event is area under curves. Model parameters described in text.
toric Anasazi farmers, and used to construct rock piles for farming purposes in semiarid New Mexico has occurred since their construction ca. 650 years ago. The derived dissolution rate, 0.8 μm/yr, is a minimum value. Variable chemical denudation rates probably reflect the impacts of several variables such as calcite crystal size, compositional impurities, biota, and surface microtopography and aspect. The model-derived value, nevertheless, is a reasonable but likely a maximum value.

3.5. Subsurface weathering of calcareous pavement clasts

The required, specified infiltration rate for the model is provided by the studies of McDonald (1994) of the infiltration behavior of gravelly soils and Av horizons of the Providence Mountains. Data from artificial wetting experiments (conducted in summer daytime conditions, in approximately air-dry soil) show that initial infiltration rates varied significantly, ranging from greater than 60 cm/h on young Holocene surfaces to 10 cm/h on older Pleistocene surfaces. Infiltration quickly decreases as the downward percolating soil water fills more pores. The rate decreases to a constant value as low as 2 cm/h within 7 to 10 min in soils on early Holocene to Pleistocene surfaces. When the rainfall rate/infiltration rate ratio is exceeded, overland surface flow is generated and these low rates are presumably maintained. Examination of pattern of rainfall distribution and amount over several years indicates that the majority of rain during the year is associated with events that last longer than 7 to 10 min and that most water infiltrates after this duration of rainfall. For example, in six of eight months when at least 4 mm of rain falls during a rainy interval (lasting < 48 h), between 52 to 88% of the total effective precipitation is probably infiltrating at this steady-state rate. Thus, such rain is responsible for most soil-water penetration much below the Av horizon, most subsurface leaching and carbonate movement. We use the steady-state C/C’ value acquired after a constant subareal dissolution rate is achieved and assume a low steady-state infiltration rate.

Although a substantial amount of infiltrating moisture moves through prominent cracks along ped faces in an initially dry Av horizon (McFadden et al., 1986), a substantial part of rainfall also must infiltrate initially along the rock–soil matrix boundary. The actual volume of the latter cannot be exactly quantified, and we are unaware of any studies that specifically address this problem. So, the measured rainfall data for the Providence Mountains is used to provide water input for individual events, although it is evident that this value must be somewhat less than the probable actual values. Finally, studies of Av horizons in the field and laboratory (Anderson et al., 1994) show that certain parts of it promote rapid throughflow of water. These parts of the horizon are essentially noncalcareous, reflecting the intensity and magnitude of leaching of carbonate in these zones (McFadden et al., 1986). Thus, the soil matrix material in immediate contact with the rock surface is characterized as noncalcareous.

Model results of subsurface carbonate-rich rock weathering indicate very small but sustained net dissolution of calcite over a depth of 0 to 5 cm in months that receive at least 4 cm of precipitation, favored by relatively slow infiltration rates and the small increases in the partial pressure of carbon dioxide associated with the low production rate specified (Fig. 9). Undersaturated conditions can be maintained despite (1) the virtually ubiquitous presence of calcite, either present as limestone or other calcareous lithologies in the parent material, or (2) the calcite present in abundant dust entrapped in such soils. In occasional spring months, when higher soil respiration rates coincide with increased precipitation, this effect is probably considerably enhanced.

Also, the calculated dissolution capacity of percolating soil water strongly decreases with depth, and thus the magnitude of dissolution also diminishes with depth (Fig. 7C, Fig. 9).

The results of model simulations also show that net rate of calcite loss (i.e., about 0.5 μm/yr) from the clast bottoms is almost an order of magnitude slower than that from the surface of larger pavement clasts. Such different rates are consistent with the formation of an increasingly ‘plate-like’ or slightly concave-up profile of subaerially exposed limestones clasts on older surfaces. This also provides an explanation for the presence of ‘cup-shaped’ clasts at depths of several decimeters commonly observed in soils formed in limestone-rich parent materials (Sowers, 1985; Treadwell, 1996). If soil pCO₂ in-
Fig. 9. Numerically simulated dissolution of calcite (mg) based on a selected data subset during a 10-s period over 0–5 cm depth for January and May. Model parameters and assumptions described in text.

increases with depth sufficiently fast (assuming a sufficiently high production rate and upward diffusion) to maintain an aggressive, descending wetting front, net calcite dissolution should be favored at the tops of large clasts encountered by relatively rapidly descending water with large gravitational potential. The process favors net dissolution and provides an explanation for the commonly observed lack of coatings of carbonate on the tops and sides of larger clasts in gravelly soils exhibiting stages I and II morphology, or even, in some cases, stages III and IV morphology (after Gile et al., 1966). Descending, soil water undersaturated with respect to calcite flows around larger stones, and some of this water must be retained on the bottom of the stone. Such water, adhering to the stone underside surface via capillary forces, becomes static. Degassing to open pores or eventual evaporation ensures precipitation of dissolved calcium primarily as pedogenic carbonate. This process, occurring repeatedly, results in the formation of increasing thicker coatings and ultimately pendants. The thickness of coatings, then, should be at least partly related to clast lithology and size as the associated clast is a source of calcium. Such a relationship has been documented by the studies of Treadwell (1996). Very small amounts of calcite must also precipitate from evaporated pore water on the tops of stones, but later infiltration events should readily dissolve it. Thus, net carbonate accumulation cannot occur on tops of stones, at least in moderately permeable soils. Coatings should only form on tops of stones in advanced stages of calcic soil formation or in other, more unusual circumstances. For example, Amundson et al. (1992) speculate that when gravelly soils are subjected to predominantly summer rainfall, very rapid soil evaporation and strong, thermally driven upward water movement, such coatings might form.

3.6. Formation of the collar

Formation of a carbonate collar at or near the soil surface requires processes that induce episodic accumulation of carbonate at or near the soil–air inter-
face that exceeds that lost during sustained, deep infiltration events. As described briefly above, we hypothesize that solar insolation, rapid evaporation of surface water following many rainfall events, and possibly the nature of the thin surface layer could favor collar formation. The seasonally hot and generally arid climate of the Mojave Desert favors seasonal evaporation of a large amount of water. In the study area, meteorological data show that, except for all but one or two winter months, the total potential evaporation substantially exceeds total rainfall (McFadden, 1982). Recent modeling studies of soil-water movement in gravelly soils in this region using the model SHAW (Simultaneous Heat and Water model, McDonald, 1994; McDonald et al., 1996) enable rigorous characterization of soil-water balance and soil-water movement. The SHAW model is a process-based model that simulates the physics of water and heat transfer in the soil-plant-atmosphere system (Flerchinger and Pierson, 1991). Processes evaluated in the SHAW model include heat flow via conduction, convection, freezing, and evaporation, water flow by Darcy flow, vapor transport, freezing, and various processes controlling evapotranspiration (e.g., wind speed, canopy albedo). Initially designed to simulate water movement in nongravelly soils, McDonald (1994) adapted SHAW to permit simulation of water movement in the gravelly early Holocene to latest Pleistocene soils of the Providence Mountains piedmont. Results show that annually up to 50% of all soil water infiltrating is lost from the Av horizon and as much as 30% from the shallowest surface A horizon (Fig. 10). Maximum solar insolation and the limited vegetation-canopy cover are the main causes of these large soil-water losses. In addition, much of the rain, particularly in the hot summer months, falls as isolated showers that produce only a few millimeters of rain. Inter-event periods are often sufficiently long to allow substantial evaporative losses from the shallowest part of the soil, even during the cooler months of the year when storms are followed by limited cloud cover or by windy conditions.

