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Calcic soils and calcretes in the southwestern
United States

By

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CALCIC SOILS AND CALCRETES

IN THE SOUTHWESTERN UNITED STATES

By GEORGE O. BACHMAN AND MICHAEL N. MACHETTE

Abstract

Secondary calcium carbonate of diverse origins, "caliche" of many authors, is widespread in the southwestern United States. "Caliche" includes various carbonates such as calcic soils and products of ground-water cementation. The term "caliche" is generally avoided in this report in favor of such terms as calcrete, calcic soils, and pervasively cemented deposits.

Criteria for the recognition of various types of calcrete of diverse origins include field relations and laboratory data. Calcic soils provide a comprehensive set of characteristics that aid in their recognition in the field. These characteristics include a distinctive morphology that is zoned horizontally and can frequently be traced over tens to hundreds of square kilometers.

The major process in the formation of pedogenic calcrete and calic soils is the leaching of calcium carbonate from upper soil horizons by downward percolating soil solutions and reprecipitation of the carbonate in illuvial horizons near the base of the soil profile. The formation of pedogenic calcrete involves many factors including climate, source of carbonate, and tectonic stability of the geomorphic surface on which the calcrete is deposited. Most of the carbonate in pedogenic calcrete is probably derived from windblown sand, dust, and rain.

Calcic soils and pedogenic calcretes follow a six-stage sequence of

morphologic development and is based on a classification devised by Gile, Peterson and Grossman in 1966. The six morphologic stages of carbonate deposition in soils are related to the relative age of the soil and are as follows:

I. The first or youngest stage includes filamentous or faint coatings of carbonate on detrital grains.

II. The second stage includes pebble coatings which are continuous; firm carbonate nodules are few to common.

III. The third stage includes coalesced nodules which occur in a friable or disseminated carbonate matrix.

IV. The fourth stage includes platy, firmly cemented matrix which engulfs nodules; horizon is plugged to downward moving solutions.

V. The fifth stage includes soils which are platy to tabular, dense, strongly cemented. A well-developed laminar layer occurs on the upper surface.

VI. The sixth and most advanced stage is massive, multilaminar, and strongly cemented calcrete with abundant pisoliths, the upper surface of which may be brecciated. Pisoliths may indicate many generations of brecciation and reformation.

In general calcic soils include stages I through III and are friable to moderately indurated; whereas pedogenic calcretes include stages IV through VI and are dense and strongly indurated. In a single pedon the morphologic stage of carbonate deposition decreases downward in the profile. The stage of development may be used in local regions for correlation and determination of relative ages of soils and geomorphic surfaces.

Some structures observed in pedogenic calcretes may be present in other types of calcrete but the horizontal zonation typical of deposits of soil processes is absent. Laminar structure in particular is not restricted to pedogenic deposits and is common in many varieties of calcrete.

Very little chemical change occurs in the noncalcareous nonclayey fractions of calcretes with age; but clay minerals within calcretes undergo a complex history of authigenesis. There is a depletion of magnesium in the calcareous portion and an enrichment of magnesium in the clayey portion of a calcrete with age. In keeping with this relationship, montmorillonite, or mixed layer montmorillonite-illite, is common in younger calcretes; whereas the high magnesium-silicate clays, sepiolite and palygorskite, are common in older calcretes. This indicates that the magnesium depleted from the carbonate is redistributed authigenically in clay minerals.

The mobility of carbonate introduces many problems in attempts to date calcretes directly. Although the relative ages of soils within a province may be determined by quantitative studies, the absolute age can at present be made only by cross reference to other datable deposits such as lava flows, pumice, ash falls, and fossil-bearing beds. Rates of calcium carbonate accumulation vary from 0.22 to 0.51 $g/cm^2/kyr$ for New Mexico. These rates exceed those of many other areas in the southwestern United States. The amount of pedogenic carbonate in a soil as well as its morphology can be used to correlate both Quaternary alluvial deposits and geomorphic surfaces. Additionally, calcic soils and pedogenic calcrete are useful in analyzing recurrent fault histories.

In many areas where climatic conditions and carbonate sources are amenable to the formation of calcic soils, relict pedogenic calcretes are not preserved. In these regions examined during this study, the absence of such calcretes is the result of tectonic instability and rates of erosion and deposition too rapid for the time required to deposit the calcrete.

Introduction

Deposits of secondary calcium carbonate of various origins are widespread in the southwestern United States. In this region the term "caliche" is broadly applied to many of these deposits without regard to their field relations, physical characteristics, and origin (Reeves, 1976). This application of the term "caliche" has also created semantic problems and misconceptions in the comparison of geologic features.

This study was undertaken in an attempt to clarify some of these misconceptions and to determine if some types of calcrete might be used as correlative stratigraphic horizons over broad regions. This study was also undertaken to determine if carbonate accumulations in soils of semiarid regions are related directly to geologic time. In theory, if this relationship could be demonstrated, many calcretes would be valuable tools in relative dating of geologic events.

Since there is a massive amount of literature, in several languages, on secondary terrestrial carbonate deposits, an exhaustive summary of previous work on these deposits is not attempted here. Goudie (1971, 1973) has summarized the theories and terminology of origin of these deposits and his work is an outstanding reference in the English language. Gigout (1960) and Ruellan (1967, 1971) have summarized the major theories of origin proposed by French workers. In the United States the work of Gile and others (1965, 1966) describes the morphology of calcic soils and is the basis for much of the classification followed in this report.

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Method of study

This study was begun in the Rio Grande depression in central New

Mexico (fig. 1) where secondary carbonate deposits of several types are
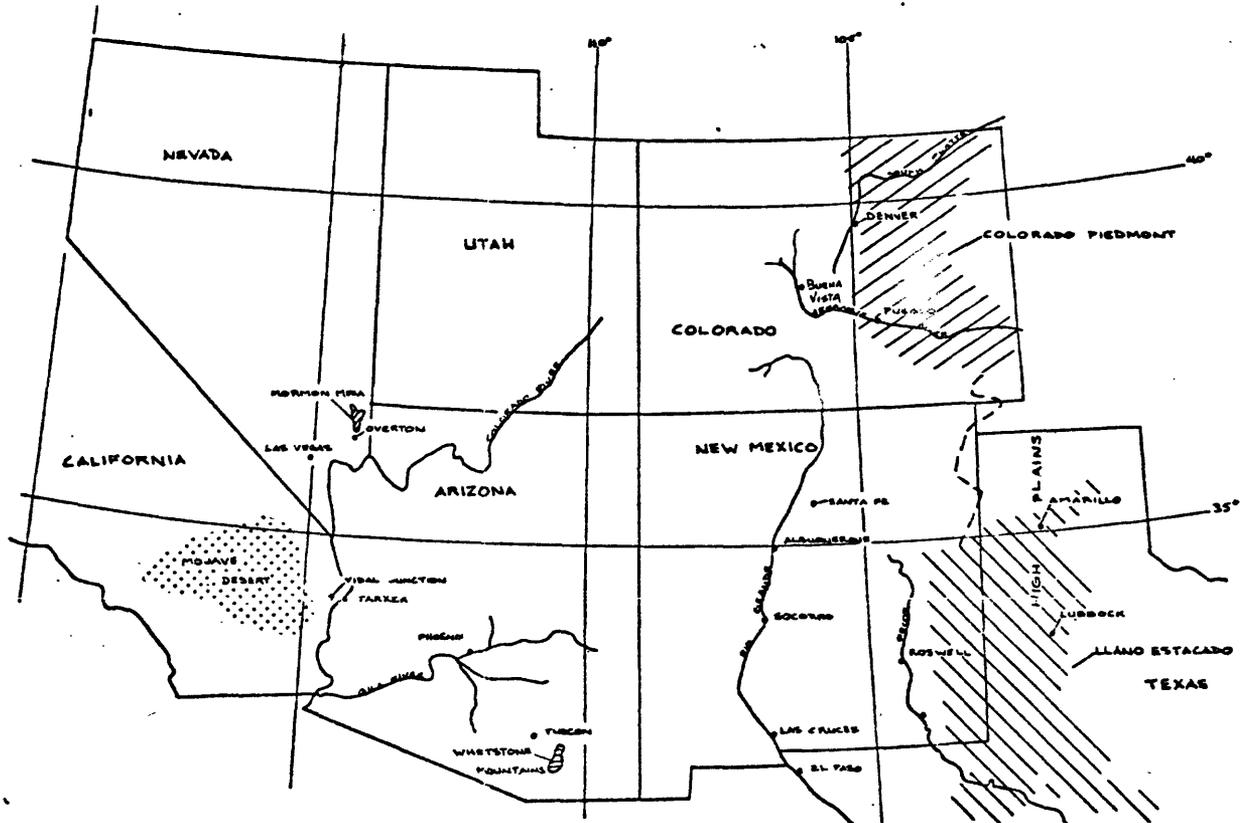
Figure 1.—Index map of part of the southwestern United States
showing major geographic features mentioned in the text.

widespread. Relict calcic soils in this area are of particular interest

because they are well exposed and continuous over broad geomorphic

surfaces. In addition some surfaces are associated with lava flows and

ash falls. Ages of these units have been obtained by K-Ar (Bachman and

Mehnert, 1978) and fission-track methods (Izett and Naesser, 1976;

Manley, 1976). These dates provide broad limits for the age of some

surfaces and their soils.

In southern New Mexico calcic soils and desert geomorphology have been studied extensively and numerous papers written by staff members of the Soil Conservation Service (SCS), Department of Agriculture (Hawley, 1975). This work has provided a broad base for our studies and consequently we have reexamined many of the exposures described in those papers. Reference to specific portions of the SCS work is made throughout this report.

Calcic soils were examined and described in both natural and manmade exposures in the central Rio Grande region of New Mexico and numerous profiles were measured and sampled in detail for additional study in the laboratory. This study was then extended to eastern New Mexico where preliminary work on Pliocene and middle Pleistocene calcic soils was previously done by Bachman (1976). Transects of the High Plains from western Nebraska southward to the vicinity of Canyon, Texas, and from western Texas across southern and western Arizona to southern Nevada and to the Mojave Desert in southern California were then conducted to examine calcic soils and carbonate deposits in a variety of climatic and physiographic conditions.

Laboratory work included the determination of $CaCO_3$ content of calcic soils, bulk densities, and both atomic absorption and spectrographic analysis for trace-element content. X-ray analysis and scanning electron photomicrographs were made of clay minerals in calcic soils and other types of carbonate deposits. Routine examinations of thin sections were made with a petrographic microscope. A specific explanation of the laboratory techniques used in this study is described in the section entitled Analytical procedures and laboratory methods.

Terminology

Although the term "caliche" has many connotations in the United States (Aristarain, 1971), more precise terms for these secondary calcium carbonate deposits have not been widely accepted. Goudie (1972) has discussed the problem of terminology and has used the term <u>duricrust</u> to include several types of deposits which are cemented within the zone of weathering. He defines duricrust as:

> A product of terrestrial processes within the zone of weathering in which either iron and aluminum sesquioxides (in the cases of ferricretes and alcretes) or silica (in the case of silcrete) or calcium carbonate (in the case of calcrete) or other compounds in the case of magnesicrete and the like have dominantly accumulated in and/or replaced a pre-existing soil, rock, or weathered material, to give a substance which may ultimately develop into an indurated mass (Goudie, 1972, p. 5).

Calcretes are widespread over the world and Goudie (1972, p. 8, table 2) has compiled a list of 35 regional and provincial terms that he considers to be synonymous with his definition of calcrete. The term "caliche" is included in this list. Although the terms "calcrete" (Lamplugh, 1902) and "caliche" (Blake, 1902) were introduced simultaneously there is such confusion as to the use of the the term "caliche" in the southwestern United States that it is avoided in this report except as quoted from other authors or as a term broadly synonymous with "calcrete."

As defined by Goudie the term calcrete would include calcic soils in various stages of development which occur in semiarid and arid regions. The term caliche is frequently used in the southwestern United States for deposits of calcium carbonate in Bca and Cca soil horizons and in the "K horizon" as defined by Gile and others (1965), but in view

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of the imprecise usage of the term "caliche" we here propose more restrictive terminology.

Where possible, it is preferable to use descriptive, nongenetic terms for secondary calcium carbonate as outlined by Netterberg (1967, quoted by Goudie, 1973) and Gile and others 1966). These descriptive terms are particularly useful in describing the morphology of pedogenic carbonate. A modification of the morphologic classification proposed by Gile and others (1966) is used in this report.

Other terms used in this report include the following:

Calcic horizon.--"A horizon of accumulation of calcium carbonate * * * . The accumulation may be in the C horizon but it may also be in a variety of other horizons" (Soil Survey Staff, 1975, p. 45). In general the calcic horizon is 15 or more cm thick and contains 15 percent or more $CaCO_3$ by volume (less than 2 mm fraction) where developed in noncalcareous parent materials. Many weakly developed calcic soils are recognized visually by the presence of secondary carbonates in the form of powdery disseminations, concretions, or thin coats on clasts.

Calcic soil.--A soil whose main attribute is the accumulation of calcium carbonate. Calcic soils are friable to moderately indurated and may have one or more K-horizons; these K-horizons may engulf other horizons in advanced stages of development. Partly synonymous with pedocal soils.

K-horizon.--Soil horizon so impregnated with calcium carbonate that its morphology is determined by the carbonate. Authigenic (secondary) carbonate coats or engulfs all primary grains in a

continuous medium (K-fabric) and this fabric makes up 50 percent or more of the volume of the horizon (Gile and others, 1965). Laminae, breccias, or pisoliths may form during advanced stages of cementation.

Textural and structural terms used in conjunction with calcic horizons include:

Nodules.--Nodular to irregular concentrations of calcium carbonate. Nodules may be soft to firm, or even hard under the hammer, widely disseminated to closely spaced, especially in a friable calcareous matrix. Individual nodules generally engulf sandy to silty matrix (fig. 14) but the carbonate cement is structureless and not laminated as in pisoliths (see pisolith below).

Platy.--Thin layers cemented with calcium carbonate, arbitrarily less than 2 cm thick, generally situated in the upper part of a plugged zone; they are usually well indurated, unlaminated (except in places where the upper surface may have weak discontinuous laminae), and best developed where exposed to surface weathering.

Tabular.--Well-cemented layers that range from about 2 to 25 cm thick. Layers are lenticular, angular blocky, discontinuous, and irregular in cross section (fig. 2).

Massive.--Well-cemented layers more than 25 cm thick. This term may be applied also to the structure of pervasively cemented deposits.

Figure 2.--The Mescalero pedogenic calcrete in western Lea
County, southeastern New Mexico. The upper part is a
tabular stage V calcrete. The lower part of the
profile shows nodular structure of stages IV and III.
Nodules at base are in a friable, calcareous sand
matrix. Hammer included for scale.

Case hardening.--Well-cemented layers deposited on the surface

of vertical outcrops (Lattman and Simonberg, 1971). Case hardening

occurs on both natural and manmade exposures and may mask other

primary structures and textures (figs. 3 and 4).