Despite these large evaporative losses of water, pedogenic carbonate accumulation does not occur in the thin, surficial A horizon. Instead, it only accumulates in the collars or sometimes in the interior of the Av horizon, whereas the A horizon exhibits evidence

Fig. 10. SHAW simulation results of the annual flow of soil water for wet and dry years and for simulations run with and without vegetation variables and transpirational-water loss for late Holocene and Late Pleistocene soils formed in granitic alluvium on the western piedmont of the Providence Mountains, California. The annual flow of soil water is superimposed over profile distributions of carbonate (fine-earth and whole-soil) and silt + clay values to illustrate relations between simulated soil-water flow and significant properties of calcic soils. Note accumulation of carbonate in upper part of Qf4 soil. Morphologic, textural, and chemical data for soils in McDonald (1994).
of net leaching of carbonates and soluble salts. So, the rapidity and magnitude of evaporation does not in itself dictate accumulation in shallow soil horizons. Net leaching of carbonate from the A horizon can be attributed to several factors. First, it is rapidly permeable due to its sandy to loamy-sand texture and single-grain character. Fines initially present in this most recently deposited eolian material are continually flushed into lower horizons by rapidly infiltrating water. Also, the large surface area/volume ratio of carbonates and the solubility of salts in eolian dust favor their rapid dissolution and thus their translocation from the A horizon. Lacking clay, carbonate or organic matter accumulation, development of aggregation and ped development is precluded. Consequently, continual re-positioning (or even locally deflation) of grains during windy periods or by rapidly infiltrating water occurs. The pedogenically dynamic nature of the A horizon does not allow the accumulation of carbonates and soluble salt, despite the large amount of evaporation.

Certain factors do favor net accumulation of pedogenic carbonate on large surficial clasts. The spatial position of most relatively large surface clasts is stable for relatively long periods of time, as shown by several types of evidence. For example, a majority of large surficial clasts on fan and terrace surfaces of desert regions, even on surfaces as young as middle Holocene, are well varnished. Whether it forms via biotic processes and contains high-resolution paleoenvironmental or geochronologic data (cf., Dorn and Oberlander, 1981; Dorn, 1991) or not (cf., Bierman et al., 1992), all researchers agree that varnish accumulation is a slow, subaerial process (cf., Denny, 1965; Harrington and Whitney, 1987; Bull, 1991). Development of varnish sufficiently thick to largely obscure the lithology of the underlying clast requires at least a few millennia of stable, subaerial exposure (McFadden et al., 1989). Therefore, if precipitation of pedogenic carbonate occurs on the surface of such stable clasts just at or below the soil–air interface, the spatial position of the carbonate is maintained. In addition, it is possible that very rapid soil evaporation rates in the surface environment are localized at the contact of pavement clasts and soil, given the thermal properties of common crustal rocks (e.g., silicates and limestone), including slow heat conductivity and heat flow. These properties enable large, dark surficial clasts to acquire surface temperatures as high as 70° to 80°C on hot summer days (Summerfield, 1991). Rock surface temperatures greatly exceed those in the adjacent surface soil and subsoil environment because it consists of small, loose particles in contact with large amounts of markedly cooler soil air, which in turn favors a lower temperature. The latter circumstances prevent surface soil horizons from achieving such high temperatures. Also, after a soil-wetting event, soil temperature is observed to drop significantly and quite quickly, whereas the surface temperature of large surface rocks is initially less affected and quickly rises following the end of a rainfall event. The proposed, very rapid rates of evaporation at the clast–soil contact should especially favor precipitation of calcite from water in adjacent soil pores immediately after cessation of rainfall (see Fig. 6).

The rate of evaporation must be sufficiently rapid to induce carbonate precipitation and to limit the loss of dissolved carbonate by withdrawal of most soil water into the adjacent soil matrix, the process hypothesized to favor continued clast-surface dissolution at lower depths. A strong temperature gradient at the rock–soil contact area might actually favor soil-water movement towards the rock surface from a distance of up to several millimeters, as evaporation and pore water evacuation creates a locally favorable matric potential gradient. This process would increase the amount of carbonate accumulated in the collar. The process would be limited to such a short distance because: (1) the strong tortuosity of the soil matrix minimizes the velocity of soil-water movement; and (2) the relatively high evaporative demand of the A horizon, coinciding with relatively small increase in matric potential in ultimately unsaturated conditions caused by elevated evaporation rates at the rock surface, would also limit the magnitude of water movement laterally to this surface. Much water in the A horizon is also lost directly to the atmosphere by water vapor diffusion, a process not associated with carbonate movement.

Yet, evidence from field observations as well as from isotopic analysis of collars presented later in this paper, support the occurrence of significant evapotranspiration loss of water at clast–soil contacts as the mechanism responsible for collar formation. The presence of collars on noncalcareous clasts (e.g.,
sandstones, basalt) in limestone-dominated pavements provide the best evidence for the hypothesized process. Noncalcareous rocks cannot themselves be the source of collar carbonate. The source of collar carbonate on noncalcareous clasts must be dissolved carbonate in pore fluid that has acquired a high \( C/C^+ \) prior to rapid evaporation. This can happen if there are enough point sources rich in calcite in the population of surface clasts to produce dissolved carbonate at a rate that prevents dilution of the accumulating surface water. The effects of the Av horizon on infiltration that lead to very slow, steady-state infiltration (McDonald, 1994) are circumstances favorable for the generation of saturated overland flow.

To numerically model this process, the zone of collar formation is considered to be the 0–1 cm depth range, as field observations indicate that this is the primary region of most active collar accumulation and on the basis of other considerations discussed above. The mass of calcite precipitated in the collar is calculated over this range assuming:

- \( A/V \) is estimated to have a value of 20;
- 30% of rainfall is evaporated in the depth range for all months, except for summer months when all rainwater is evaporated;
- monthly carbonate losses from the rock surface are calculated using the strategy described in the previous section;
- the dissolved carbonate concentration \( (C^-) \) of the evaporating pore water is set by the value \( C_{0.5 \text{ cm}} \);
- infiltration and evaporation of soil-water 1 mm from the rock surface is assessed;
- evaporation and carbonate accumulation is calculated per ml of reacted surface.

These assumptions or estimated parameter values are considered to be generally conservative. Evaporative losses are based on results from soil-water modelling using SHAW. Modeling simulates collar formation at an annual rate of 0.5 \( \mu \text{m/yr} \) (Fig. 11). The thicknesses of collars formed at this rate are generally similar to those observed by Sena et al. (1994) and those we have observed elsewhere in pavements of desert soils in the Mojave Desert, Nevada, and New Mexico.

Several factors prevent the accumulation of carbonate on the clast surface with depth following the carbonate dissolution that occurs during sustained infiltration events. First, increased thermal insolation at these slightly greater soil depths and therefore slightly cooler rock surface temperatures should be conducive to decreased evaporation rates. Second, the soil matrices of Av horizons are strongly clay- and silt-enriched, a soil texture that should strongly influence soil-water movement into and through this horizon. The presence of large, vertical, tensional cracks in dry Av horizons favors rapid movement of water directly through the horizon, allowing the Av horizon to remain relatively dry during the initial period of wetting (McFadden et al., 1986). These factors favor the development of a strongly negative matric potential gradient that would cause soil-water movement into the dry ped interior. The evolution of fine, platy soil structure would facilitate lateral transport of soil water into the ped (Anderson et al., 1994). The very small amounts of calcite that can precipitate on the surface of large rocks in the pavement at greater depth would be that in strongly held, hygroscopic soil moisture. Such calcite should be readily dissolved during subsequent, sustained infiltration events. The transport of dissolved carbonate into the ped not only accounts for the formation of an isolated, distinct collar, but also partly accounts for the accumulation of pedogenic carbonate in the Av horizon.