Laminae.--Thinly laminated, alternating, medium- to light-gray

pinkish layers that average about 1 to 3 mm in thickness. Layers

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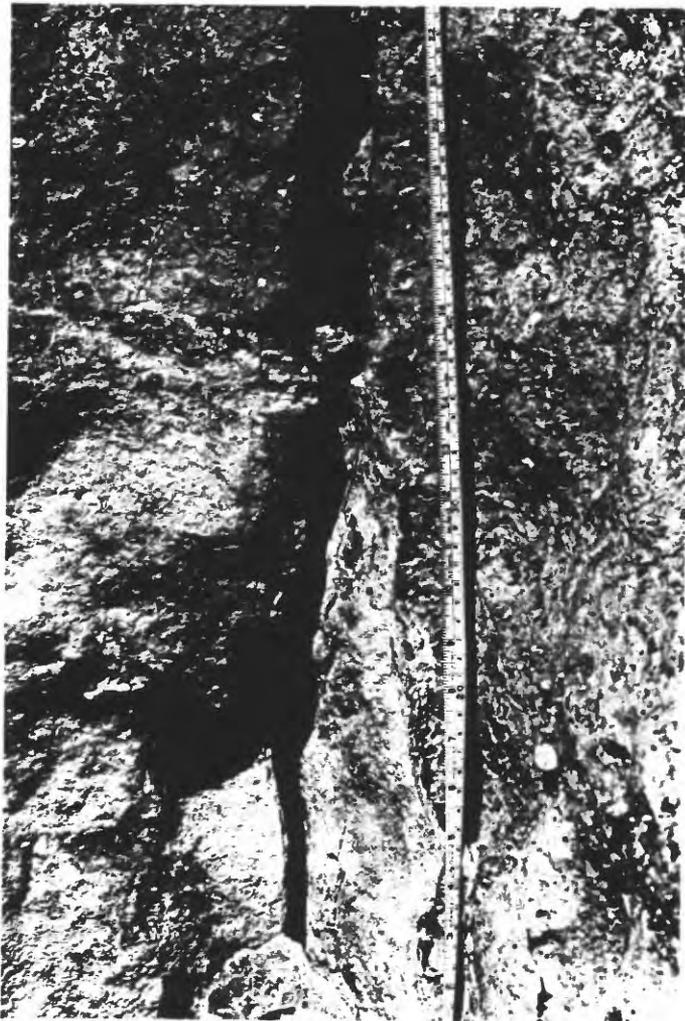
Figure 3.--Case hardening along a vertical joint in the Mormon Mesa pedogenic calcrete. Case hardening consists of vertically laminated, nearly pure $CaCO_3$, 1.0-1.5-cm thick. The case hardened portion extends into joint and, where present, masks other internal soil structures.
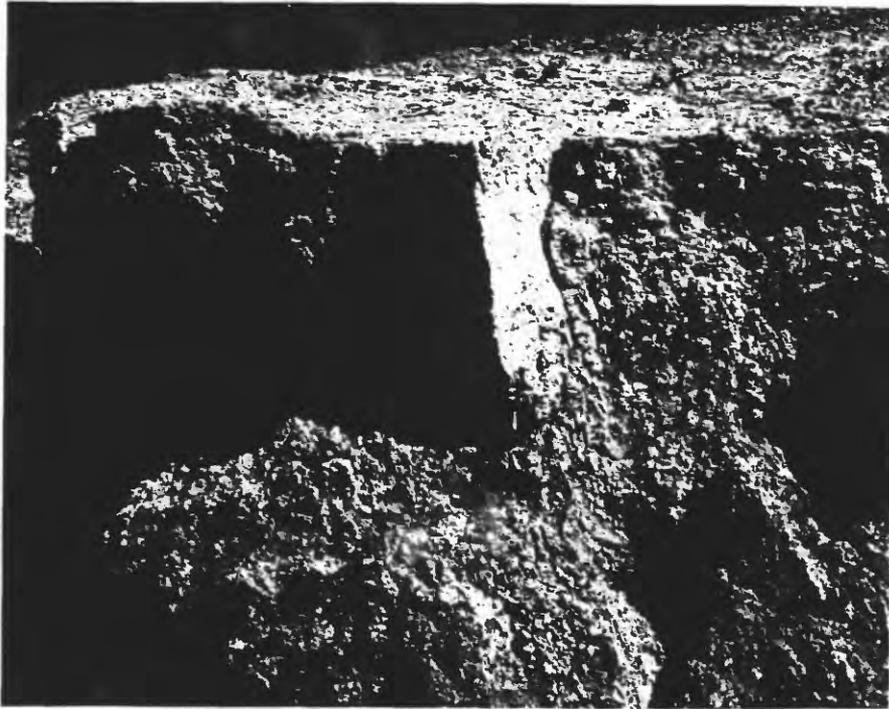
Figure 4.--Case hardening on surface exposure of La Mesa soil. The case hardening appears as a smooth, vertical surface plastered on the exposure. At this place the exposure is about one meter thick. Southern Dona Ana County, New Mexico, west of El Paso, Texas.

may be simple (couplets) or multiple (3 or more laminae per set). They may occur as a discontinuous to continuous cap on tabular or massive calcrete and are usually related to well-developed, plugged calcic horizons or pervasive cementation. They are very fine grained to micritic. They usually occur on horizontal surfaces but may fill vertical fractures as veinlets, occur as part of advanced case hardening (fig. 3), or form the walls of pipes (fig. 6).

Pisoliths.--Subangular to spheroidal carbonate masses that may range from 0.5 cm to more than 10 cm in diameter. They are characterized by concentric banding and an internal structure of

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disrupted laminae, or disrupted concentric banding, that is relict from previous generations of pisoliths. Some pisoliths in ancient calcretes incorporate portions of smaller pisoliths and suggest many generations of development (fig. 5).

Figure 5.--Cemented pisoliths exposed on upper surface of Ogallala pedogenic calcrete, Chaves County, southeastern New Mexico.

Pipes.--Vertical tubular cavities, generally funnel-shaped in cross section, that penetrate plugged horizons, and may be overlain by platy to tabular calcrete deposits. They may be as much as 1 m in length and more than 0.5 m in diameter at the top. Their walls are usually laminated (fig. 6).

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Figure 6.--Pipe in K horizon of La Mesa soil. Pipe has
    vertical, laminated walls. Locality is west of Las
    Cruces, New Mexico.

Petrocalcic horizon.--"The calcic horizon tends in time to
become plugged with carbonates and cemented into a hard, massive,
continuous horizon that we call the petrocalcic horizon. Such
horizons seem to be mainly in soils older than the Holocene. In
the early stages of development, a calcic horizon has lime that is
soft and disseminated or that has accumulated in hard concretions
or both. The petrocalcic horizon is a mark of advanced soil
evolution" (Soil Survey Staff, 1975, p. 46). The term "petrocalcic
horizon" is used very little in this report inasmuch as it overlaps

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the later stages of calcic soil development discussed here and may also be confused with features that are pervasively cemented.

Pervasively cemented deposits.--Massive, strongly cemented deposits of alluvium. Laminar horizons may be present on the upper surface or as fracture fillings but the horizontal zonation characteristic of soil morphology is not present. Fanglomerates and stream gravels in semiarid and arid regions may be pervasively cemented by dense calcium carbonate, especially in areas where drainages cross calcareous bedrock. Soil processes may have contributed to the pervasive cementation but soil morphology is masked by the massive structure. Some soils may accumulate in younger materials overlying the zone of pervasive cementation. Pervasive cementation is predominantly the result of the deposition of calcium carbonate from surface water or ground water circulating in the vadose zone. Zones of "pervasive cementation" are partly synonymous with "petrocalcic horizon" and "ground-water cementation."

Solution-faceted clasts.--Carbonate clasts in alluvial deposits whose upper surface has been partially dissolved. The dissolved carbonate is precipitated as a light-colored secondary deposit on the lower part of the clast (Bryan, 1929) and is micritic and markedly different in texture from the carbonate host (fig. 7). The faceted surface may have a central boss or it may be rough and irregular as a result of differential solution of accessory or secondary minerals in the original carbonate. Solution-faceted clasts are most common on the surface, or within

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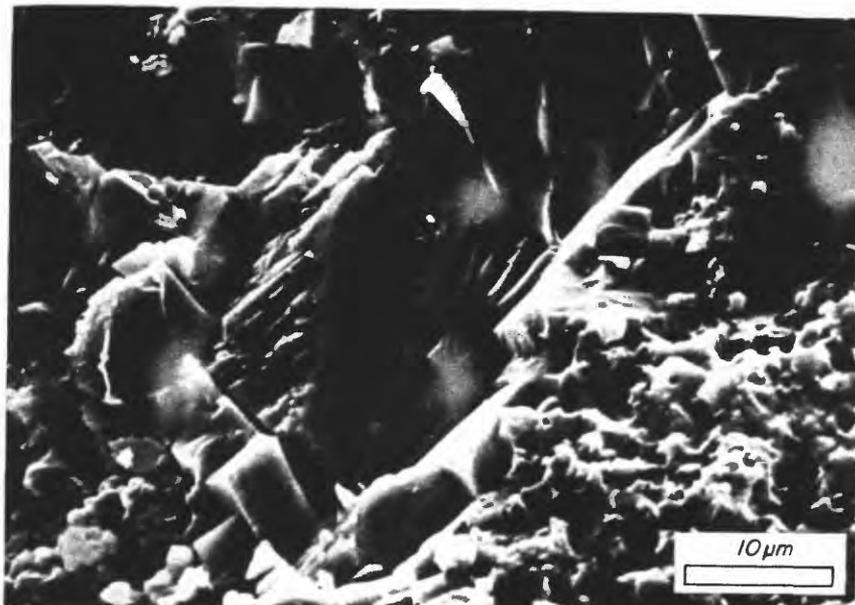
Figure 7.--SEM photograph of solution-faceted limestone
    pebble.   Base of pebble (upper left hand part of
    photograph) displays coarse rhombohedral cleavage;
    white pebble coatings has very fine grained micritic
    texture.   10 micron bar shown for scale.

porous layers of pervasively cemented deposits (fig. 8). Solution-

faceted pisoliths are common in ancient calcretes. These faceted

pisoliths and the accompanying reprecipitated carbonate may

resemble horn corals (fig. 9).

Figure 8.--Solution-faceted clasts in fanglomerate in southern Nevada, near Overton.

Figure 9.--Solution-faceted pisoliths, Mormon Mesa, Nevada. The upper surface of the original pisolith has been almost completely dissolved and the carbonate redeposited on the lower surface resulting in forms that resemble horn corals.

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Criteria for recognition of various
types of calcrete

Criteria for the recognition of various types of calcrete include both field observations and laboratory data. Field relations are usually the most reliable and definitive, but in some cases, especially where exposures are isolated, physical characteristics (including those of microscopic scale), calcium-magnesium ratios, clay mineralogy, and the trace-element content may provide important clues to the origin and type of calcrete in question.

Soil characteristics of pedogenic calcrete and calcic soils provide a comprehensive set of field relations that aid in their recognition. Unfortunately, many other types of calcrete are much more difficult to recognize. The origin of some deposits may be indeterminable especially when those deposits are polygenetic.

Ideally, relict calcic soils have the following distinguishing characteristics:

1. Concentration of calcium carbonate decreases progressively downward in the deposit below a carbonate maximum that lies near the top of the calcareous zone.

2. One, or several, morphologic characteristics are present. Where more than one of these characteristics are present they are zoned horizontally, usually with more advanced stages of development near the top of the calcareous zone.

3. At many places where the deposit underlies a geomorphic surface its morphology is relatively persistent and can be traced laterally over extensive areas--possibly tens to hundreds of

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square kilometers.

4. In keeping with the morphologic characteristics, the pedogenic calcium carbonate content of a soil is generally comparable when traced laterally. Some changes occur as climatic or geologic provinces are transected and as the soil has been affected by differential stripping.

5. Dry color of these deposits ranges from about 7.5YR 7/4 to 10YR 8/3. These colors are described in the literature as salmon pink or pink to white. The colors alone are not conclusive evidence of pedogenic origin but may be used in conjunction with other properties to determine the origin of calcrete.

Field relations and the geomorphic expression of calcretes vary with their origin. Pedogenic calcretes underlie extensive geomorphic surfaces that have been subject to soil-forming processes for long periods of time (fig. 10). Pervasive cementation may require less time to develop and occurs as cement in alluvium on piedmont slopes. Both types of these calcretes are usually resistant to erosion and may cap erosional remnants (fig. 10, 11, and 12). Where calcretes cap erosional remnants close examination of the morphology of the deposit is necessary to determine its origin.

The upper surface of plugged laminar calcic horizons is commonly undulatory. The depth of depressions on these surfaces varies but locally depressions may penetrate the calcic soil partly or completely. Some of these depressions are part of a drainage system and originate in local erosional channels; the others have interior drainage and are the

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Figure 10.—Aerial view of the Llano de Albuquerque surface looking
southwesterly from near Belen, New Mexico. Badlands topography in
the foreground dissects Quaternary beds of the upper part of the
Santa Fe Group (silt, sand, and gravel). The white band along the
margin of the surface is the relict Llano de Albuquerque calcic
soil. In the background are the Ladron Mountains (on the right)
and the Magdalena Mountains (on the left).
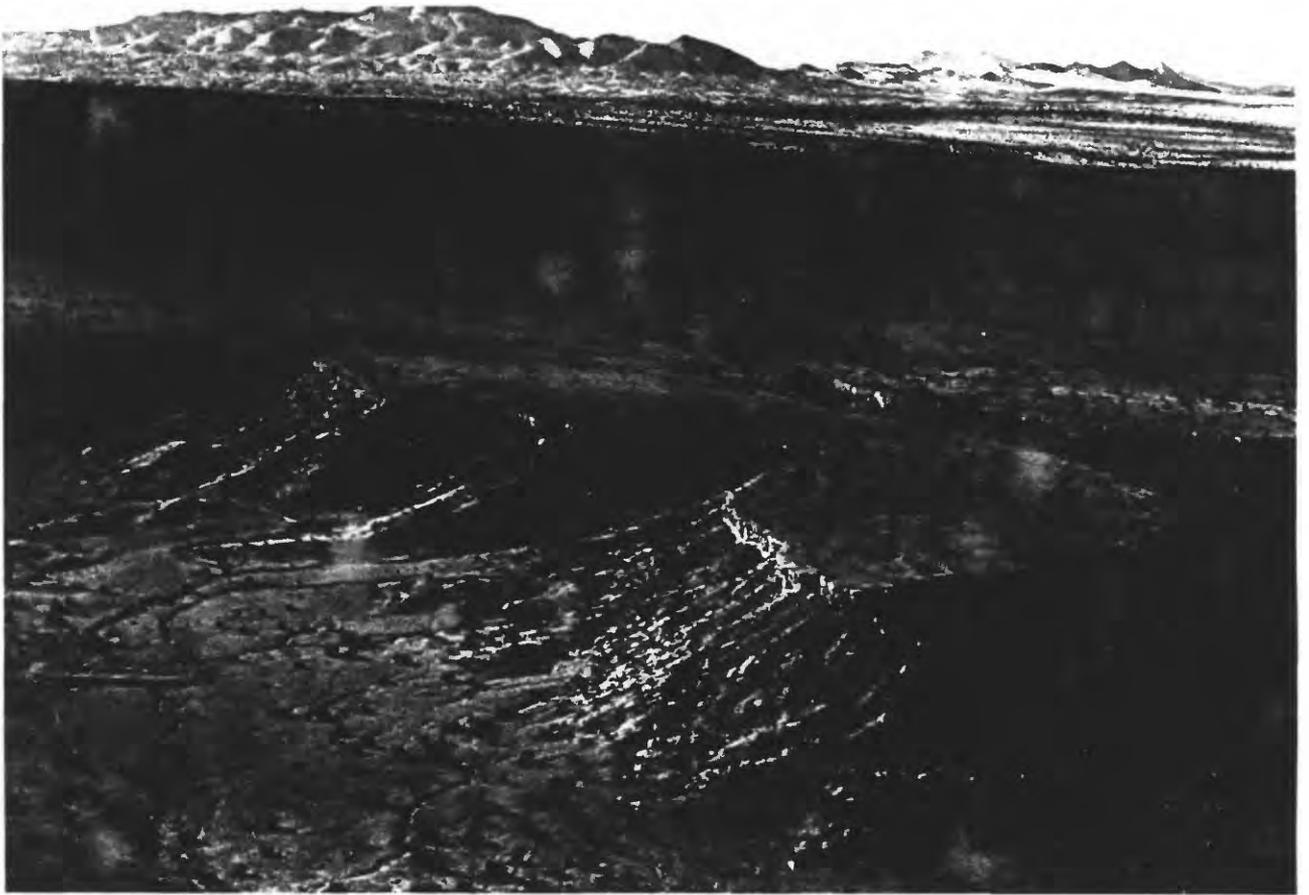
Figure 11.--Exhumed travertine-capped surface in La Jencia basin along the south side of Rio Salado, central New Mexico. The deposit underlying the surface grades from cemented alluvium at its base to relatively pure calcium carbonate near its top. The total deposit is as much as 20 m thick in places. The travertine surface is known to be exhumed because valley fill more than 70 m thick rests on it in places. This is an example of a geomorphic surface capped by a calcium carbonate cemented zone that is not genetically related to pedogenic calcrete.
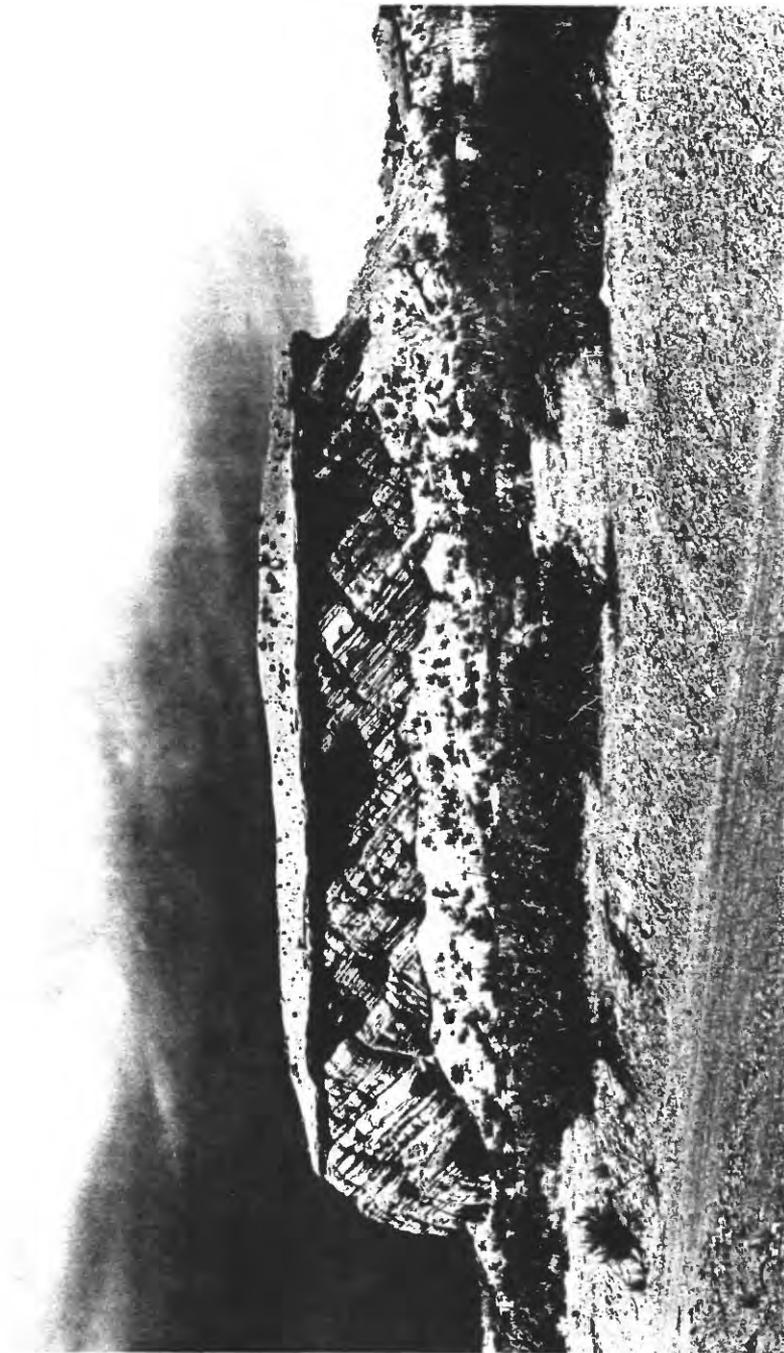
Figure 12.--Upper Pleistocene alluvial deposit (unit E of Machette, 1977) unconformably overlying older fanglomerates of the Popotosa Formation (Miocene; lower part of Santa Fe Group) near Socorro, New Mexico. The basal part of the alluvium is well-cemented with $CaCO_3$, and where the overlying alluvium is eroded, forms a pervasively cemented calcrete.

the result of root penetration into the calcic horizon.

Closed depressions on calcrete surfaces range from 5 m to more than a kilometer in diameter. These surficial features are called playas, dolines, and, in the northwestern Sahara, dayas (Clark and others, 1974). In the southwestern United States these depressions are most common on the Mescalero and Ogallala surfaces. They are circular to elliptical in plan and are partly filled with fine-grained sediments. These features have been formed by partial dissolution of the calcrete, probably by root growth (fig. 13). They are distinguished from collapse
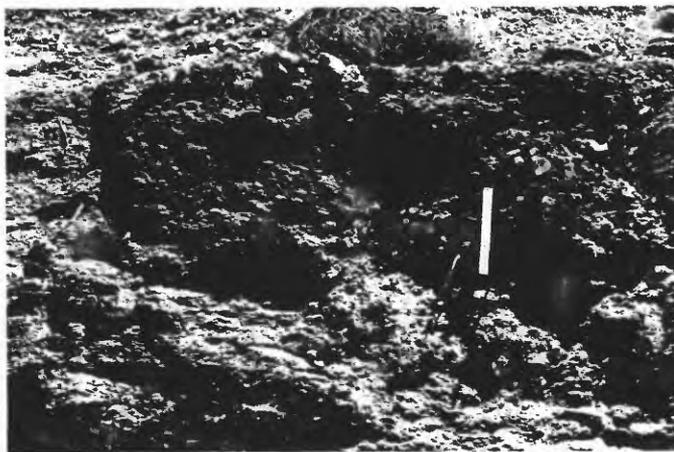
Figure 13.--Depression in the upper surface of the Mescalero pedogenic calcrete southeastern New Mexico, filled with rootlets of mesquite (Prosopis juliflora) and fine-grained sediments. The surface has been etched by mesquite growth. Thirty-cm-long ruler shown for scale.

sinks, the result of dissolution of underlying soluble deposits, on the basis of the association of collapse breccias with the latter features.

Alined swales are elongate depressions common in southeastern New Mexico on the surface of the Ogallala calcrete. They range from about 35 to 100 m wide and as much as 16 km long, and are usually less than 13 m deep. They are generally oriented about S. 60° E. and reflect orientations of ancient fields of sief dunes during latest Pliocene or early Pleistocene time (Price, 1958; Bachman, 1976). It is believed that the depressions represent interdune areas of more intensive plant growth where surface solution and deflation were dominant processes. Swales with this orientation are not present on middle Pleistocene surfaces in that area; therefore they must have originated in late Pliocene time.

Microscopically, advanced stages of calcic soils contain a higher proportion of micrite to microsparite or sparite. Detrital grains are not in contact with one another but are separated by carbonate cement and are generally well sorted in the upper horizons of relict calcic soils. This appears to be a reflection of the pedogenic processes. In pervasively cemented deposits, microscopically detrital debris is poorly sorted, not in contact, and sparite and microsparite are usually dominant over micrite. Laminae may be present on the upper surface or in fractures of the deposit and solution-faceted pebbles are common in many layers within the deposit.

Spring deposits and travertine are usually characterized by megascopic, irregularly shaped pores, but these porous zones may grade laterally into more densely cemented alluvial deposits near their margins. This gradation may be the result of contamination by the alluvial detritus. In pure travertines detrital grains are generally

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rare; although the basal part of a travertine deposit may cement coarse alluvial deposits. This type of cementation is indistinguishable from other types of pervasively cemented deposits where the overlying travertine has been stripped by erosion or completely dispersed in alluvial debris. The contribution of algae to the deposition of travertine has not been studied during this work.

Origin of calcic soils and calcretes

Major theories of the origin of calcrete have been reviewed by Goudie (1973) and these theories are outlined only briefly here. There are many types of calcrete and a single origin cannot be assigned to all types. Therefore, we here discuss mainly our own observations and interpretations of the origin and morphologic evolution of pedogenic calcretes and pervasively cemented deposits.

Pomel (1890, p. 193) observed the extensive calcareous and gypsiferous crusts in surficial deposits in North Africa. He stated that these hard crusts are probably forming at present and that they are the result of the evaporation of saline solutions that have risen to the surface by capillarity.

In the southwestern United States, a similar theory involving the "upward capillary flow of calcareous water, induced by constant and rapid evaporation at the surface in a comparatively rainless region" (Blake, 1902, p. 225) has been widely accepted for the origin of "caliche."

Capillarity is probably a local, adjunct process in the formation of some pedogenic calcretes. However, the major soil process is the leaching of carbonates from upper soil horizons by downward percolating water. Carbonates precipitate in illuvial horizons (near the base of the B horizon and in the C horizon) as soil water evaporates. In advanced stages of soil development, carbonate may engulf both underlying and overlying parent material. In many areas we have observed pedogenic calcretes that are tens to hundreds of meters above the present water table and the upward transport of carbonate solutions

from the water table to the calcrete zone by capillarity is improbable. Gile and others (1966, 1971) state that capillarity and ground-water flow have never played a significant role in [Quaternary] calcic soil genesis in the Las Cruces, New Mexico, area.

The soil horizons in arid to semiarid regions are commonly dry and powdery except after rainstorms. Trenches in soils in these regions 3 to 4 days after intense rainstorms of short duration show soil moisture penetrating as much as 10 cm into the upper part of the Cca horizon. There is an abrupt interface between the soil moisture in the B and upper part of the C horizon and the dry, powdery carbonate in the underlying Cca horizon. In early stages of calcic soil formation, before K horizons are plugged to downward moving solutions, the Cca horizon may mark the mean depth of moisture penetration during formation of those horizons.

The formation of calcic soils and pedogenic calcrete is dependent on many factors (Jenny, 1941) including climate, source of carbonates, and tectonic stability. Precipitation and evaporation vary from one region to another within semiarid climates and control soil moisture distribution. The season during which rain falls (that is, warm or cool), rate of evaporation, and the mean annual temperature are major factors in calcic soil formation. In addition, calcic soils are directly related to the texture and calcium carbonate content of parent materials (Birkeland, 1974, p. 232-233). Extreme desert climates are not conducive to carbonate accumulation because there must be sufficient rainfall for carbonate-bearing soil solutions to infiltrate soil horizons, however, evaporation must exceed precipitation for these

solutions to precipitate carbonate in the vadose zone. At the other extreme too much precipitation leaches carbonates from the soil profile.

Many writers have attempted to relate the distribution of calcrete to climate (Goudie, 1973, p. 96-111), however, both the wide variety of deposits that have been included in calcrete, caliche, or croute and the varying age of these deposits suggest that many of the postulated relationships between modern climate and calcrete distribution may be deceptive. Major climatic changes have occurred over large areas during Quaternary time and many of the calcretes present today may have formed in response to paleoclimates (Watts, 1976).

In east-central New Mexico, for example, there is abundant evidence that numerous ponds and lakes were present in topographic depressions during the interval about 18,000 to 13,000 yrs B.P. (Leonard and Frye, 1975). These ponds and lakes "were maintained by increased precipitation and/or decreased evaporative loss resulting from lowered annual mean temperatures, or more likely by suppression of the summer extreme high temperatures relative to those prevailing today" (Leonard and Frye, 1975, p. 30). At present mean annual rainfall in this region is about 320 mm. Potential evaporation data is not available for eastern New Mexico but in the vicinity of Las Cruces it averages about 2,300 mm per year. (New Mexico State Engineer, 1956a, 1956b). Mean annual temperature in this area averages about 15 to $16^{\circ}C$ (table 1). Calcretes are widespread in this area and occur on surfaces of late Pliocene to late Pleistocene age. Calcic soils are presumed to be forming in east-central New Mexico presently and pervasive cementation and case hardening are known to be occurring today. Since Pliocene time

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Table 1.--Mean annual precipitation and mean annual temperature
in four areas of New Mexico

[Number of recorded years shown in parentheses. Las Cruces data from
the Jornada Experimental Station; other data from New Mexico State
Engineer, 1956a, 1956b.]

Locality--------------	Las Cruces	Albuquerque	Roswell	Carlsbad
Mean annual precipi- tation in mm-------	225	204.5	354.6	328.4
No. years precipi- tation recorded----	38	75	77	54
Mean annual temperature in degrees C----------	15.04	13.08	15.26	17.22
No. years temperature recorded------------	29	62	59	60

there may have been arid intervals during which calcrete did not form,
but there is no evidence that the region has ever been so humid that the
calcrete was completely leached out of the soil.

Similarly, in parts of the Sahara Desert large freshwater lakes
were present at least from 22,000 to about 3,500 yrs ago (Faure, 1966).
The water budget necessary to maintain such lakes would have been
conducive to the formation of pedogenic calcrete. Ancient calcretes are
present in the central Sahara yet pedogenic calcretes do not appear to
be forming today (Meckelein, 1959). On the Arabian Peninsula erosional
remnants of calcrete underlie Holocene deposits (D. L.Schmidt, written
commun., 1977). "The deposit indicates that the area received more
rainfall in the recent past, when the caliche formed, than at present."
There is no evidence that "caliche is forming in this area under the

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arid climatic cycle now prevailing over the Arabian Peninsula" (Hadley, 1976, p. 23). In eastern Saudi Arabia landforms and calcretes formed during "marked and repeated climatic alternations between wet and dry throughout the Pleistocene" (Chapman, 1974, p. 129).

The only reliable correlations between the present climatic regime and the formation of calcrete are in areas where calcrete is presently forming or is known to have formed during historic time. For example, during the war years 1939-1945 agricultural fields in Algeria were idle. After hostilities had ceased and farming was resumed it was found that a thin, but hard, crust had formed (Pouquet, 1966, p. 218). In this case the type of crust was not indicated and its presence may be related more to precipitation from shallow ground water than to pedogenic processes. Other examples are cited by Goudie (1973, p. 107-111) and he summarizes this problem by stating that "the fact that many calcretes are fossil forms suggests they formed under conditions different from those represented by present-day climatic indices, though the widespread nature of the 500 mm isohyet-humid boundary of calcrete relationship is striking" (Goudie, 1973, p. 105).

Gile (1975, 1977) has discussed the morphology of Holocene soils in arid and semiarid climates of southern New Mexico. He observed that the soil moisture in an arid basin (annual precipitation about 200 mm) during Holocene time has been sufficient to move carbonate from the surface into the soil, forming a surficial noncalcareous zone with a carbonate horizon beneath it. The thickness of the upper noncalcareous zone increases towards the mountains where there is an increase in precipitation (from about 250 to 400 mm precipitation per year near the

mountains). This suggests a direct correlation between the depth of the noncalcareous zone of a pedogenic calcrete and precipitation.

Pervasive cementation of alluvial deposits results in massive layers of calcium carbonate that may be dense and very hard under the hammer. The carbonate cement is relatively uniform throughout and is distributed along original bedding planes. These deposits commonly lack the horizontal zonation present in calcic soils. Pervasive cementation is common near the base of fan and channel trench deposits on piedmont slopes.

We believe that most of the carbonate in pervasively cemented deposits is carried by ground water or surface runoff. Dissolved calcium carbonate, derived from limestone or dolomite bedrock, is carried down piedmont slopes and precipitates in porous alluvium in the vadose zone as evaporation occurs.

We have observed this process in the southern Sacramento Mountains of New Mexico. During spring the runoff flows over carbonate bedrock of Paleozoic age. Large amounts of carbonate are dissolved by these surface waters, and as the small streamlets evaporate, carbonate precipitates along channels in fan deposits. Although the surface water appears to sink into the alluvial sand, the last 4 or 5 m of surface flow contains a translucent flocculant of calcium carbonate. These flocculated masses are elongate and as much as 1 to 2 cm in length. They dissolve with violent effervescence with the application of weak hydrochloric acid.

Along the terminus of these streamlets is a spongy mass of algae and calcium carbonate that may range from 1 to 3 m in width. At the

outer borders, the mass grades from a weakly cemented crust to a hard cement deposited during previous seasons of runoff. The result is a massive, structureless body of cemented deposits that armors the bottom of an arroyo.