The change in pore size and pore type at the very abrupt \( A/\text{Av} \) horizon boundary presumably initially...
limits the rate of soil-water movement from the A into the Av horizon. Such movement can occur only after the A horizon has been largely saturated, when its matric potential is less negative than that of the Av, which would allow movement of water into this much finer horizon. Such soil-water movement would enable transport of at least some dissolved carbonate derived from surface clast dissolution into the interior of the vesicular horizon and thus account for some of the pedogenic carbonate in the horizon. Of course, during certain periods of the year when the soil is repeatedly wetted, a substantial amount of dissolved carbonate is ultimately transported to the deeper calcic horizons (McDonald, 1994; McDonald et al., 1996) (Fig. 10).

Other studies of pavements also illustrate the important effects of the thermal behavior of pavement clasts on soil water and pedogenesis. Many researchers, for example, have noted the presence of noncalcareous, reddened pavement-clast undersides that form due to the accumulation of pedogenic Fe oxides. These coatings are found on diverse lithologies, including quartzites, which indicates that the major source of the iron oxides and other materials is external. The formation of these coatings and associated reddened B horizons has been attributed to the moist microenvironment favored below large clasts in the pavement (McFadden and Bull, 1981; McFadden, 1982). Recent studies document the condensation of moisture on the bases of pavement clasts on cool nights following rainy periods (Helms et al., 1995). In this case, it is the colder temperatures of the rock compared to the surrounding soil in certain times of the year that presumably favors the condensation of essentially distilled water, but the process must also be related to the large volume of the clast that would block upward moving vapor as well as the large water-holding capacity of the Av horizon.

Certain micromorphic observations also support the hypothesized scenario of collar formation. Most of the carbonate in the collar is microlaminar, and few larger skeletal grains are present. If initial infiltration is characterized by the fast dissolution of exterior carbonate in only the incipient stage of engulfing matrix grains, such grains could be entrained later by rapidly infiltrating rainwater and swept away. After the rainfall event, rapid, evaporative precipitation of calcite from pore fluid on the remaining surface of the clast as described above would produce a largely grain-free, thin layer of calcite. Repetition of this would continue to preclude progressive incorporation of large grains in the matrix.

Finally, because Av horizon development is largely vertical and accretionary, the depth of locus of collar accumulation on larger clasts must also change. The accretion would cause the gradual burial of previously formed collar carbonate. Calculated subsurface dissolution rates of calcite are quite slow, so buried collar material could persist for centuries, depending on, among other factors, its initial thickness. Given the development of thick Av and non-gravelly AB horizons in the Holocene, this process partly explains the existence of relatively wide collars reported by Sena et al. (1994).

3.7. Isotopic carbon and oxygen composition of the collar: implications for collar genes

The carbon isotopic composition of pedogenic carbonate has been shown in numerous studies to strongly reflect the isotopic composition of soil carbon dioxide (Cerling, 1984; Amundson et al., 1988; Cerling et al., 1989; Quade et al., 1989; McFadden et al., 1991a,b). The analysis of the isotopic composition of C in carbonate collars can also be used to test the hypothesis of collar formation described in this paper. With soil depth, the isotopic composition of soil CO₂ is increasingly influenced by biogenic CO₂ produced from plant respiration and bacterial oxidation. The isotopic composition of the carbon depends on the proportion of plants utilizing different photosynthetic pathways (e.g., C₄ or C₃) and the extent of mixing with atmospheric CO₂. Using the gas diffusion model described previously to describe the theoretical concentration and isotopic composition of soil CO₂ with depth, Cerling (1984) demonstrated that the observed values of isotopic compositions of pedogenic carbonate and modeled values agree closely. Isotopic studies of pedogenic carbonate have been applied to other aspects of calcic soil evolution, including the role of climatic change (Magaritz et al., 1981; Schlesinger, 1985; McDonald and McFadden, 1994; Wang et al., 1996), elevation and plant community type (Amundson et al., 1988; Quade et al., 1989), and their age (Amundson et al., 1994; Mc-
Donald and McFadden, 1994; Wang et al., 1996. Methods of analysis of isotopes in pedogenic carbonate used in this study are described in the aforementioned publications.

Well-developed carbonate collars exist in the pavements of middle Holocene fan deposits composed dominantly of limestone and lesser amounts of chert derived from the Spring Range, Nevada, in pavements of soils of various ages in the Catamarca Province, Argentina, and from shallow carbonate pendants in soils associated with young Holocene basaltic volcanic flows in Utah (Table 2). Given the model for isotopic carbon composition in pedogenic carbonate described above, with an assumed paleo-CO$_2$ $\delta^{13}$C value of $-6.5\%o$, $\delta^{13}$C value of $3.4\%o$ for pedogenic carbonate formed at the soil surface is predicted (assuming the Deines, 1980 $\alpha$ CO$_2$–CaCO$_3$ fractionation factor for 25°C). This value is also very close to the surface value projected on the basis of extrapolation of $\delta^{13}$C values of carbon in carbonate coatings from progressively deeper parts of the soils. The $\delta^{13}$C values of carbonate collars and shallow pendants shown in Table 2, however, are generally much heavier than $3.4\%o$. The best explanation for this is at least partly the kinetic effects on isotopic fractionation associated with rapid evaporation and degassing that produce values well above those that would be expected from equilibrium fractionation. Data in Table 2 and Fig. 12 also show that $^{13}$C and $^{18}$O values closely correlate. Again, this is probably a kinetic effect, as the light isotope off-gasses preferentially in both cases. Profile results shown for SM-2 (Fig. 13) also show strong enrichment of $^{18}$O in carbonate collars and coatings. Soil carbonates formed in regions with high potential evapotranspiration and low rainfall typically exhibit strong $^{18}$O enrichment when compared to local meteoric water, which is most likely the result of evaporative enrichment. Thus, even if only equilibrium fractionation were involved, the heavy $^{18}$O values shown in Table 2 indicate that up to 80–90% of the soil water evaporated during the precipitation of carbonate.

These conclusions are consistent with the proposed mechanism of rapid, evaporation-driven collar formation. Other isotopic data should be collected to further test this hypothesis. For example, the $^{87}$Sr/$^{86}$Sr ratio of the carbonate collars from limestone should be relatively similar to that of the associated limestone that is hypothesized to form the primary source of the carbonate. This prediction can be tested if the strontium composition of the regional dust fallout is sufficiently different from that of the

Table 2
Stable isotopic data for carbonate collars from desert soils

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{13}$C (PDB)</th>
<th>$\delta^{18}$O (PDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISV-1c*</td>
<td>+3.5</td>
<td>+0.8</td>
</tr>
<tr>
<td>ISV-1d</td>
<td>+5.9</td>
<td>+3.1</td>
</tr>
<tr>
<td>Arg. 199a</td>
<td>+3.2</td>
<td>+0.3</td>
</tr>
<tr>
<td>ISP-3*</td>
<td>+0.6</td>
<td>−2.2</td>
</tr>
<tr>
<td>ISP-1</td>
<td>+4.8</td>
<td>+1.9</td>
</tr>
<tr>
<td>ISP-4</td>
<td>+9.9</td>
<td>+6.6</td>
</tr>
</tbody>
</table>

*Pavement clasts from a soil associated with gravelly alluvial unit of probable middle Holocene age on the piedmont of the Spring Range, near Indian Springs, Nevada. Deposits are about 3 m thick and overlies carbonaceous-rich materials referred to as the ‘Black Mat’ that yielded an approximately 9400 yr $^{14}$C age (J. Quade, pers. commun., 1995). Calcareous Av horizon associated with pavement is 5 cm thick and overlies a thin Bwk horizon and the 2Bk horizon.

*Pavement clasts from a soil associated with gravelly alluvial unit of possibly middle Holocene age in the Catamarca Province, Argentina. The Av horizon is 3 cm thick and overlies a 17 cm thick Ck horizon and a 2Ck horizon that exhibits Stage I carbonate morphology.

*Carbonate in shallow, horizontal fractures in approximately 500 yr old Ice Springs volcanic flow, central Utah.
limestone, as has been documented in some calcic soils studied by Quade et al. (1995). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of collars on noncalcareous pavement clasts also should reflect a large contribution from limestone. The kinetics should be quantitatively evaluated to determine just how heavy a C or O isotopic value can be produced via rapid evaporation and degassing, and whether or not these values are consistent with those observed. Also, determination of the age of the carbonate collar from its $^{14}\text{C}$ content using a recently developed model (Amundson et al., 1994; Wang et al., 1996) would provide an additional test of the collar formation hypothesis. The predicted concentration of isotopically heavy $^{14}\text{C}$ in the collar via strong evaporation and concentration might produce, for example, a very slightly younger-than-expected ages for the precipitated carbonate.

3.8. Carbonate accumulation in Av horizons: implications of the proposed model of collar formation

In previous modeling studies (McFadden, 1982; McFadden and Tinsley, 1985), the net accumulation of carbonate in the Av horizon simulated by modeling of soils formed in hot, arid climates was attributed not only to the limited leaching, but also to the impacts of calcareous dust entrainment and the rapid development of a horizon with a larger available water-holding capacity. The modeling indicated that a calcic horizon should form a few decimeters below the surface in a semiarid climate. In these studies the ‘leaching index’ (Li) of Arkley (1963) was used to characterize soil-water balance. The more rigorous method of calculating soil-water balance provided by the model, SHAW, shows that even in the arid-to-semiarid climate of the Providence Mountains, the fraction of rainfall that infiltrates below the Av horizon ranges between 50% and 65%, far less that indicated by estimates based on Li. These circumstances and the proposed model of collar formation imply that the properties of the Av horizon more strongly influence soil hydrology and calcic soil-forming processes than was recognized in the earlier studies.

Using SHAW to estimate soil-water movement, the current, average accumulation rate of calcite in dust for this region, 1.3 mg/$10^4$cm$^2$ per year (Reheis et al., 1995; Reheis and Kihl, 1995), as a proxy for carbonate input rate throughout the Holocene and the solubility for the 0 and 5 cm depths calculated previously, the net gain or loss of carbonate in the Av horizon (0–5 cm) can be determined using a modified version of the compartment model of McFadden (1982) and McFadden and Tinsley (1985). The results indicated that about 2/3 of externally derived carbonate is translocated to depths well below the Av horizon, while the carbonate content of the Av would increase at the rate of $6.2 \times 10^{-5}\%$/yr. Maintaining this soil-water balance and dust input rate for 10,000 years would produce an Av horizon with a carbonate content of about 6%. Thus, carbonate accumulation in the shallow Av horizon occurs despite a climate substantially moister than that associated with soils of the drier, hotter eastern Mojave Desert, emphasizing the large impact of the Av horizon’s character on processes of soil-water movement.

The measured carbonate contents of Av horizons associated with soils of differing age, in different parent materials, and forming under semiarid thermic to arid hyperthermic areas on the Providence Mountains piedmont (McDonald, 1994), in the Cima area (McFadden et al., 1986; Royek, 1991), in the Soda Mountains piedmont (McFadden, unpublished data), in the Whipple Mountains piedmont (McFadden, 1982) and in the western piedmont of the Los Pinos Mountains, New Mexico (Treadwell, 1996) are shown in Fig. 13. The actual carbonate contents of the Av horizon vary significantly, ranging from virtually no carbonate to 27.5%. A trend of net carbonate accumulation in Av horizons is evident in only three of the eight sequences; other sequences display trends of net accumulation followed by a net decrease, no net accumulation, or net loss of carbonate.

Fig. 13. Changes in the carbonate contents of Av horizons from soil chronosequences in the Mojave Desert and for a chronosequence in New Mexico. The carbonate contents of the Av horizons of some soils in the Providence Mountains study areas represent averages of data for two soils of the same geomorphic surfaces. See text for discussion of climatic regimes, parent material composition and other aspects of the chronosequences.
Interpretation of these data is complicated by several factors. First, dust composition locally could be quite variable, as is indicated by modern measurements of dust composition over much of this area (Reheis and Kihl, 1995). Second, dust flux and composition has probably varied, perhaps significantly in some regions, during the late Quaternary. Third, as suggested by McFadden et al. (1986) and addressed later in this paper, much of the Av horizon of Pleistocene soils may be of Holocene age, complicating the interpretation of the data as reflective of purely time-dependent trends, irrespective of variation in other soil-forming variables. Finally, significant periods of potentially wetter climate during the Holocene lasting decades that are documented in the Transverse Ranges (Enzel et al., 1989; Enzel et al., 1992) may have also occurred in the Mojave Desert, with the potential to influence soil-water balance and thus the development of calcic soils in the region (McFadden et al., 1990; McDonald, 1994).

The data shown in Fig. 13, nevertheless, illustrate several important relationships between carbonate accumulation and soil age, climate, and parent material. When the parent material contains very little or no carbonate and in the semiarid regions (Providence QM, PM, Cima areas), mostly only relatively small to moderate amounts of carbonate accumulate in the Av horizon. The amounts are generally smaller than those predicted by modeling; but, its presence demonstrates that dust is the primary source of the pedogenic carbonate in these soils, a conclusion of many previous studies that relied on other types of evidence. The relatively low carbonate contents probably reflect: (a) the lack of any other source of pedogenic carbonate other than dust (or dissolved calcium in rainfall), and (b) local soil-water balance and soil respiration conditions that are apparently conducive to the movement of most carbonate through the Av horizons.

In contrast, when the parent material contains moderate carbonate content (Whipple Mountains, Silver Lake) or abundant carbonate content (Providence Mountains LS, Los Pinos Mountains), the Av horizons typically have relatively abundant carbonate (Fig. 13). The trend of increasing carbonate content in Av horizons of progressively older soils observed in sequences in the hottest, driest regions may partly reflect contributions of carbonate from dissolution of the parent material in pavement, but also probably reflects the effects of sustained, limited leaching. Such an environment represents the ‘moisture-limited condition’ described by Machette (1985) and simulated by modeling studies (McFadden, 1982; McFadden and Tinsley, 1985; Mayer et al., 1988). The very large carbonate contents in the Av horizons of the youngest Holocene soils in carbonate-rich alluvium (largely limestone) implies that part of the carbonate is nonpedogenic, detrital material and that large part of the dust entrapped in the horizon is derived from the local, highly calcarious materials. The maintenance of high carbonate contents greater than can be explained by continued dust input in increasingly older Holocene soils, however, is at least partly attributable to carbonate derived by dissolution of limestone clasts in the pavement through mechanisms described in the previous section. In soils with such carbonate-rich Av horizons, infiltrating soil water may ultimately acquire sufficiently high concentrations of dissolved calcium to favor flocculation of clays, thereby inhibiting movement of clay below the Av horizon and thus limiting accretionary soil development (McDonald, 1994).

The decreasing carbonate contents of Av horizons of older Pleistocene soils in these sequences may be caused by several factors. Rates of calcareous dust entrapment probably decline with increasing pavement development associated with older soils (McDonald, 1994; McDonald and McFadden, 1994; McDonald et al., 1998). The currently semiarid climate should also be conducive to leaching of at least some carbonates from or through the Av horizon. The reduced rate of carbonate input and favorable soil hydrology should, therefore, eventually favor net losses of carbonate from the Av horizon, despite the abundant, previously accumulated carbonate and the abundance of carbonate in the pavement.