Examples of pervasive cementation occur in the extensive fan deposits surrounding the Whetstone and Tombstone Mountains in southern Arizona and in the fan deposits south and west of Las Vegas, Nevada (fig. 1). The latter have been called petrocalcic horizons by Cooley and others (1973). Arroyo deposits are firmly cemented in places along Penasco Creek and in the vicinity of Roswell, New Mexico. The Penasco flows through limestone terrain of late Paleozoic age.

Many surficial carbonate deposits of the southwestern United States that have been called "caliche" are travertine and lacustrine deposits. The origin of some other "caliche" is less clear but many of these enigmatic "caliche" deposits are associated with fault zones and may be related to ground-water movement.

Origin of carbonate in calcic soils and calcretes

It is apparent that the carbonates in calcic soils accumulate as a result of the movement of soil solutions. The ultimate origin of the carbonate may be diverse and in many deposits is problematical. Thick relict calcretes exposed at the surface or overlain by a relatively thin cover of eolian sand or weakly developed soils present a specific problem. Volumetrically, it is impossible to derive all the calcium carbonate in the relict calcic soil from the overlying sediment by normal processes of weathering (see calculations by Gardner, 1972).

It is improbable that such widespread calcic soils as those underlying the Llano de Albuquerque surface (fig. 10) were deposited by capillary solutions rising from the ground-water table. This soil is several hundred meters above the present water table in most places. Carbonate content in the profile in this calcrete decreases downward and the source of the carbonate must be sought in proximity to, and overlying, the calcic soil.

The relict calcic soil on the Llano de Albuquerque has from 100 to 125 g of calcium carbonate in a 1-cm^2 column through profiles that range from about 1.5 to 2.5 m in thickness. The overlying windblown sand is rarely over 5 to 10 m thick and averages 2 to 3 percent calcium carbonate and 1.5 to 1.6.g/cm^3 in bulk density. To derive the Llano de Albuquerque calcite from stationary horizons in the overlying sand would require complete leaching of all calcium carbonate from a sandpile 20 to 42 m thick.

Brown (1956) postulated that pedogenic calcretes on the High Plains in western Texas were deposited in an aggrading eolian environment. He

stated that "the wind and rain bring in all the materials that form the soil and its associated caliche and deposit these materials on the soil surface" (Brown, 1956, p. 14). Variations on this hypothesis have since been proposed by many writers (Gile, 1967; Ruhe, 1967; Gardner, 1972; Lattman, 1973).

Our observations are in agreement with this hypothesis. We believe that much of the calcium carbonate in calcic soils is derived from windblown sand, dust, and rainwater. Small quantities of calcium carbonate are leached from the sand during wet seasons and are deposited in the underlying soil horizons by downward percolating solutions. During dry seasons the sand is reworked and moved about on the surface and a new source of calcium is constantly introduced into the region. Aerosolic dust (Syers and others, 1969) provides a more calcareous but less voluminous supply of Ca^{++} to the soil. Rainwater itself is also a source for calcium carbonate. The calcium content of rain is variable over the United States but in the arid southwest the Ca^{++} in rain reaches concentrations of more than 4 mg/l (Junge and Werby, 1958). With time this concentration of soluble calcium would make a substantial contribution to the soil. Gardner (1972) calculated that more than one-quarter of the calcium in the Mormon Mesa "caliche" (calcic soil) could have been derived from rainwater sources.

Parent materials do provide some calcium carbonate to calcretes. This is observable particularly in alluvial deposits derived from calcareous bedrock. Solution faceting of carbonate pebbles releases soluble carbonates to surface water and supplies on important source of cement. However, most of the carbonate in pedogenic calcretes which

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underlie extensive geomorphic surfaces is probably derived from eolian

sand, aerosolic dust, and rainwater.

Morphology of calcic soils and pedogenic calcrete

A developmental sequence as well as physical characteristics of pedogenic carbonate in soils of semiarid regions, has been described by Gile (1961). We have used much of his terminology in the field to define physical characteristics. The "K horizon" was later defined "for soil horizons of prominent carbonate accumulation" (Gile and others, 1965). The K horizon has a diagnostic fabric where "fine-grained authigenic carbonate occurs as an essentially continuous medium [K-fabric]. It coats or engulfs, and commonly separates and cements skeletal pebbles, sand, and silt grains" (Gile and others, 1965, p. 74). Juncture of carbonate coatings or of cement is sufficient to define the K-fabric.

We have found the concept of the "K-horizon" useful in the description of soils where carbonate is a prominent constituent in spite of the fact that the K horizon may not always be relegated to a specific position in the profile in the sense of the A, B, and C horizons. Based on carbonate content and morphology, the K horizon includes subhorizons that may be qualified by standard soil symbols for layers and subordinate characteristics (that is, K23m horizon). In regions such as the southwestern United States where calcic soils are widespread, the use of this soil nomenclature is invaluable both in separating the carbonate horizon from other horizons and in ranking calcic soil horizon development of calcic soil horizons.

Gile and others (1966) have defined four stages that show the relative morphologic sequence of carbonate deposition in calcic soils. They summarized the stages in tabular form (table 2). The concept of

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Table 2.--Stages of the morphogenetic sequence of carbonate

deposition in calcic soils

[Modified from Gile and others, 1966, p. 348, table 1]

| Stage | Diagnostic carbonate morphology | |
	Gravelly soils	Nongravelly soils
I	Thin, discontinuous pebble coatings.	Few filaments or faint coatings.
II	Continuous pebble coatings, some interpebble fillings.	Few to common nodules.
III	Many interpebble fillings.	Many nodules and internodular fillings.
IV	Laminar horizon overlying plugged horizon. (Thickened laminar and plugged horizons.)	(Increasing carbonate impregnation.) Laminar horizon overlying plugged horizon.

Table 3.--Stages in the morphogenetic sequence of carbonate

deposition used in this report

Stage	Diagnostic carbonate morphology
I	Filaments or faint coatings. Thin, discontinuous coatings on lower surface of pebbles.
II	Firm carbonate nodules few to common but isolated from one another. Matrix may include friable interstitial accumulations of carbonate. Pebble coatings continuous.
III	Coalesced nodules in disseminated carbonate matrix.
IV	Platy, massive indurated matrix. Relict nodules may be visible in places. Plugged. May have weak incipient laminae in upper surface. Case hardening common on vertical exposures.
V	Platy to tabular, dense and firmly cemented. Well developed laminar layer on upper surface. May have scattered incipient pisoliths in laminar zone. Case hardening common.
VI	Massive, multilaminar and brecciated, with pisoliths common. Case hardening common.

these morphogenetic stages is useful, but by combining textural and structural features with depositional stages we have recognized at least six stages in a morphological sequence (table 3). These are more easily recognized in nongravelly soils but the later stages in particular may be recognized in either gravelly or nongravelly soils.

There are two major differences between our classification and that of Gile and others (1966). First, our stages I through V are generally equivalent to their stages I through IV except that we have introduced the factor of structure. This factor creates an additional morphogenetic stage that refines the nature of cementation. Secondly, we recognize the pisolitic stage VI as a late part of the natural sequence in the formation of pedogenic calcrete.

The sequence of development of these stages is relatively clear through stage IV and into stage V. All these stages are gradational and readily observed in the field. The recognition of stage VI as part of this sequence has required more extensive observation over broad areas of the southwestern United States where older (early Pleistocene to Pliocene) calcic soils are preserved.

Stages I through III (fig. 14) are formed by downward moving carbonate soil solutions. Deposition of the carbonate occurs by evaporation near the mean annual depth of soil-water penetration and carbonate content increases with time. Nodules form along vertical fractures (figs. 14, 15) at junctures where permeability in the parent material increases. Carbonate deposition builds upward on the soil as permeability of the horizon decreases during successive waves of cementation.

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Figure 14.--Calcium carbonate morphology in two soils near
Las Cruces New Mexico. The upper soil is developed in
Isaacks' Ranch alluvium and has stage II carbonate
which forms dispersed nodules. The lower soil, which
has stage II (in the buried B horizon) and stage III
carbonate, is developed in the Jornada II alluvium.
Tip of mechanical pencil, 15 cm in length, marks top
of buried B horizon.

Figure 15.--Carbonate distribution in a sandy clay.
Nodules of calcium carbonate occur as isolated masses
within the soil, while vein-filling carbonate follows
former root channels and fractures.

Calcic soils may form on bedrock if the parent material is permeable to soil waters. At many places, Pliocene and younger soils are cut across bedrock in southeastern New Mexico. During early stages of calcic soil formation on sandstones or shales (fig. 16) its distribution follows rock structures; whereas, in later stages it engulfs rock structures.

With the formation of stage IV the calcareous horizon is plugged to downward percolating solutions and deposition occurs in remaining pores and fractures. At this stage deposition is upward, parts of the overlying B horizon are engulfed, and soil solutions flow for short distances laterally on the upper surface of the K-horizon. As soil moisture evaporates laminae are formed. During this stage all vestiges of nodules are lost in the upper part of the profile and the carbonate develops a relatively homogeneous texture and platy to tabular structure (fig. 2). Sand grains and pebbles are common in the matrix but carbonate deposition expands the distance between grains. Detrital grains appear to "float" in a carbonate matrix.

Stage V is typified by dense and firm cementation, platy to tabular structures, and laminae on the surface. A K1 horizon is rarely seen in stage V development in the southwestern United States inasmuch as the surface of the soil is unconformable. The K21m horizons of the Mescalero and La Mesa soils in southern New Mexico are examples of well developed stage V. Where stage V is developed, horizons below the K21m are progressively less well developed and the K2m horizon may be a stage IV in its lower part, and the K3m and K3 horizons may have characteristics of stage III, or even stage II.

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Figure 16.--Mescalero pedogenic calcrete on red sandstone
of Triassic age in southeastern New Mexico. Soil
carbonate follows bedding and joint planes; the
resultant soil structures are largely controlled by
the parent material.

At many places stage VI calcrete bears little resemblance to earlier stages of pedogenic calcretes. Stage VI is massive, multilaminar, and well cemented. Abundant pisoliths are the distinguishing characteristic of this stage. In the southwestern United States stage VI calcic soils are most prominent as the "caprock" of the Ogallala Formation on the High Plains of New Mexico and on Mormon Mesa in southern Nevada.

The origin of pisoliths and the progressive development from stage V to stage VI is exhibited on the upper surface of stage VI calcic soils. After the soil is completely plugged to freely downward moving solutions, subsequent solutions move laterally on the surface of a calcic horizon or follow fractures within the horizon. The carbonate of the calcic horizon is dissolved by weak carbonic acid solutions and is redeposited as laminar layers on the surface of the calcic horizon and in fractures as a result of evaporation or evapotranspiration.

Alternate wetting and drying of plugged and laminar calcic horizons results in swelling and cracking of the calcrete (Gile, 1961). Where exposed to surface weathering, a platy structure is formed that fractures into prisms, polygons, and irregular fragments of calcrete that litter the surface (fig. 17). These fragments may be partly dissolved and $CaCO_3$ is reprecipitated as a cement that engulfs fragments lower in the profile or as coatings on individual fragments. Solution is most rapid on the angular and irregular edges of the fragments, tending to round the fragments. Where these rounded fragments are coated by calcium carbonate and recemented they appear as pisoliths in the calcrete groundmass.

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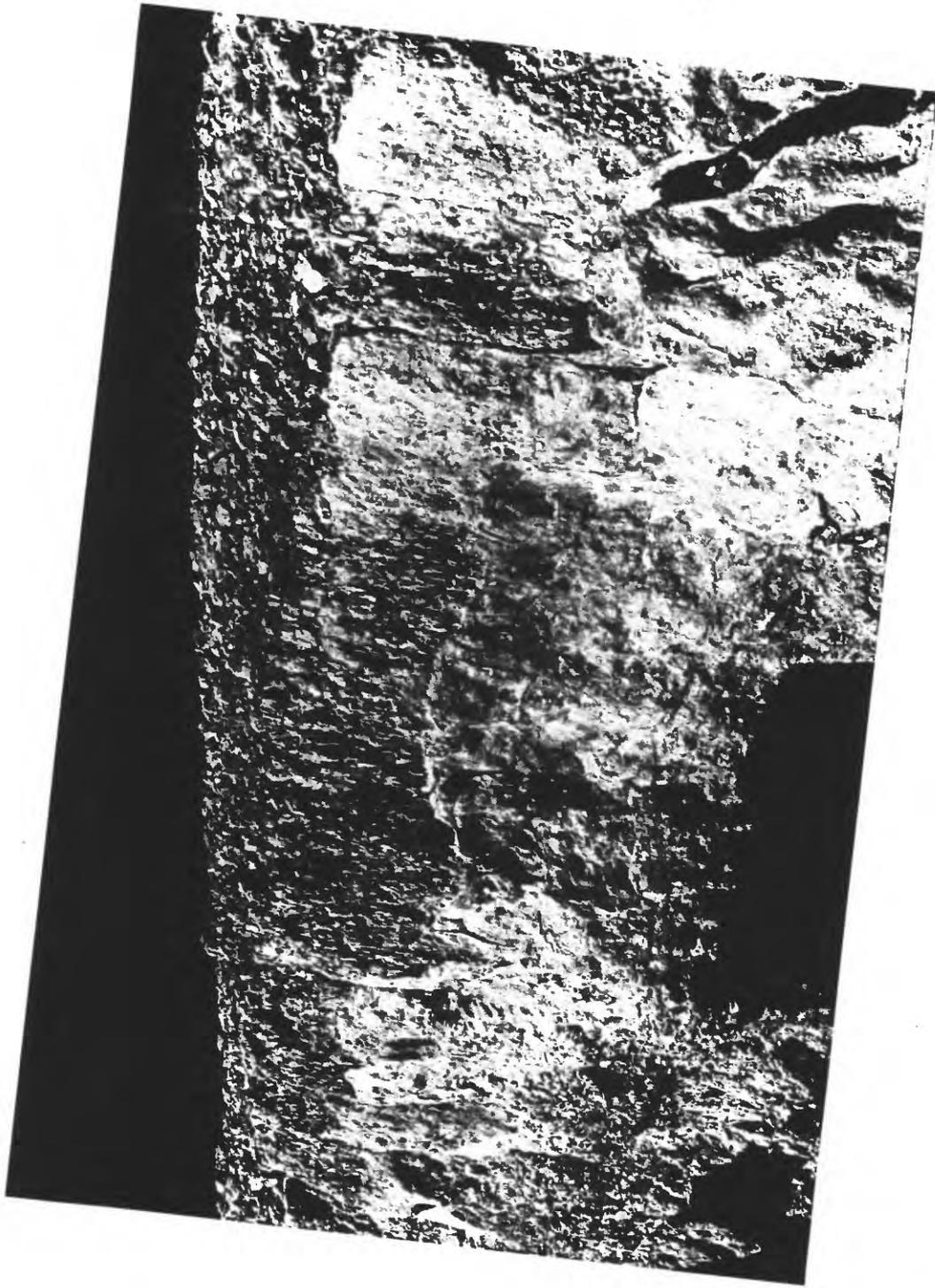
Figure 17.--Upper surface of calcrete, Mormon Mesa, Nevada, showing brecciated debris and pisoliths overlying strongly cemented calcrete. Brecciated horizon ranges from about 15 to 30 cm thick. Case hardening prominent on lower part of these exposures.

Pisoliths that are a complex aggregate of fragments of former pisoliths can be found at Mormon Mesa and on the "caprock" of the Ogallala Formation of the High Plains. These exhibit many generations of fracturing, partial solution, and recementation. Pisolitic structures in the High Plains caprock may be as much as 10 cm in diameter. Some are coated with an iron-manganese-clay(?) stain which may be analagous to the desert varnish that develops on desert pavement (Potter and Rossman, 1977).

Geographic and stratigraphic distribution of calcretes

Calcretes of various types are well developed in many semiarid regions of the world. The best known are in the High Plains region of the United States, Argentina, the Kalahari of South Africa, extensive areas in North Africa, and in adjacent Mediterranean countries. Goudie (1971) has published a detailed regional bibliography of calcretes.