The anomalously shallow pedogenic carbonate accumulation in these desert soils and pavements reflect the increasing impact of the evolution of Av horizon properties on soil-water movement and composition. The carbonate contents of Av horizons of oldest soils may ultimately represent a type of dynamic, pedogenic equilibrium state, reflecting conditions in which carbonate gains are approximately equaled by carbonate losses. The time required to achieve this state, and the value of the associated
carbonate content, will be a function of several variables, including the dust composition and input rate, the proportion of calcareous sources in the pavement, the climate, and finally, the actual age and maximal degree of development possible of the Av horizon itself. For example, a significant part of the Av horizon of Pleistocene soils may have formed well before the Holocene, suggesting the possibility that many of its properties are artifacts of sustained pedogenesis in a substantially different climate (McDonald, 1994; McDonald and McFadden, 1994; McDonald et al., 1998).

4. Age of the vesicular horizon: thermoluminescence age dating results

As discussed previously, vesicular horizons contain only very small amounts of organic carbon, the large majority of which are roots or very recently accumulated and only slightly decayed organic material. This and the virtual absence of strongly decayed humic materials preclude radiocarbon dating by conventional methods. Collar carbonates probably do not meet the closed-system conditions required by the $^{238}$U–$^{234}$U–$^{230}$Th dating method. Luminescence dating provides an alternative to these techniques. Most common silicate minerals contain lattice defects which become potential sites of electron storage and a subsequent source for a luminescence signal (Wintle and Huntley, 1979). This signal is mostly acquired by exposure to ionizing radiation produced by decay of isotopes present in surface environments. Eolian deposits are often ideal for thermoluminescence (TL) analysis because light exposure prior to deposition maximizes solar resetting of the inherited luminescence signal (Forman et al., 1998). Following burial, silicate grains act as long-term dosimeters, and thus the luminescence signal increases with time reflecting a prolonged exposure to environmental radiation. Time-stored luminescence can be liberated by heating or by light exposure through various laboratory techniques, a feature that is used as a basis for TL dating or optical dating (O.D.). TL dating and O.D. are most useful for dating sediments less than 100 ka, with a precision of between 5 to 20% (Forman et al., 1998).

The large majority of the material in the vesicular horizon is accumulated dust which contains significant amounts of appropriate silicate minerals subject to a substantial opportunity for solar resetting. Pedogenically modified sediments, however, with accumulations of clay, silt and carbonate complicate TL dating or O.D. through alterations of the radionuclide concentration, disruption of the crystal structure through chemical weathering, and by introduction of newly incorporated, younger sediments (Forman et al., 1998). Because thin-section observations strongly suggest minimal chemical weathering of mineral grains that are the source of luminescence emissions, the impact of this factor is considered unlikely to greatly impact TL dating of the vesicular horizon. Thus, the principal problem to be considered with concern to interpreting Av horizon dates is the progressive accumulation of new minerals in Av and the complex aggregation of grains observed in the micromorphologically complex fabric. The TL ‘ages’ acquired may be roughly analogous to mean-residence time ages from dating of progressively accumulated organic carbon in soil A horizons, such as Mollic epipedons. But the TL ages will establish the minimum age of a soil horizon and elucidate rates and processes of Av horizon development.

Av horizons and associated eolian blankets on flows of the Cima Volcanic Field are an appropriate setting to attempt TL dating of soils, because various studies provide independent ages of the flows (Dohrenwend et al., 1984; Wells et al., 1985, 1995) and many studies of soils and sediments in the area have been conducted. TL, OSL ages of Av horizons or adjacent soil horizons (Bwk and Btkb) from flows of very different ages have been obtained (Table 3). The deeper soil B horizons are not as subject to illuviation and the introduction of younger material or soil mixing as is the Av horizon. The ages of these horizons, therefore, should more closely correspond to (1) the actual age of the buried soil upon its burial, plus the residual age of the surface at the time of its burial, and (2) the age of the material that blanketed the buried soil given the depths in the profile. In general, these ages strongly support the hypothesis that the most recently accumulated eolian blanket on the flows as well as the soil formed in it is latest Pleistocene to Holocene (Wells et al., 1985; McFadden et al., 1986, 1987). The event hypothesized to have triggered deposition of the blanket was the climatic change to an increasingly arid and hot
Table 3

Luminescence data and apparent age estimates for soil horizons, Cima Volcanic Field, California

<table>
<thead>
<tr>
<th>Field No.</th>
<th>Lab sample No.</th>
<th>Soil Horizon</th>
<th>Equivalent dose method</th>
<th>Light exposure</th>
<th>Temperature (°C)</th>
<th>Equivalent dose (grays)</th>
<th>U²⁺ (ppm)</th>
<th>Th⁴⁺ (ppm)</th>
<th>K₂O³⁺</th>
<th>A⁴⁻</th>
<th>Dose rate⁵⁻</th>
<th>Apparent⁶⁻ TL age estimate (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F90-Y16</td>
<td>OTL529</td>
<td>Av</td>
<td>TL-Total bleach</td>
<td>8h UV</td>
<td>280-400°C</td>
<td>26.9 ± 4.3</td>
<td>3.4 ± 0.6</td>
<td>12.2 ± 1.5</td>
<td>2.87</td>
<td>0.05 ± 0.01</td>
<td>5.1 ± 0.3</td>
<td>5.0 ± 1.0</td>
</tr>
<tr>
<td>F90-Y16</td>
<td>IRSL529</td>
<td>Av</td>
<td>OSL-infrared</td>
<td>3-59 seconds</td>
<td>26°C</td>
<td>25.9 ± 0.9</td>
<td>3.4 ± 0.6</td>
<td>12.2 ± 1.5</td>
<td>2.87</td>
<td>0.05 ± 0.01</td>
<td>5.4 ± 0.3</td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>F90-Y10</td>
<td>OTL530</td>
<td>Bwkb</td>
<td>TL-Total bleach</td>
<td>8h UV</td>
<td>250-400°C</td>
<td>63.3 ± 6.9</td>
<td>3.3 ± 0.5</td>
<td>11.0 ± 1.4</td>
<td>3.26</td>
<td>0.05 ± 0.01</td>
<td>5.3 ± 0.3</td>
<td>12.0 ± 1.5</td>
</tr>
<tr>
<td>F90-Y11</td>
<td>OTL534</td>
<td>Bwk</td>
<td>TL-Total bleach</td>
<td>8h UV</td>
<td>250-400°C</td>
<td>68.0 ± 22.8</td>
<td>2.4 ± 0.6</td>
<td>13.7 ± 1.7</td>
<td>3.11</td>
<td>0.04 ± 0.01</td>
<td>5.0 ± 0.3</td>
<td>13.5 ± 4.0</td>
</tr>
<tr>
<td>Black Tank Flow</td>
<td>Av</td>
<td>TL-Total bleach</td>
<td>8h UV</td>
<td>270-370°C</td>
<td>4.0 ± 0.2</td>
<td>2.6 ± 0.3</td>
<td>7.0 ± 0.2</td>
<td>2.7</td>
<td>0.14 ± 0.02</td>
<td>5.3 ± 0.2</td>
<td>&lt; 1</td>
<td></td>
</tr>
</tbody>
</table>

¹All TL measurements were made with a 5-58 filter (blue wavelengths) and HA-3 filters in front of the photomultiplier tube. Samples were preheated to 124°C for 2 days prior to analysis. No anomalous fading within analytical resolution was detected for preheated samples after 30 ± days of storage.

²Hours light exposure to define residual level. "UV" is light from a 275 watt General Electric sunlamp bulb, dominated by ultraviolet emissions.

³Temperature range (TL) or seconds after infrared excitation (OSL) used to calculate an equivalent dose.