This study has concentrated on calcretes in the southwestern United States where secondary carbonate deposits of many types are known as "caliche." We have attempted to differentiate the various types of deposits by physical characteristics, field occurrences, and origin. The study of field relations of calcretes has resulted in many observations on geographic and physiographic distribution. In this region the major factors that appear to control the distribution of calcretes are climate, source and abundance of carbonate, and relative long-term erosional and tectonic stability.

Calcretes are widespread on the High Plains and in the Pecos and Rio Grande Valleys in New Mexico. These calcretes are amenable to study because of their varying ages and field relations. Progressive stages of development of pedogenic calcretes are particularly well exposed in stream terraces, on coalesced alluvial fan surfaces, and as relict soils on older Pleistocene and Pliocene landforms.

The morphologic stage of calcrete development is a physical characteristic that may be used for correlation of soils and geomorphic surfaces only within local areas. These stages are not correlative on an interregional scale. The stage of development is dependent on local factors such as climate, availability of carbonates, and texture of

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parent materials. For example, in southeastern New Mexico where carbonate bedrock is widespread, morphologic stages of calcrete develop more rapidly than in central New Mexico where carbonate parent material is less abundant (fig. 18).

The oldest and best known calcrete in the southwestern United States is the "caprock" or "rim rock" underlying the Llano Estacado of the southern High Plains. This is a pisolitic pedogenic calcrete that also caps the Ogallala Formation of Miocene and Pliocene age from northwestern Kansas and eastern Colorado southward to southeastern New Mexico and western Texas (fig. 19) and has been called the Ogallala "climax soil" (Frye, 1970). The bulk of the soil formed after Ogallala deposition and before the extensive erosion that characterized Pleistocene time in that region. It probably developed a distinctive pisolitic texture before Pleistocene time inasmuch as calcrete clasts with this pisolitic texture are found in Pleistocene deposits far from present exposures (Bachman, 1976; Hawley and others, 1976). On the basis of a K-Ar dated basalt that appears to lie on this surface, the pisolitic calcrete may be more than 3.4±1.0 m.y. old (Trauger, 1973). We have examined this area and found that the pisolitic calcrete is present on both sides of the flow but field relations are not conclusive as to its stratigraphic position relative to the basalt flow.

The Ogallala calcrete averages at least 2 to 6 m thick and weathers to a prominent ledge. The upper 0.5 to 1.0 m of the soil is dense and pisolitic and grades downward into poorly cemented or friable sand at the base of the exposures.

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EPOCH	AGE, in m.y.	Upper Arkansas River Valley, Colorado:	Colorado Piedmont:	Albuquerque, New Mexico:	San Acacia, New Mexico:	Los Cruces, New Mexico:	Roswell-Carlsbad New Mexico:	Vidal Junction, California and Overton, Nevada:
PLIOCENE	1.8	III	Ogallala Formation	Ortiz-n.r.s. VI ?	2/ Rincon ?	Ogallala Formation VI	Mormon Mesa
		1/ Nussbaum Alluvium	Nussbaum Alluvium ?	V ?			2/ Q1a alluvium
PLEISTOCENE	1.0	1/ Nebraskan Alluvium	Rocky Flats Alluvium	?		V	
		1/ Kansan Alluvium	Verdos Alluvium IV	Llano de Albuquerque	Cliff	upper La Mesa / lower La Mesa	Mescalero	Q1b alluvium
	0.4							
		III 1/ Illinoian Alluvium	Slocum Alluvium III	Llano de Monzano / Tercero alto-n.r.s. III	Unit H / Unit G / Unit F	IV 2/ Tortugas	2/ Blackdom	Q2a alluvium
	0.2							
	0.1	1/ Bull Lake outwash II	Louviers Alluvium / younger loess	Segunda alto / Primero alto II	Unit E / Unit D	Picacho	2/ Orchard Park	Q2b alluvium
HOLOCENE	0.01	1/ Pinedale outwash I	Broadway Alluvium / Piney Creek Alluvium	young alluvium I	Unit C / Unit B	Isaacks' Ranch II / Fillmore I	Lakewood	Q3 alluvium / Q4 alluvium

Notes:
1/ Soil data interpreted from unpublished reports
2/ Soils developed on calcareous deposits
n.r.s. No relict soils

Source modifications:
- Colorado Piedmont: Modified from Scott (1963) and Machette and others (1976)
- Upper Arkansas River Valley: Scott (1975; written communication, 1977), and R R Shroba, written communication (1977)
- Albuquerque: Modified from Lambert (1966)
- San Acacia: Modified from Machette (1977) and Bachman and Machette (1977)
- Las Cruces: Modified from Gile and others (1971); Hawley and others (1976); Hawley, written communication (1977)
- Roswell-Carlsbad: Modified from Bachman (1976) and Hawley and others (1976)
- Vidal Junction: Modified from Gardner (1972) and Bull (1974)

Figure 18.--Correlation diagram for various alluviums or geomorphic surfaces corresponding maximum soil-carbonate development (stage) in New Mexico and adjacent areas. Ages of alluvium and surfaces based on published and unpublished data, soil data largely from this study.

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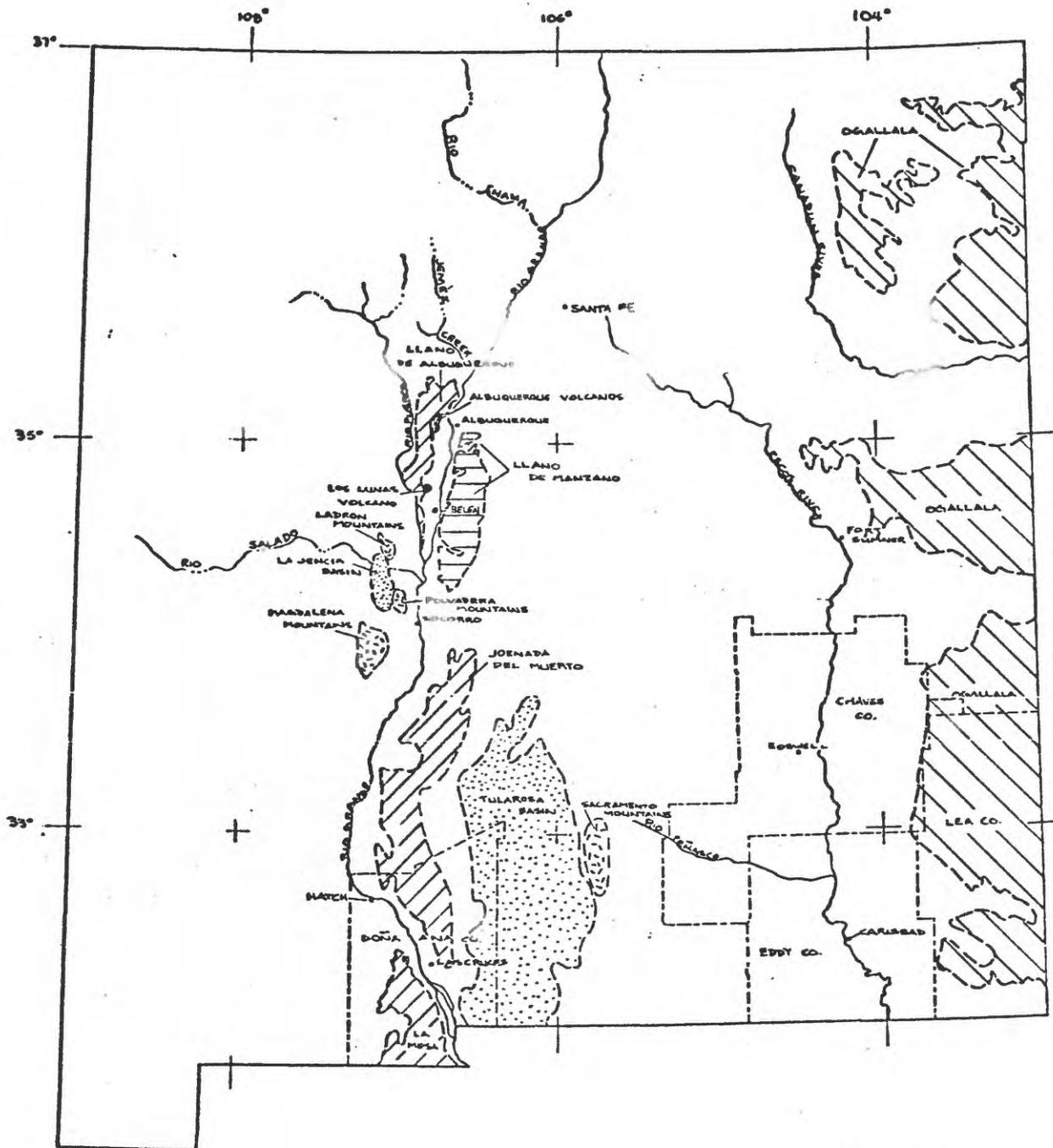
Figure 19.--Index map showing major geographic and geo-
logic features in New Mexico.

The next younger pedogenic calcrete is widely distributed in central and southern New Mexico and southwestern Texas and is considered to be about 500,000 yrs old. This calcrete is preserved over hundreds of square kilometers in southeastern and southern New Mexico, where it includes the "Mescalero caliche" of Bachman (1976) between the Ogalalla Formation and the Pecos River (fig. 19), and southwestern Texas. In central and southern New Mexico it is the relict calcic soil that underlies the Llano de Albuquerque, La Mesa, and parts of the Jornada del Muerto geomorphic surfaces.

The estimated age (500,000 yrs) of the most widespread of these constructional surfaces is based on K-Ar dates, tephrochronology, and fossils (Hawley and others, 1976; Bachman and Machette, 1977; Bachman and Mehnert, 1978). These surfaces have been traced or correlated within basins from localities where there is evidence for their age. A broad bracket for the age of the Llano de Albuquerque surface (fig. 10) is provided by mafic flows at Los Lunas Volcano that are interbedded with sediments of the Santa Fe Group that underlie the geomorphic surface. The Los Lunas flows range from about 1.1 to 1.3 m.y. old (Bachman and others, 1975). In addition, the Tsankawi Pumice Bed of the Bandelier Tuff (ca. 1.1 m.y. old) underlies this surface (Bachman and Mehnert, 1978). Basalt flows about 0.19 m.y. old (Bachman and others, 1975) unconformably overlie the surface to the north near Albuquerque, New Mexico.

The Llano de Albuquerque surface has been traced southward along the west side of the Rio Grande and correlated southeastward across the Rio Grande with the Jornada del Muerto surface. The Bishop ash (about

0.7 m.y. old, Izett and Naeser, 1976) rests in a swale on this surface at the Grama site (Seager and Hawley, 1973). Field relations are not conclusive at this locality but we believe that the ash fall is stratigraphically lower than the relict calcic soil of the Jornada del Muerto and the soil is younger.

The Jornada del Muerto surface is largely correlative with La Mesa surface and the Pearlette type O ash (about 0.6 m.y. old) underlies La Mesa soils (Hawley and others, 1976). In addition, bones and teeth of middle Pleistocene Equus and Cuvieronius occur within the sediments that underlie the La Mesa surface (Hawley and Kottlowski, 1969, p. 92).

This evidence suggests that a broad valley floor surface was formed considerably earlier than 200,000 yrs ago and somewhat less than 600,000 yrs ago. Based on the geomorphic relations between the younger basalt flows and the geomorphic surface (Llano de Albuquerque) we have therefore assumed that these major surfaces became stable about 500,000 yrs ago.

Petrography of calcretes

More than 100 thin sections of various types of calcrete, travertine, and petrocalcic horizons were examined during this study. Pedogenic calcretes of stage IV through VI received the most attention because the progressive development of these stages is not always clear in the field without having seen many subtle changes in exposures. The thin section study helped to substantiate field observations.

Generally the calcium carbonate in stages I through III is powdery and microcrystalline. Micritic texture is common in the matrix of later stages as cementation occurs. Microsparite is common in the laminar layers where commonly it alternates with micrite. Microsparite also occurs in minute veinlets where it may be accompanied by microscopic masses of opal. The microsparite crystallizes in minute vugs (fig. 20) and irregular crystalline texture is in contact with the opal.

Ooids that range from about 0.04 to 0.4 mm in diameter are common in the last three stages. Usually they have a faint nucleus of microsparite and a single layer rind of micrite. Some ooids have multiple nuclei (fig. 21) and occasionally some have a nucleus of detrital grains (fig. 22). Ooids may occur in clusters or individually but they appear to be most prevalent in the micritic cemented areas. Where present in laminar horizons they appear to be relict textures that have been isolated by microsparite.

Silt and sand grains are usually abundant in all pedogenic calcretes. These detrital grains commonly include quartz, sodic feldspar, plagioclase, biotite, and, occasionally, weathered amphiboles, that are well sorted. They average about 0.1 to 0.2 mm in diameter.
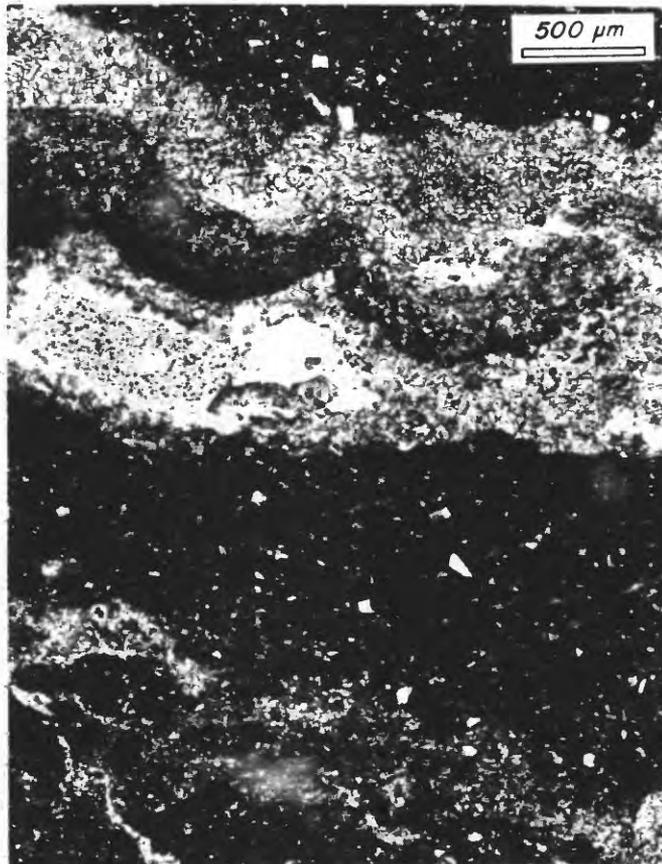
Figure 20.--Laminar zone near upper surface of pedogenic
calcrete (x32). Laminae alternate between layers of
microsparite and sparite (white layer) and micrite
(dark layer). Detrital grains are much more abundant
in micritic layers but opal may be present in the
sparry layer. 500 micron bar shown for scale.
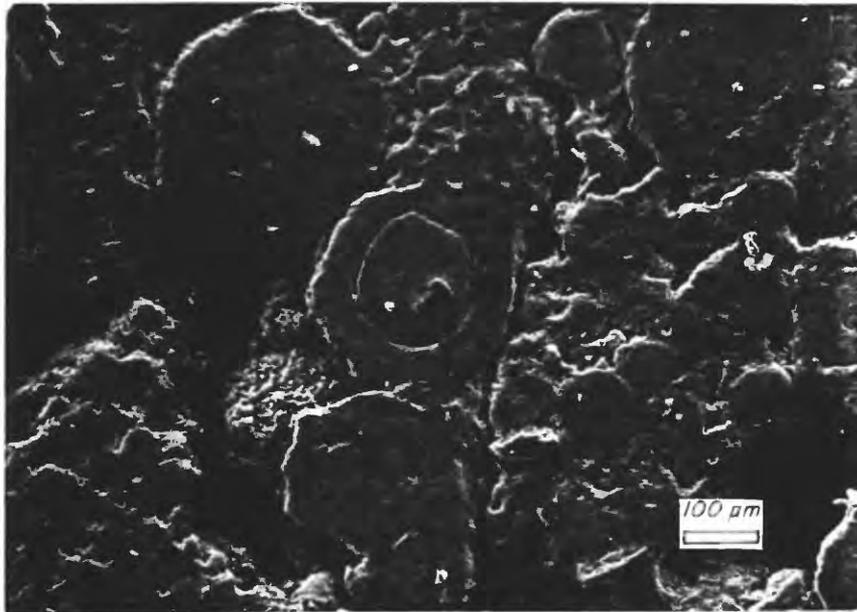
Figure 21.--Scanning electron microscope photograph of
     ooids showing two stages of growth and coalescing
     ooids (x280).   Quartz inclusion in center of ooid.
     Sample of calcrete from Estancia Basin, 3 km west of
     Willard, New Mexico. Sample was etched in 10 percent
     HCl solution. 100 micron bar shown for scale.
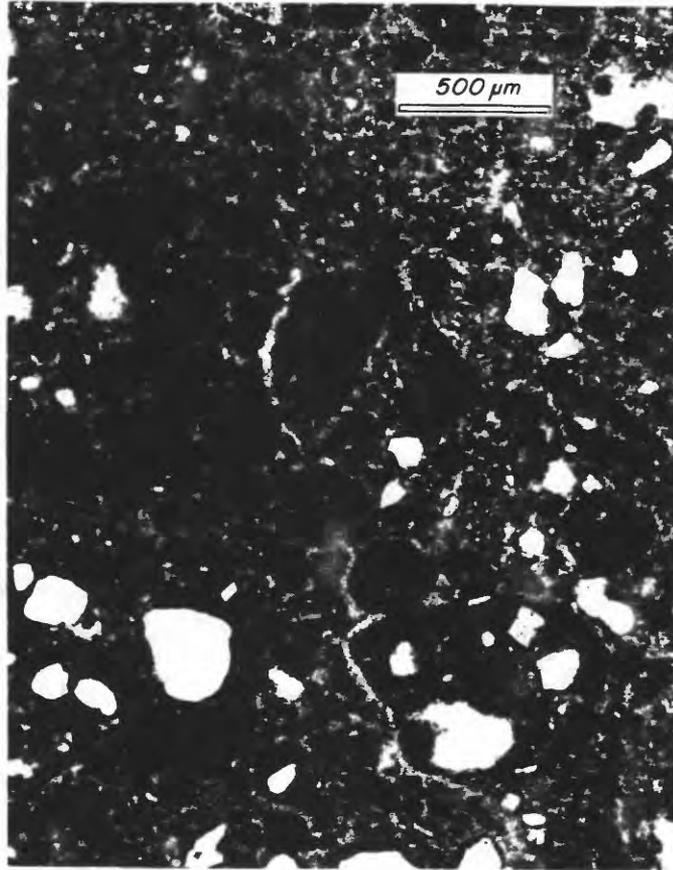
Figure 22.--Ooids in calcrete (x40). The large ooid in
    the lower right portion of the field has multiple
    nucleii of ooids and detrital grains. One grain of
    quartz in this ooid has been etched by the calcium
    carbonate. 500 micron bar shown for scale.

They are rarely in contact with one another and the distance between grains increases with increasing in cementation. At most stages of cementation the grains appear to "float" in the carbonate matrix. Detrital grains are sparse to rare in laminar zones but may be arranged in crude bands generally parallel and adjacent to the laminae (fig. 20). In other parts of the cemented matrix the detrital grains are randomly disbursed. Some silt grains may be etched by carbonate (fig. 23). The pisoliths characteristic of stage VI include rounded fragments of micrite with laminar rinds or fragments of former laminar zones that have been rounded and later enveloped by laminar rinds (fig. 24). Detrital grains may be concentrated in irregular zones in the matrix or they may be included in the nucleus of a micritic pisolith. They were not noted in the laminar rinds of pisoliths. Ooids may be present in the matrix of calcretes of stage VI but these ooids do not appear to be dimunitive pisoliths because of the difference in size and structure (fig. 25). Pisoliths vary greatly in size and an individual pisolith may record many stages of brecciation and recementation.

Most laminae in pisoliths have some yellowish-orange layers and are presumed to contain iron oxide compounds. At one locality on the Ogallala calcrete about 40 km east of Hagerman and at localities east of Fort Sumner an iron-manganese oxide stains the rim of many pisoliths (fig. 5).

"Vadose pisoliths" in Permian limestones in southeastern New Mexico described by Dunham (1972) are not closely comparable to the fabric of stage VI calcretes. Esteban (1976, p. 2052) enumerated some of these differences:

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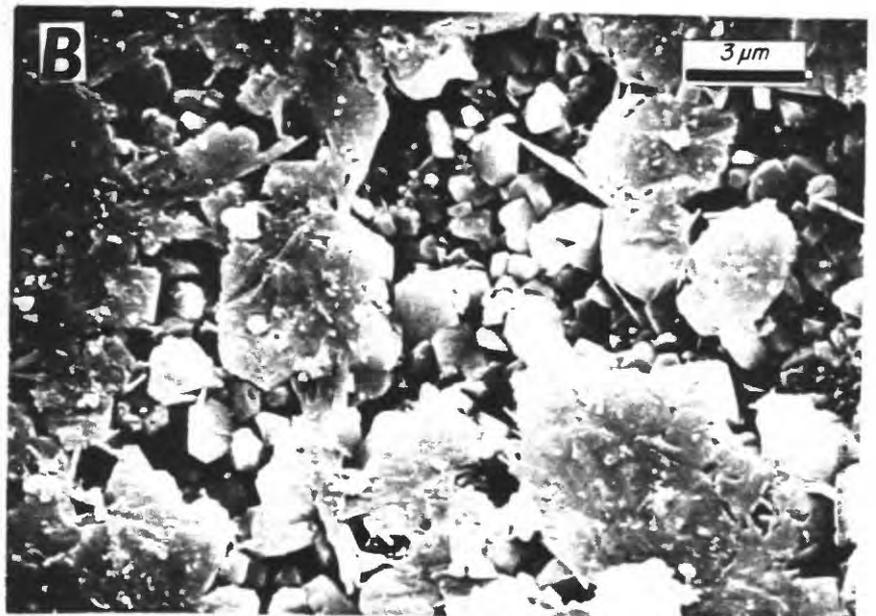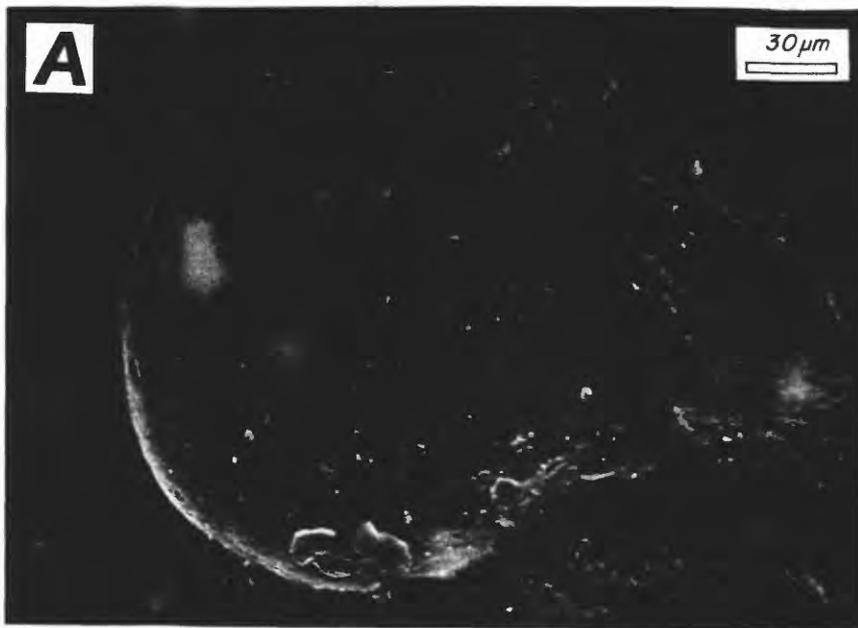
Figure 23.--A. SEM photographs of contact between sand grains (forms cavity) and soil matrix. 30 micron bar shown for scale. B. Fine-grained rhombs of calcite are plastered against former grain well. Matrix area still remains relatively porous, although the sample is from the K21m horizon of the Mormon Mesa calcic soil; 90 percent $CaCO_3$ and bulk density of 2.5 g/cm^3. Lath-shaped crystals are palygorskite, an authigenic Mg-Al silicate clay mineral. Three micron bar shown for scale.
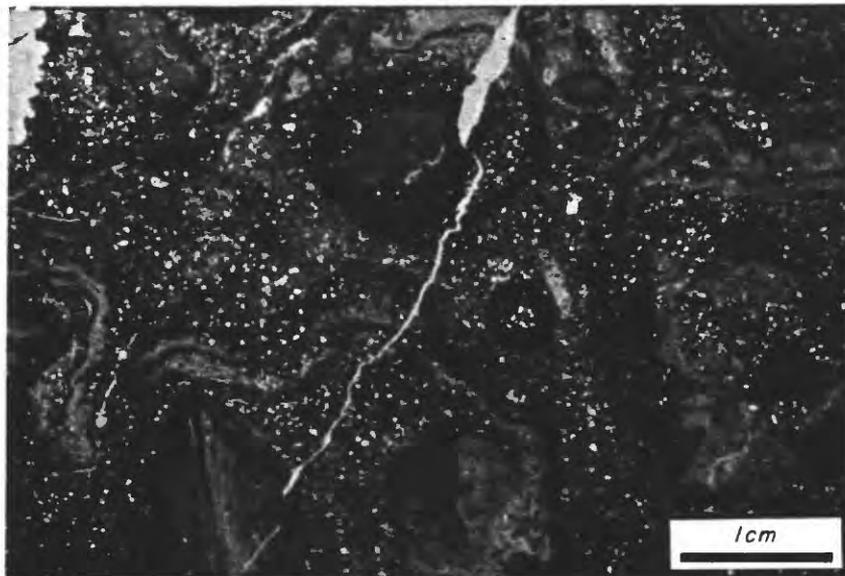
Figure 24.--Pisoliths cemented in (x2) Ogallala "caprock,"
    southeastern New Mexico.   Some pisoliths indicate
    multiple stages of growth; others retain the laminar
    structure of previous laminar layers.   The dark rinds
    on some pisoliths are films of manganese and iron
    compounds. One cm bar shown for scale.
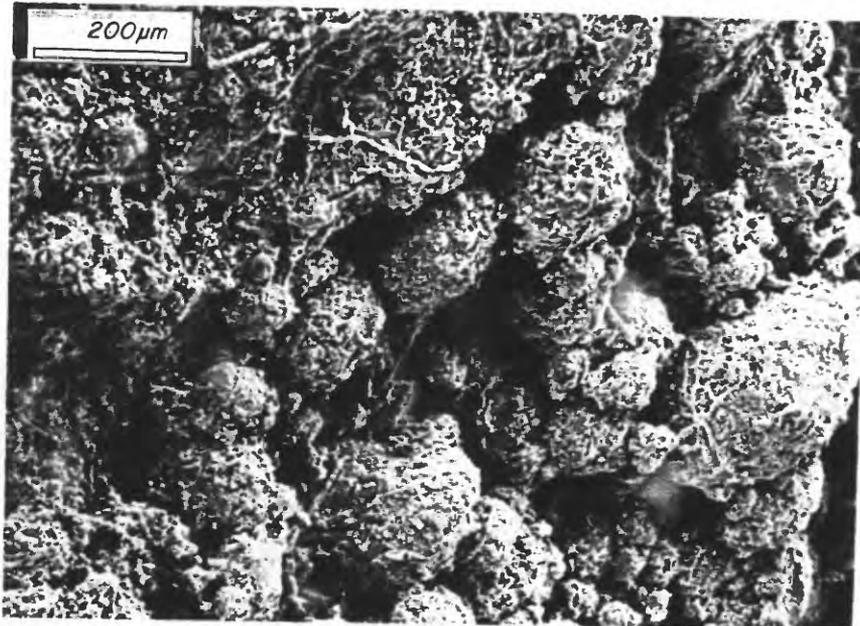
Figure 25.--Scanning electron microscope photograph of
ooids showing crystalline structure of surfaces
(x100).   Elongate, hairlike structures may be
palygorskite coated with carbonate crystals. Ooids
may contain trace amounts of Zn.   Sample is from
calcrete of unknown age in Estancia Basin, 3 km west
of Willard, New Mexico.   Sample was fractured and
cleaned in ultrasonic bath.   Two hundred micron bar
shown for scale.

1. Caliche [calcrete] pisoliths are micritic, indistinctly laminated, and rarely have more than five laminae. "Vadose pisoliths" may have 10 to 30 laminae that are distinct and composed of thin micrite layers alternating with microspar that have relics of radial-fibrous or bladed crystals.

. 2. There is an abundance of fine-grained calcareous material, mostly micrite with a clotted peloidal texture in calcretes. Micrite appears to be common only in pisolith nucleii and laminae in "vadose pisolite."

We agree with most of these observations by Esteban and we are particularly impressed by the more numerous laminae surrounding "vadose pisoliths" as compared with the few laminae that surround pisoliths in stage VI pedogenic calcretes.

The origin of pisoliths in calcretes is discussed in an earlier section. The origin of ooids in these continental deposits is more of an enigma. Ooids in South African calcretes are believed to have been formed by descending carbonate solutions that are checked in their descent and drawn upward by capillary action. Evaporation and soil suction cause precipitation of concentric coatings of carbonate mud around individual grains (Siesser, 1973).

Dunham (1971) has divided cementation of carbonates into an "even style" characterized by water-filled pore space in the phreatic zone and an "uneven style" characterizing pore space with immiscible fluid phases in the vadose zone. Furthermore, he related a "pore-rounding habit" to the vadose zone. Dunham (1971, p. 298) stated that "water for growth exists mainly in the corners of pore space, especially at grain

contacts, where water can be most tightly held by capillarity.
* * * The water-air interface (the meniscus) is the controlling element
in each of the several aspects of the uneven style of cementation." He
termed this "meniscus cement." It appears that during evaporation of
soil moisture the last phase would be a reduction of the moisture to
droplets of solution from which precipitation would occur. The ooids
could be deposited from the droplets.

Geologic significance of calcic soils and calcretes

There are many implications for the presence or absence of relict calcic soils in arid and semiarid regions. Some of these have direct application in the deciphering of tectonic, erosional, and climatic history.

The presence of a mature pedogenic calcrete underlying extensive geomorphic surfaces implies a delicate balance between a relatively stable tectonic and erosional terrain during the time required to form the calcrete. If conditions are favorable in a region for the formation of calcic soils and these soils are not present, evidence should be examined for tectonic instability or unusually rapid rates of erosion.

We have studied several areas where pedogenic calcretes underlying geomorphic surfaces have been displaced locally by faulting (Bachman and Machette, 1977; Machette, 1978). These include localities on the Llano de Albuquerque and Llano de Manzano surfaces in the central Rio Grande Valley (fig. 19). However, faulting at these localities has not been sufficient to trigger extensive erosion and the major surface has been preserved. Where the age of the calcic soil can be reasonably estimated, these soils provide a maximum limit for time of faulting.

In many areas in the southwestern United States only weak calcic soils and poorly developed B horizons are present along river terraces on some relatively large fans. A typical example is a young fan deposit along the eastern side of the Polvadera Mountains north of Socorro, New Mexico (fig. 19), the surface of which is graded to the flood plain of the present Rio Grande. Surfaces at the distal end of this fan are of two ages. The oldest surface has a weakly oxidized cambic B horizon

with a weak stage II horizon of carbonate accumulation. This soil is overlain by a weak desert pavement. Deposits of the younger surface bury the older surface. The younger surface also has desert pavement but the carbonate consists of stage I coatings on pebbles. These surfaces are thought to be latest Pleistocene and Holocene in age, respectively. The fan surface probably resulted from constructional deposition after very recent (Holocene) faulting along the mountain front.