⁴Uranium and thorium determined by thick source alpha counting (Huntley and Wintle, 1981). K₂O values derived for sediments by flame photometry at the Radiogenic Isotope Laboratory, Dept. of Geological Sciences, The Ohio State University.

⁵The measured alpha efficiency factor as defined by Aitken and Bowman (1975).

⁶Dose rate estimate assumes average moisture content during burial period of 5 ± 2%, similar to present conditions. Also, a cosmic ray contribution of 0.18 grays/ka is included.

⁷All errors are at one sigma and calculated by averaging the errors across temperatures or seconds.
climate, concomitant development of playas, and increased eolian activity. Recent TL ages from dune deposits in the central Mojave Desert also indicate increased eolian activity at that time (Lancaster, 1994), providing further support for this hypothesis.

The luminescence age estimates from Av horizons of ca. <1 ka and 5 ka are not easily interpreted. These ages are inferred to reflect a mixture of luminescence ages of materials accumulated and transported to the interior of the Av horizon since the horizon formation. Consequently, part of the Av horizon could be quite old, whereas some of the horizon could be much younger, having only recently accumulated. A conservative conclusion drawn from these ages is that much of the Av horizon on the older flow must be at least 5 ka old, and probably much older in order to yield this ‘mean age’. Similarly, much of the material in the Av horizon of the soil on Black Tank Flow, must be as old as 1 ka. The recency (<1 ka) of Av formation inferred from one luminescence age estimate is supported by the presence of similarly developed Av horizons on late Holocene surfaces in the Mojave Desert (cf., McFadden et al., 1991a,b). Luminescence age estimates of ca. 5 ka for Av horizon development on a lava flow with an age of 560 ka, indicates eolian enrichment sometime in the Holocene. Older luminescence ages at depth (25 cm) of ca. 12 ka (Table 3) suggest the possibility of even older Late Pleistocene eolian additions. This provides some support for co-evolution of Av horizons and pavements during the late Quaternary (McDonald, 1994; McDonald and McFadden, 1994; McDonald et al., 1998). These luminescence age estimates underscore the continuous supply of at least some eolian materials to landforms during the Late Pleistocene, with increased flux inferred during the early to middle Holocene.

More specific data regarding age of Av horizons from TL dating will require further studies that, for example, involve microsampling and dating of parts of the Av horizon or the obtaining of ages from Av horizons from a suite of soils in chronosequences. Yet, TL dating results from this study strongly indicate the prolonged period of formation of the Av horizon and demonstrate its stability and maintenance at the surface during pedogenesis for many thousands of years. Thus, the Av horizon can remain strongly coupled to clasts in the co-existing and evolving pavement for a period of time sufficiently long to permit the accretion of carbonate collars up to several cm thick, through mechanisms simulated by numerical modeling.

5. Discussion and conclusions

5.1. The carbonate collars — Av horizon link

Numerical simulation studies supplemented by field, isotopic, and chronologic evidence support a proposed model for the development of carbonate collars, which in turn provides additional information relevant to processes of the vesicular, and calcic horizon development. The key factors that favor collar-forming conditions include: (1) the essentially impermeable, calcareous clasts in the pavement that focus much of the initially infiltrating water with increasingly larger amounts of dissolved calcite along the stone–soil contact; (2) the increase in calcite solubility with depth produced by upward diffusing, respired carbon dioxide and favorable dissolution rates; (3) the generation of saturated overland flow that enables transport of dissolved calcite to other parts of pavement, enabling collar formation on non-calcareous lithologies in the pavement; (4) the hydrologic character of the Av and A horizons; and (5) the rapid evaporation of surface water, due to both the timing of rainfall (hot, dry summer daytime events) and the thermal properties of pavement clasts. Relatively rapid rates of carbonate collar formation indicated by the numerical model are consistent with field data that indicate roughly similar rates (Sena et al., 1994). Their continued growth requires the calcareous source and the continued, long-term coupling of the clast and the Av horizon to enable carbonate precipitation at approximately the same site. The presence of wide collars up to a width of 10 cm (Sena et al., 1994), however, is at least partly attributable to slow, upward growth of an increasingly thicker Av horizon and underlying, transitional nongravelly horizon(s). This phenomenon would be associated with the very large clasts embedded deeply in abandoned surfaces. With cumulic growth, the locus of collar formation on clast surfaces would ascend. The abandoned collar carbonate, subject to very slow rates of dissolution in the progressively...
deeper, subsurface environment, would form part of an increasingly wider collar.

Carbonate collar development might be limited, or perhaps precluded in certain circumstances. For example, limestone clasts in pavements over large areas of semiarid and arid southern Israel are extensively mantled by lichen (Danin et al., 1982), a condition that likely limits carbonate dissolution by direct rainfall, preventing collar formation.

This study also demonstrates the importance of biotic, pedogenic processes in the formation of carbonate collars. Only through soil respiration can a pattern of soil carbon dioxide content develop with depth that will enable dissolution of calcite from the bottoms of surface clasts, even limestone clasts. The proposed model of collar formation does not, however, require biologic processes to force the precipitation of pedogenic calcite. Modeling results show that physicochemical processes described above are sufficient to generate circumstances that favor carbonate accumulation at or near the surface on stable surface clasts. This is also the explanation most consistent with the isotopic data. Once carbonate precipitation is favored by appropriate soil-water compositions, however, microbial organisms may well play significant roles in controlling the morphology of pedogenic calcite (e.g., needle fiber habit) that reflects a biologically mediated process (Wright, 1990; Verrecchia, 1990; Monger, 1990; Monger and Adams, 1996; Gile et al., 1995). Such biologic processes strongly influence the spatial distribution, quantity and micromorphology of carbonate within the developing calcic horizon. Additional studies of calcite in collars and in Av horizons must be conducted to determine the extent of biologic influences on these characteristics. A few researchers revived the hypothesis that microbial activity may be the process most responsible for the accumulation of carbonate in desert soils (Monger, 1990; Monger et al., 1991; Verrecchia, 1990). The overall pattern and depth of accumulation of pedogenic carbonate in large numbers of calcic soils (Yaalon, 1983; Retallack, 1994), the prevalence of noncalic soils in relatively humid regions, the results of numerical modeling studies discussed earlier, the magnitude of carbonate accumulation (Marion, 1989) show that the primary factors responsible for pedogenic carbonate accumulation are favorable soil-water balance and the incorporation of calcareous dust. Soil-water balance is most closely related to climate. Thus, we propose that it is unlikely that microbial processes are primarily responsible for the formation of collars or pedogenic carbonate in Av horizons.

The presence of collars, the accumulation of carbonate in the Av horizon, and the compositional evolution of the horizon demonstrate that the Av horizon is in many instances essentially hydrologically isolated from underlying horizons. The strong influences exerted by the Av horizon on runoff/infiltration ratios of associated fan surfaces also has important implications for fan surface evolution by producing surface runoff (Wells et al., 1987; McDonald, 1994; McDonald and McFadden, 1994; McDonald et al., 1998). Such surface runoff, in turn, may influence the character of Av horizons subject to runon and infiltration. Recent studies provide evidence of variable Av horizon development in some areas that is attributable to the influence of a pattern of surface or shallow flow related to local surface topography as well as other factors (Anderson et al., 1994).

On the basis of the properties and inferred genesis of the Av horizon, the designation of this surface horizon of these gravelly, desert soils as an A horizon is not especially appropriate, given the formal definition of the master A horizon. Because of the very light color of the Av horizon, it meets some of the requirements of the E horizon (formerly the ‘A2’ horizon), so in some studies it was inappropriately recognized as such (Gile and Grossman, 1979; Gile et al., 1981). The horizon primarily possesses characteristics of a B horizon (especially in the ped interior), however, and the thin overlying layer of loose material would accordingly merit CB or a Bw designation, given its origin as recently deposited, but fines-, carbonate-, and soluble salt-depleted eolian material. The subjacent, nongravelly layer that typically occurs below the Av horizon of older Holocene and Pleistocene soils is either (1) pedogenically modified eolian material formed largely during the first

---

2 A horizons are mineral horizons that formed at the soil surface, have humified organic matter mixed with mineral material and are not dominated by properties characteristic of B or E horizons (Buel et al., 1989).
stages of accretionary accumulation of eolian material (McFadden et al., 1986), or (2) material flushed or leached through the A horizon after the A horizon has attained a strongly developed state (McDonald, 1994; McDonald and McFadden, 1994; McDonald et al., 1998). Formation of the layer, usually referred to as some type of B horizon (e.g., Bwk or Btky), probably reflects aspects of both processes. The pedogenically modified gravelly parent material, buried by these cumulic soil horizons, is a 2Bt or 2Bk horizon, but is not a 2Bth horizon, because the overlying younger layer is not 50 cm thick.

5.2. Vesicular horizons, carbonate collars, and surficial geomorphic processes

For how long will carbonate collars and the associated A horizon continue to form? This must largely depend on the long-term stability of the surface clasts. Various mechanical weathering processes, such as salt shattering, cause the diminution of exposed surface clasts on alluvial fan surfaces subsequent to their abandonment, an important mechanism in the process of pavement development (Cooke, 1970; Mabbutt, 1977; Ritter, 1986; Summerfield, 1991; Cooke et al., 1993). Clasts with collars subject to these processes would be subject to new circumstances that would either destroy the collar or even preclude development of another collar.

Processes of stone tilting or overturning also may significantly influence carbonate collar development. On many pavements clasts with reddened, subaerial surfaces that have variably strong varnish veneers are indicative of clast reorientation. Such movement of clasts has been attributed to bioturbation and overland flow, or perhaps even displacement by larger mammals traversing the surface (Sena et al., 1994). Processes that increase surface runoff may also disrupt the pavement itself. For example, the formation of increasingly clay- and carbonate-rich soils on Pleistocene surfaces in the Mojave Desert significantly increased their potential to produce runoff due to decreased soil permeability. This process can lead to local erosion of the A horizon, exposing part of a previously formed collar (see Fig. 3A). The presence of only weakly developed pavements on some older Pleistocene or Pliocene surfaces that typically exhibit strongly developed pavements may thus reflect the progressive increase in overland flow and locally extensive surface erosion by sheet flow (Wells et al., 1985, 1987; McDonald, 1994). These circumstances would likely limit or even preclude collar formation.

Sena et al. (1994) attributed the presence of tilted carbonate collars to processes of pavement disruption. On the basis of the model of collar formation presented in this paper, such tilting will subaerially expose part of the collar and it should dissolve quickly, probably within centuries. The part of the tilted collar projected below the zone of active collar formation should dissolve, but only relatively slowly. A new collar will form if the source of dissolved carbonate remains. Therefore, the presence of a well preserved tilted collar associated with minimal new collar development implies that the tilting occurred relatively recently, probably within the past few decades or centuries. With increased time, the formation of the new collar and the persistence of much of the tilted, older collar should produce overlapping, crossing collars. A well preserved, subsurface collar should also be present. A feature with the predicted form has been observed on a pavement where preferential erosion on the downslope side of the clast was the probable cause of the inferred tilting (Fig. 14).

From the model results, we can also hypothesize that if processes producing tilting have operated on pavements throughout their existence (albeit at variable rates), surficial evidence of tilting prior to $10^3$ years ago from tilted collars should be rare or absent; but, subsurface tilted collars are likely preserved. Future studies of pavement evolution similar to the study of Sena et al. (1994) will help to test the model of collar evolution proposed here. If the model as presented is essentially correct, more detailed evaluation of spatial and temporal patterns of collar size, clast size and lithologic association and degree and magnitude of preservation of tilted collars in pavements will provide important insights into processes of pavement evolution.

Studies of rarely observed collars present in pavements underlain by parent materials with little or no limestone also could provide data useful in geomorphic studies. The presence of such a collar implies that the original carbonate source must have been a carbonate coating previously extant on the clast. On
very young geomorphic surfaces, the presence of carbonate-coated clasts may simply reflect erosion of gravelly calcic horizons and the redeposition of such clasts in gravel bars formed in downstream locations. The presence of such collars on moderately to well developed pavements, however, suggests that the clast’s coating initially formed in a subsurface calcic horizon and that the clast has arrived at the surface through some other geomorphic process. For example, the surface may have been subject to enhanced bioturbation or erosion, followed by surface stabilization and collar development on locally isolated clasts. Such collars are likely transient, because there is no additional source of carbonate to replenish carbonate lost from the coating during successive infiltration events. Model results suggest that an initially thick coating would favor development of a collar sufficiently thick to persist for a few thousand years.

5.3. Climatic change and vesicular horizons

A consideration of the distribution of Av horizons in Holocene soils in the western United States provides insights into the critical factors that currently favor its development. For example, Av horizons do not form or are only weakly developed on smooth surfaces associated with fine-grained deposits, such as sand dunes or loess because of (1) the lack of an appropriately rough surface to entrap the dust and trigger its formation, and (2) the lack of the gravel veneer that protects the evolving Av horizon from deflation and raindrop impact. Dust influx is also a critical factor. Very fast dust influx produces thick loess deposits and not Av horizons. The extensive, dust-producing playas and beaches formed after desiccation of pluvial Lake Lahontan in Nevada, for example, caused burial of surrounding landscapes with such deposits (Chadwick and Davis, 1990); their soils lack pavement or well developed Av horizons. Vegetation on these surfaces also illustrates the role of climate as a key variable. In most currently semiarid to subhumid areas in the western United States, geomorphic surfaces associated with gravelly deposits have only weak or no pavements, typically darkened Ohric A horizons or occasionally Mollic A horizons with granular structure. The development of these epipedons reflects sufficiently high rainfall and infiltration to promote development of greater vegetation cover and deep translocation of

Fig. 14. Intersecting, overlapping carbonate collars formed on a volcanic clast from a stone pavement. Note dissolution features exhibited by subaerially exposed part of tilted collar. The clast was originally located near the margin of a Late Pleistocene terrace above a 20-m scarp. The terrace is one of several terraces of Palo Duro Wash, a major drainage of the Los Pinos Mountains, New Mexico, recognized and mapped by Treadwell (1996).
fine materials to lower soil horizons (cf., McFadden and Weldon, 1987). In addition, this environment appears to be conducive to bioturbation (e.g., burrowing of small mammals), a process that probably minimizes or prevents Av horizon formation.

As climate plays such a critical role in Av horizon and pavement evolution, what roles have the climatic changes that occurred in the late Quaternary played in the development of this horizon? It seems reasonable to presume, at minimum, that their formation rate was accelerated during and after the Pleistocene-to-Holocene climate change as has been proposed in previous studies (McFadden et al., 1986, 1989). At elevations now above the modern upper limit of creosote shrubland in the Mojave Desert, where pavements and Av horizons are weak or lacking, it is unlikely that Av horizons were forming during the effectively wetter climate of the last glacial period. But in areas currently favorable to Av horizon formation, Av horizons must have formed at times before the Holocene during similarly arid conditions. In the Cima Volcanic Field, for example, Av horizons are present in soils instantly buried by pyroclastic materials during older, Pleistocene volcanic eruptions (Wells et al., 1985). McDonald (1994) hypothesizes that an Av horizon, once formed, may be maintained as an intact horizon that passively rises with the associated pavement with most cumulic soil development occurring below it. But such intact Av horizons, had they been present on older Pleistocene soils, would have been subject to conditions presumably far less favorable to Av horizon development during the most recent, relatively long glacial period of the Late Pleistocene. How could such Av horizons have been preserved over many tens of thousands of years?