The tectonic block on which this fan is deposited appears to be subsiding; near the mountain front calcic paleosols are presumed to be present in the subsurface. However, a similar surficial relationship could occur on a recently uplifted block. In this case paleosols would be stripped away by erosion and the youngest surface would be constructed on an erosional unconformity.

Horizons associated with calcic soils
and pedogenic calcretes

In soil nomenclature the "B" is a master horizon whose dominant features include illuvial concentrations of clay minerals, iron, or aluminum. Alteration obliterates original depositional structure and colors of the horizon are darker, stronger, or redder than overlying and underlying horizons. There is no diagnostic property by which all kinds of B horizons can be identified (Soil Survey Staff, 1975, p. 460).

Major types of B horizons in arid and semiarid regions of the southwest include the natric, cambic, and argillic horizons. The natric is a sodium-rich variety of argillic horizon that occurs generally in playa regions of the southwest and is not discussed here. However, the cambic and argillic horizons are common in association with calcic soils and K horizons.

In the southwest the cambic B horizon is generally characterized by loamy sand texture, reddish hue, and an indication that at least some carbonates have been removed. It is a weakly developed B horizon and can indicate the relative age of a geomorphic surface. In southern New Mexico some soils about 2,600 years old have not developed a cambic B horizon; whereas weak cambic B horizons are present in soils less than 5,000 years old (Gile and Grossman, 1968). This indicates that reddish hues and minor redistribution of carbonate (weak, stage I, calcic horizons) can form in an arid to semiarid environment within 5,000 years. Calcic horizons of stage II or greater development have not been documented in Holocene deposits in the southwestern United States.

The argillic B horizon is characterized by layer-lattice silicate

clays that have accumulated by illuviation (Soil Survey Staff, 1975, p. 19). Argillic soils form in calcic soils at a slower rate than in low carbonate soils probably because clay formation can be impeded by the presence of calcium carbonate and argillic horizons can be masked and engulfed by carbonate accumulations (Gile and Hawley, 1972).

Arguments about whether or not argillic horizons can develop in arid soils have been summarized by Dregne (1976, p. 180). Prerequisites for the formation and preservation of argillic horizons generally include stable landscapes relict from moist regimes and low concentrations of carbonates. Clay skins that form on sand grains and ped surfaces may be disturbed by repeated wetting and drying, adsorption of calcium carbonate, and root and faunal activity (Gile and Grossman, 1968). Therefore, argillic horizons in arid regions may have weakly developed clay skins even though the soil developed originally under more humid conditions.

The B horizon in arid regions does have potential as a means of determining the age of a soil but the process of illuviation and source of clay in B horizons is so poorly understood at present that much fundamental work remains to be done. We have not contributed to research on this subject except to note the presence of weakly developed B horizons, or their absence, in areas of recent tectonic activity. Tectonic stability is certainly a prerequisite for the development of strong B horizons in semiarid and arid regions.

Chemistry of calcic soils and calcretes

General chemical characteristics of calcretes

Goudie (1973) cites about 300 chemical analyses of calcretes from around the world, the averages of which help to characterize their general chemical attributes (table 4). Chemical analyses of pedogenic calcretes by Vanden Huevel (1966), Aristarain (1970), and Gardner (1972) indicate the importance of calcium carbonate relative to other constituents. Together these four analyses are representative of mature, well developed calcretes, typically developed on surfaces of middle Pleistocene to Pliocene age. Also included for comparison in table 4 is the average chemical analysis of 345 marine limestones (Clark, 1924). Calcium carbonate is the predominant constituent of calcretes, each of the analyses having similar CaO contents. Goudie (1973) cites maximum CaO values of 52.2 percent (South Africa) and 51.4 percent (India), and maximum $CaCO_3$ contents of 91.0 percent (Cyprus), 95.6 percent (North Africa), and 99.4 percent (Australia). The best developed pedogenic calcretes of the southwestern United States are on the La Mesa surface, near Las Cruces, New Mexico; the Mescalero surface and Ogallala Formation, in eastern New Mexico and western Texas, on the Reynosa surface, in southwestern Texas, and on the Mormon Mesa surface in southern Nevada. These calcretes consistently have maximum $CaCO_3$ contents that range from 75 to 85 percent.

Although $CaCO_3$ is the dominant constituent of calcretes, SiO_2, Al_2O_3, and Fe_2O_3 may also be present in substantial quantities, especially in young calcic soils. Marine limestones are low in clastic content, the noncarbonate fraction averaging about 8 percent by weight

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Table 4.—Chemical analyses of some calcretes

[Also shown, for comparison, is the average chemical composition of 345 limestones.]

Oxide	Goudie, 1973 Average of 300 calcretes	Vanden Huevel, 1966 K21m, La Mesa, N. Mex.	Gardner, 1972; 1a K2n, Mormon Mesa, Nev.	Aristarain, 1970; 2-3 K2m, Ogallala, Caprock, N. Mex.	Clark, 1924 Average of 345 limestones
CaO----------	42.62	44.2	[1]42.64	45.40	42.61
SiO2---------	12.30	16.9		13.20	5.19
MgO----------	3.05	.64	[1].51	.35	7.90
Al2O3--------	2.12	2.13		1.44	.81
Fe2O3(+FeO)--	2.03	.65	[1].43	.53	.54
K2O----------		.48	[1].67	.22	.33
Na2O---------			[1].19	.11	.05
TiO2---------		.09		.09	.06
CO2----------		[1]35.60		36.01	41.58
Other--------				1.94	1.02
Total-------		100.07		99.29	100.09
CaCO3-------	79.28	[1]77.5	[1]79.4	[1]81.8	[2]94.5

[1] Values calculated from data of respective authors.

[2] Value based on CO2 content; includes MgCO3.

(table 4), whereas the clastic content of calcic soils and pedogenic calcretes decrease as they become more calcareous (fig. 37). The SiO_2, Al_2O_3, and Fe_2O_3 contents (and other oxides, except MgO) reflect the parent material mineralogy in calcretes. Very little chemical change occurs in the noncalcareous, nonclay fraction of calcretes with age. Clay minerals within calcretes which can have a complex geochemical history of authigenesis will be discussed later in this report.

Most calcretes are characterized by calcium carbonate, although some exceptions are cited in the literature and these might better be considered as other types of duricrusts. Magnesium carbonate contents are generally low in calcretes; Goudie (1973) cites 3.05 percent MgO as the world mean for calcretes (table 4). High magnesium carbonate calcretes do occur, locally, in some areas and Goudie (1973) provides a review of their distribution and chemistry. These "dolocretes or magnesicretes," range from about 17 to 45 percent $MgCO_3$, although Goudie (1973, table 7) cites dolocretes in Kenya with 80 percent $MgCO_3$. Analyses of calcretes in North America (Gile, 1961, Vanden Heuvel, 1966; Aristarain, 1970; and Gardner, 1972) typically have MgO contents that range from 0.2 to 5 percent. The maximum MgO content within a calcrete usually occurs in association with attapulgite or sepiolite (Vanden Heuvel, 1966), Mg-Al silicate clay minerals. This aspect of calcrete chemistry, the association of MgO and genesis of clay minerals, is discussed in a later section.

Silica is the second most abundant element in calcretes. Silica is a chemical constituent of quartz, feldspar, and other framework grains, and can occur as authigenic opal and chalcedony, or as a silica gel.

Reeves (1976) discusses the geochemistry of silica in calcretes but may have overemphasized the importance of silica, at least on a regional basis. In cases where authigenic silica is an important cementing agent of calcretes, these may more appropriately be called silici-calcretes (Lamplugh, 1907), silcretes (Goudie, 1973), or duripans (Soil Survey Staff, 1976).

Less abundant oxides in calcretes are Al_2O_3, Fe_2O_3 (and FeO), MnO, K_2O, NaO, and TiO_2. These oxides represent, to a large degree, the parent material in which a calcrete formed. MnO may be important, locally, as an agent in forming black patinas on pisoliths and brecciated fragments in older calcretes such as those developed on the Ogallala Formation (fig. 5).

In general, most of the oxides mentioned above are more abundant in calcretes than limestones. Obvious exceptions are relatively pure travertines, which by definition (Goudie, 1973) might be included with calcretes, and impure arkosic or cherty limestones.

Calcretes may contain abundant water-soluble salts, such as gypsum, phosphates, organic matter, and occasionally iron sulfide or glauconite (Ward and others, 1970). Soluble salts are often found downwind from playas. Reeves and Suggs (1964) report as much as 30 percent gypsum in some caliches downwind from closed basins in Texas and Mexico. Weber (1973) describes gypsite caliche 2 m thick in central New Mexico, but our observations indicate that the gypsite is most likely lacustrine and has been modified (slightly calcified) by pedogenesis. Both of these gypsiferous "caliches" might better be called gypcretes, inasmuch as gypsum is their primary component. Lattman and Lauffenberger (1974)

proposed a biogenetic origin, bacterial reduction of $CaSO_4$ to $CaCO_3$, for gypcretes that occur in the Las Vegas Basin of southern Nevada. They are thick and well developed only where they overlie the gypsiferous Miocene and Pliocene Muddy Creek Formation, and in parts of southern Nevada their hypothesis may be valid. The Mormon Mesa "caliche" (Gardner, 1972) does not overlie gypsiferous beds as Lattman and Lauffenberger report (1974, p. 141), but rests on slightly calcareous to noncalcareous, fine- to medium-grained arkosic to quartzitic sands. The Mormon Mesa "caliche" is not associated with gypsum as are some immediately to the west in the Las Vegas Basin, and based on our fieldwork is known to have a pedogenic origin.

Calcic soils constitute a specific type of calcrete, those formed by pedogenic processes, and as such their chemistry is different from other types of calcretes. Likewise, the chemistry of calcic soils is unlike that of most other soils inasmuch as calcic soils are characterized by massive accumulations of calcium carbonate. As the carbonate accumulates detrital framework grains are physically forced apart, resulting in expansion of the soil. The original framework grains of a calcic soil may represent only 5 to 10 percent of the volume of a soil horizon.

Only two detailed investigations of pedogenic calcretes by Vanden Huevel (1966) and Aristarain (1970) are of particular interest to this study. These analyses are from areas in which we have studied and sampled many soils. We have supplemented data for Vanden Heuvel's work and made descriptions of soils that Aristarain studied to help interpret certain aspects of his chemical data.

Aristarain (1970) studied the chemisty of the "Ogallala caprock," a relict pedogenic calcrete formed on the Miocene and Pliocene Ogallala Formation, which is particularly well exposed in western Texas and eastern New Mexico. Using Barth's (1948) standard cell method (160 oxygen atoms per cell), as modified by Keller (1957), Aristarain calculated the mobility of various elements in the Ogallala caprock. Al_2O_3 was assumed to be the most immobile oxide and as such was considered constant for his calculations. Aristarain (1970, p. 210) cites Keller (1957) who suggests that Al_2O_3 is immobile in the presence of Ca^{++} and Mg^{++}, strong (clay) flocculating agents.

Numerous problems arise in Aristarain's treatment of soil chemistry. First, the use of a standard cell method, although modified for a constant index element (Al_2O_3), is not acceptable for calcic soils because they are aggradational, that is they are continually growing volumetrically. Second, Aristarain's data is in weight percent and he made no attempt to assess elemental concentrations on a weight-volume basis using bulk density data. Additionally, fundamental in all investigations of soil chemistry is the establishment of a chemical baseline; the initial concentration of elements or oxides in the parent material. Aristarain's (1970, table 2) lowest samples from each profile contain from 19 to 44 percent CaO; these values are typical of moderately well developed calcic soil horizons (K2m, K3m, or K3 of Gile and others, 1965). Thus, Aristarain's comparison of relative element mobilities is of limited value. Finally, the use of Al_2O_3 as an index element may not be valid. Al_2O_3 is essentially insoluble in the normal range of pH, 4-9 (Loughnan, 1969), but above pH 9.5 Al_2O_3 solubility

increases rapidly. Microsoil pH, especially in arid and semiarid environments, may reach 10.

Aristarain (1970, fig. 5) reported net gains in the soil profile for Ca, C, and O ($CaCO_3$), H (water), Mg, Fe, S, and P while Ti, Na, and K did not show prominent trends. There were no net losses. His results are largely the effect of holding Al_2O_3 constant, an element that is somewhat mobile.

For the purpose of this report we have used Aristarain's (1970, table 2, profile 1) data with TiO_2 as the index-oxide. Titanium (Ti) is a commonly used index element. It exists in various forms in soils: TiO_2, $Ti(OH)_3$, $Ti(OH)_4$, and in solid solution with Fe and Mg-bearing minerals; all of which are essentially insoluble above a pH of 4.5 (Loughnan, 1969). We selected profile 1 because the lowest sample (1-4) contained the least CaO of all basal samples (this reflects a lower $CaCO_3$ content), and we had previously sampled this profile and made analyses for $CaCO_3$ content and Ca:Mg ratio, as well as x-ray diffraction and SEM photos of the clay minerals. In addition to his profile samples 1-1 (Cca), 1-2 (IIK2mb), 1-3 (IIK31mb), and 1-4 (IIK32b) we calculated the chemical analysis of the parent material (IICn, Ogallala Formation) by removing all but enough CaO required (2.8 percent) to form 5 percent $CaCO_3$ (fig. 26). This is the average $CaCO_3$ content of sand from the Ogallala which we sampled from 5 to 10 m below the surface near his locality. At Aristarain's soil locality younger eolian sand (Aristarain, 1970, sample 1-1, Cca) lies unconformably on the IIK2mb horizon and is derived, in part, from the lower, older soil. Fragments of the IIK2mb horizon are present throughout the younger sand and give
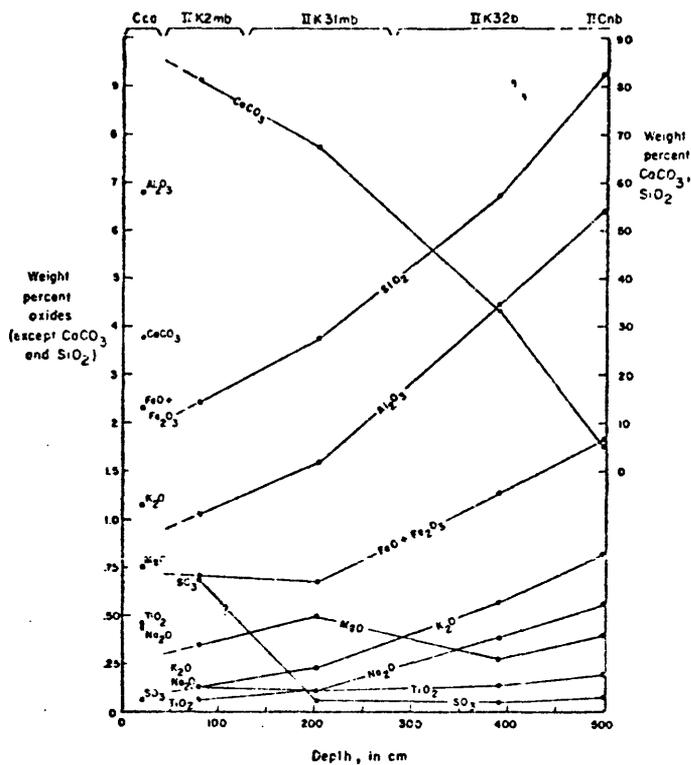
Figure 26.--Weight percent oxides and CaCO₃ for a pedogenic calcrete developed on the Ogallala Formation in southeastern New Mexico. Data taken from Aristarain (1970, table 2, profile 1). The sulfate value (reported as SO_3^{--}) for the IIK2mb horizon is considered anomalous when compared to other soil analyses (Aristarain, 1970, table 2). Oxides with values of less than 0.1 percent are not included.

this horizon an anomalously high $CaCO_3$ value.