The survival of Av horizons in such times might be explained in several ways. For example, once Av horizons and stone pavements have formed, their profound effect on soil hydrology may persist, despite changes to wetter climates. The thermal characteristics of dark, stone pavements should also continue to favor enhanced soil-water evaporation and decreased effective infiltration. Thus, the colonization of such surfaces by plants in a wetter climate may have been prevented by maintaining unfavorable water infiltration–depth relations and soil-water compositions. These characteristics play important roles in determining presence or absence of many species in arid landscapes, as they possess varying physiological adaptations to different edaphic environments (McAuliffe, 1994). Unfortunately, packrat middens from caves or other favorable nesting sites do not provide records representative of pavements of fan surfaces, making it difficult to easily test this proposal. The potentially important effects on spatial patterns of changing plant community distribution arising from an evolving soil state, however, have potentially significant paleoecological as well as geomorphological implications.

Even presuming favorable circumstances for their persistence, what was the relative impact of the last major glacial–interglacial climatic change on the development of Av horizons? Several lines of evidence reported here show that the impact was substantial. The simplest interpretation of the TL ages is that most of the Av horizon material of soils on a middle Pleistocene volcanic flow is Holocene. Mass-balance analyses described earlier in this paper suggest limited alteration of this material, and the overall character of the soil properties strongly indicates pedogenesis in a largely hot, arid regime that predominates throughout most of the Holocene. Limited alteration is also indicated by Av horizon colors. The colors of Av horizons of soils on the oldest Pleistocene soils have colors the same as those of the youngest weakly developed Av horizons of late Holocene soils, 10YR 7/3. The interior ped color is occasionally slightly redder, but only to a color acquired by B horizons in deserts after only a few thousand years (McFadden et al., 1991a,b). In B horizons of desert soil chronosequences, strongly increasing redness is a hallmark of increasing soil age, the result of sustained pedogenesis in a hot, dry soil environment that favors ferrihydrite formation and rapid formation to anhydrous hematite (McFadden and Hendricks, 1985). As the most shallow soil horizon should be subject to a large amount of oxygenated, infiltrating moisture, it is difficult to identify a process that could explain why the horizon would not become redder, especially given the abundant amount of ferrous iron in the horizon (McFadden et al., 1986). Thus, it seems that, although rates of Av horizon formation and net rates of dust incorporation may be comparatively slow on smoother surfaces of older pavements compared to younger,
topographically rougher surfaces (McFadden et al., 1986; Gerson and Amit, 1987), horizon formation continues through slow but progressive accretion via processes documented by Anderson et al. (1994). The Pleistocene-to-Holocene climatic change profoundly influenced soil development in this region, regardless of geomorphic surface age. Remarkably, parts of Av horizons now associated with older Pleistocene soils at elevations below 700 to 800 m may well have survived the last, and perhaps other previous, long intervals of glacial climate. Ultimately, this may provide the answer to the vexing question of how, despite large and frequent climate changes, many desert pavements have remained intact for much of the Quaternary.

Acknowledgements

The senior author is very grateful to Dr. Roger Scurlock for numerous, insightful discussions concerning the behavior of chemical systems and relevant reaction rates and important, thought-provoking comments. Discussions with Dr. Joseph McAuliffe concerning soil and plant ecologic relationships in desert regions have also been quite beneficial. We would also like to thank Dr. Rivka Amit and two other anonymous referees for insightful, critical and ultimately very helpful reviews.

References


Danin, A., Gerson, R., Marton, K., Garty, J., 1982. Patterns of limestone and dolomite weathering by lichens and blue-green
geology and their palaeoclimatic significance. Palaeogeogr.,
Palaeoclimatol., Palaeoecol. 37, 221–233.

Deines, P., 1980. The isotopic composition of reduced organic
carbon. In: Fritz, P., Fontes, J.C. (Eds.), Handbook of Envi-
ronmental Geochemistry, 1. Elsevier, Amsterdam, pp. 329–
406.

Denny, C.S., 1965. Alluvial fans in the Death Valley region,

Dohrenwend, J.C., McFadden, L.D., Turin, R.D., Wells, S.G.,
1984. K–Ar dating of the Cima volcanic field, eastern Mojave
Desert, California: Late Cenozoic volcanic history and land-
scape evolution. Geology 12, 163–167.


Dorn, R.I., Oberlander, T.M., 1981. Microbial origin of desert

Drever, J.I., 1991. The Geochemistry of Natural Waters (2nd ed.).

Atmospheric circulation during Holocene lake stands in the
Mojave Desert: evidence of regional climate change. Nature
342, 44–48.

Enzel, Y., Brown, W.J., Anderson, R.Y., McFadden, L.D., Wells,
S.G., 1992. Short-duration Holocene lakes in the Mojave
River drainage basin, southern California. Quat. Res. 38,
60–73.

with vesicular structure in deserts. Geomorphology 18, 162–
172.

effects on variability of soil temperature and water. Agric. For.


Frissei, M.J., Reingier, P., 1974. Simulation of Accumulation and
Leaching in Soils. Wageningen Centre for Agriculture, Publi-
cation and Documentation, Wageningen.

Gerson, R., 1975. Karst and fluvial denudation of carbonate
terrains under sub-humid Mediterranean and arid climates —
principles, evaluation and rates (examples from Israel). In:
Proc. Int. Symp. Standardization of Field Research Methods of
Karst Denudation (Corrosion). Dep. of Geography, Philosophi-
cal Faculty, Univ. of Ljubljana, pp. 71–79.

Gerson, R., Amit, R., 1987. Rates and modes of dust accretion
and deposition in an arid region: the Negev, Israel. In: Fostick,

Western Deserts. Soil Sci. 139, 468–481.


Goosens, D., 1995. Effect of rock fragments on eolian deposition

cients from the electrical conductivity of natural aquatic sys-


rubification in Pilot Knob Valley, Mojave Desert, California:
potential for use in dating Late Quaternary surfaces in arid

counting for measuring Th-230 and Pa-231 contents of ocean

Jenny, H.J., Leonard, C.D., 1935. Functional relationships be-
tween soil properties and rainfall. Soil Sci. 38, 363–381.

Jessup, R.W., 1960. The Stony Tableland soils of the Australian
arid zone and their evolutionary history. J. Soil Sci. 11,
188–196.

Kiefer, R.H., Amey, R.G., 1992. Concentrations and controls of
soil carbon dioxide in sandy soil in the North Carolina coastal
plain. Catena 19, 539–559.

Kline, J.R., 1973. Mathematical simulation of soil—plant relations-

Lancaster, N., 1994. Studies of Quaternary eolian deposits of the
Mojave Desert, California. In: McGill, S.F., Ross, T.M. (Eds.),

MA, 340 pp.

States. In: Weide, D.L., Faber, M.L. (Eds.), Soils and Quater-
ary Geology of the Southwestern United States. Geol. Soc.

nodules in soils: 18O/16O and 13C/12C ratios and 14C

Marion, G.M., 1989. Correlation between long-term pedogenic
CaCO3 formation rate and modern precipitation in deserts of

regional model for soil CaCO3 (caliche) deposition in south-
western deserts. Soil Sci. 139, 468–481.

Mayer, L., McFadden, L.D., Harden, J.W., 1988. Distribution of
calcium carbonate in desert soils: a model. Geology 16, 303–
306.

McAuliffe, J.R., 1994. Studies of Quaternary eolian deposits of the

McDonald, E.V., 1994. The Relative Influence of Climatic Change,