All oxide contents decrease progressively in abundance upwards from the unaltered parent material (IICnb horizon), with the exception of MgO. This decrease in oxide contents is largely the result of volumetric dilution of detrital grains by $CaCO_3$.

There are two major components in a calcic soil or pedogenic calcrete: 1) the calcareous fraction which usually has some Mg associated with the $CaCO_3$ in solid solution, and 2) the detrital or noncalcareous fraction of the soil. The noncalcareous fraction consists of the parent material and any noncalcareous authigenic or weathering products that might have formed.

We have removed the carbonate component from Aristarain's (1970) data (profile 1) and recalculated the chemical analyses of the remaining components. We have allotted either all the CaO or CO_2, whichever was least abundant, and an appropriate amount of the other compound, to form $CaCO_3$. The remaining oxides and water were recalculated on a 100 percent basis. Using TiO_2 as an index-oxide and adjusting its concentration to one, all other oxide values become concentration ratios of TiO_2 (fig. 27). The concentrations of Al_2O_3, SiO_2, and K_2O are relatively stable in the upper one-half of the profile (IIK2mb-IIK31mb horizon), but increase in the basal part (IIK32mb horizon). Na_2O and $FeO+Fe_2O_3$ are at their maximum in the IIK2mb and decrease in the IIK31mb. MgO shows a marked association with $CaCO_3$ (fig. 26), both being most concentrated at the top of the profile (IIK2mb). MgO, which is 2.6 times as abundant in the IIK2mb as in the IIK32mb, is present in two modes within the soil, the carbonate phase, and in clay minerals.
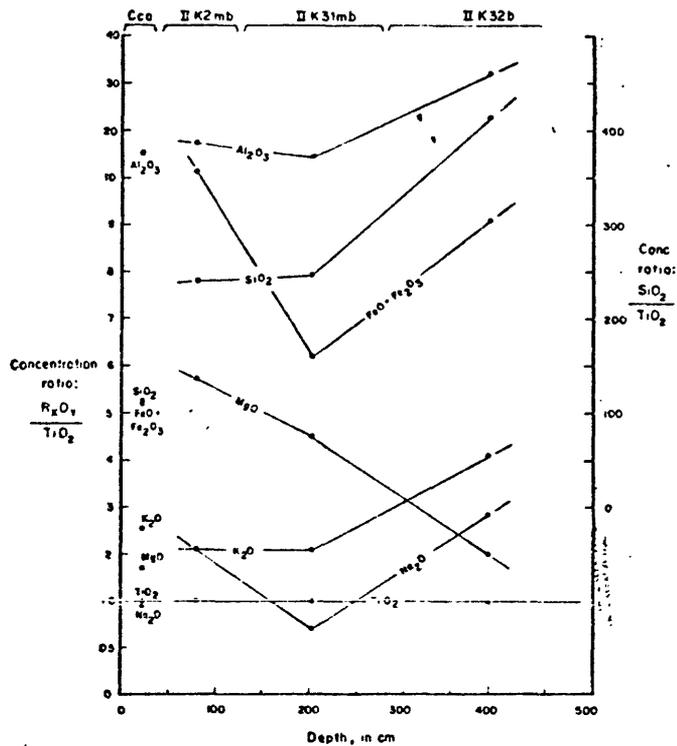
Figure 27.—Concentration ratios for vario⁻ oxides in the
noncalcareous component of a pedogenic calcrete
developed on the Ogallala Formation (Aristarain, 1970,
profile 1). TiO_2 content is arbitrarily set at 1.0,
all other oxides represent their concentration
relative to TiO_2.

X-ray diffraction of soil clay minerals and SEM photographs confirm the presence of both palygorskite and sepiolite, pedogenic Mg-Al silicate clay minerals. If the authigenic MgO is removed (fig. 26), the other oxide contents increase proportionately and the overall net changes in oxide elements are reduced. K_2O, SiO_2, and Al_2O_3 show losses in the profile, while $FeO + Fe_2O_3$ and Na_2O are greatly enhanced in the uppermost part of the profile. Perhaps these oxide concentrations reflect the presence of an engulfed B horizon within the upper K horizon, the B horizon being relict from former moister climates.

Vanden Huevel (1966) analyzed the chemistry and mineralogy of a pedogenic calcrete on the La Mesa surface near Las Cruces, New Mexico (fig. 19). His main purpose was to document the presence and interpret the genesis of sepiolite and palygorskite (attapulgite) in the calcareous zone of the soil. We used Vanden Huevel's chemical analyses, supplemented by SCS soil data (Gile, 1961; Gile and others, 1971), and our own soil analyses, to construct a net gain-loss diagram for the soil and to examine oxide mobilities. The weight-percent chemical analyses and recalculated chemical analyses, Ca:Mg ratios, bulk densities, and percent $CaCO_3$ are shown in Table 5. By allotting CaO and CO_2 to $CaCO_3$ as we did for Aristarain's profile, and an appropriate amount of Mg in solid solution with the $CaCO_3$, we recalculated chemical analyses for the noncalcareous phase of the soil (table 5). As in Aristarain's profile (fig. 26) the presence of $CaCO_3$ results in a dilution effect although MgO does not follow this trend but shows a marked accumulation in the middle part of the profile.

The concentration ratios for the La Mesa pedogenic calcrete are

Table 5.—Weight percent oxides of whole rock (WR) and noncalcareous (NC) phases for a La Mesa pedogenic calcrete.

[Whole rock data are from Vanden Huevel (1966); bulk density, percent CaCO₃ and clay contents are from this study and Gile (1961, table 1, Soil No. 1). CaO contents of the noncalcareous phase of the soil is set at 0.83 percent and is based on parent material CaO and CaCO₃ contents. Ca:Mg ratio of CaCO₃ is based on AAS determinations, rounded to units of 25. Noncalcareous analyses are calculated on a 100 percent basis. Weight of individual oxides in the soil are based on the oxide content, horizon thickness, and horizon bulk density. Total weight is calculated from the WR data using present horizon thicknesses and bulk densities. Original weight is calculated from WR analyses of the parent material (IIC2b horizon), using 117cm as the original soil—parent material thickness.]

Horizon	A	B1t	B21t		B22tca		IIK21imb		IIK22mb		IIK23mb		IIK31mb		IIK32b		IIK33b		IIC1cab		IIC2b		Weight of individual oxides IIK21imb–IIC1cab 48-272 cm	
Sample No.	14977c / 4978c / 4979c	14978c / 14979c	14982c		14983c		14991c		14992c		14985c		14986c		14987c		14988c		14989c		14990c		Total (g)	Original (g)
Depth in cm	0-5	5-25	25-36		36-48		48-50		50-74		74-102		102-150		150-185		185-236		236-272		272+			
Bulk density in g cm³	1.65e	1.82	1.70		1.53		2.20		1.90		1.70		1.66		1.65		1.73		1.70e		1.64			
Type of analysis	WR	WR	WR	NC	WR	NC	WR	NC	WR	NC	WR	NC	WR	NC	WR	NC	WR	NC	WR	NC	WR	NC	WR	Total Original in g
Percent CaCO₃	0	0	1	—	16	—	89	—	75	—	64	—	51	—	52 (?)	—	41	—	13	—	2	—		
Percent clay	9.7	11.0	14.7	14.8	14.0	16.7	4.0	36.1	6.6	26.4	6.2	17.8	9.3	18.9	—	—	—	—	4.6	5.3	4.4	4.5		
SiO₂	79.90	78.45	77.20	79.65	65.70	78.36	8.06	72.21	19.10	77.39	29.60	78.81	36.40	75.07	41.90	76.89	46.40	75.96	74.90	84.38	81.00	84.86	163.13	154.76
Al₂O₃	8.84	9.59	9.82	10.13	9.10	10.86	1.34	12.00	2.20	8.91	2.84	7.56	3.01	6.20	3.47	6.37	3.85	6.30	6.99	7.87	7.56	7.92	14.49	14.44
Fe₂O₃	2.81	2.97	3.05	3.15	2.60	3.10	.56	5.01	.67	2.71	.67	1.78	.68	1.40	.79	1.45	.85	1.39	1.47	1.65	1.59	1.67	3.30	3.04
TiO₂	.49	.50	.49	.51	.39	.47	.07	.63	.08	.32	.11	.29	.11	.23	.13	.24	.13	.21	.27	.30	.28	.29	.54	.51
K₂O	2.59	2.62	2.64	2.72	2.11	2.52	.25	2.24	.48	1.94	.72	1.92	.73	1.51	.86	1.58	.93	1.52	1.95	2.20	2.22	2.33	3.65	4.22
MgO	.44	.43	.47	.49	.47	.56	.07	.63	.45	1.82	1.09	2.90	3.67	7.57	3.96	7.27	4.98	8.16	.98	1.10	.78	.82	10.93	1.49
CaO	.92	.97	.85	.88	.73	.87	.09	.83	.20	.83	.31	.83	.40	.83	.45	.83	.51	.83	.74	.83	.83	.87	1.72	1.59
Ignition loss	2.10	2.15	2.39	2.47	2.73	3.26	.72	6.45	1.50	6.08	2.22	5.91	3.49	7.19	2.93	5.37	3.44	5.63	1.47	1.66	1.18	1.24	10.18	2.25
Subtotal	98.09	97.66	96.91	100.00	83.83	100.00	11.16	100.00	24.68	100.00	37.56	100.00	48.49	100.00	54.49	100.00	61.09	100.00	88.77	100.00	95.44	100.00	207.94	182.35
Ca:Mg	—	—	25		25		200		150		125		100		75		50		25		25			—
MgO	0	0	.02	—	.29	—	.25	—	.28	—	.28	—	.28	—	.33	—	.11	—	.22	—	.07	—	1.20	.27
CaO	0	0	.54	—	7.16	—	49.41	—	41.90	—	34.59	—	28.30	—	24.85	—	21.39	—	5.48	—	1.68	—	96.88	6.41
CO₂	0	0	.44	—	5.85	—	39.01	—	33.13	—	27.33	—	22.44	—	19.76	—	17.12	—	4.52	—	1.38	—	77.02	5.29
Percent CaCO₃	0	0	1.00	—	13.30	—	88.67	—	75.31	—	62.25	—	51.02	—	44.94	—	38.94	—	10.21	—	3.13	—	175.13	12.06
Total	98.09	97.68	97.91	100.00	97.13	100.00	99.83	100.00	99.99	100.00	99.81	100.00	99.51	100.00	99.43	100.00	100.03	100.00	98.99	100.00	98.57	100.00	383.04	194.35

⅟ Average value

shown in figure 28. With the exception of the uppermost calcareous horizon (IIK211mb) of the buried soil, Fe_2O_3, SiO_2, Al_2O_3, and K_2O remain relatively constant in the profile. Fe_2O_3 increases and SiO_2 decreases near the top of the buried soil. These two chemical changes may reflect the presence of an engulfed B horizon which is a common feature of older calcic soils in the southwestern United States. Besides $CaCO_3$, the other compound which shows a marked gain is MgO. MgO is slightly depleted in the IIK211mb horizon, as are most of the other oxides (fig. 28). The TiO_2 content of the noncalcareous phase of the IIK211mb horizon is 0.63 percent; two to three times as much as in the lower horizons. The concentration of oxides in the IIK211mb may be low as the result of overcompensation when adjusting an anomalously (?)high TiO_2 content (table 5).

The comparison of oxide contents on a weight-volume basis is preferable to a weight percent basis. Figure 29, which is similar to figure 28, is a plot of unit-weight of oxides, in g/100 cm^3, in each horizon of the soil profile; TiO_2 is the index oxide. By observing the oxide weight in a profile relative to that of the parent material, the oxides weight gain or loss is that deviation from the chemical baseline of the parent material.

Assuming that TiO_2 is immobile in this soil environment, its present concentration in the soil is largely the result of dilution by $CaCO_3$. The total TiO_2 present in the buried soil may be calculated from the chemical analyses, bulk density data, and horizon thicknesses. By redistributing the total TiO_2 (0.535 g) at its original concentration (0.0476 g/cm^3) in the parent material, the resulting thickness of 117 cm
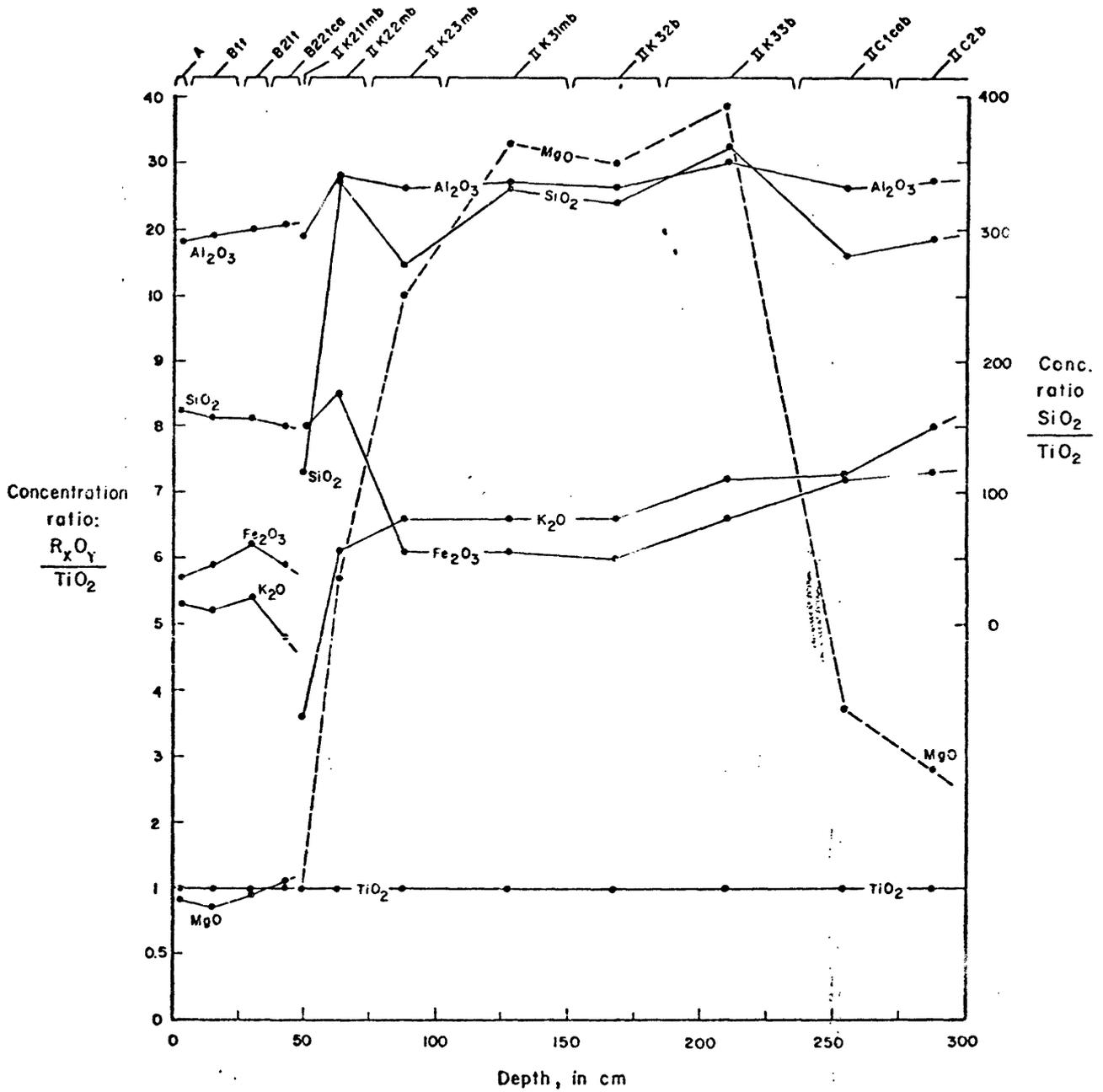
Figure 28.—Concentration ratios of oxides for the La Mesa
pedogenic calcrete. TiO_2 is assumed to be constant,
arbitrarily set at on. all other oxides represent
their concentrations relative to TiO_2.
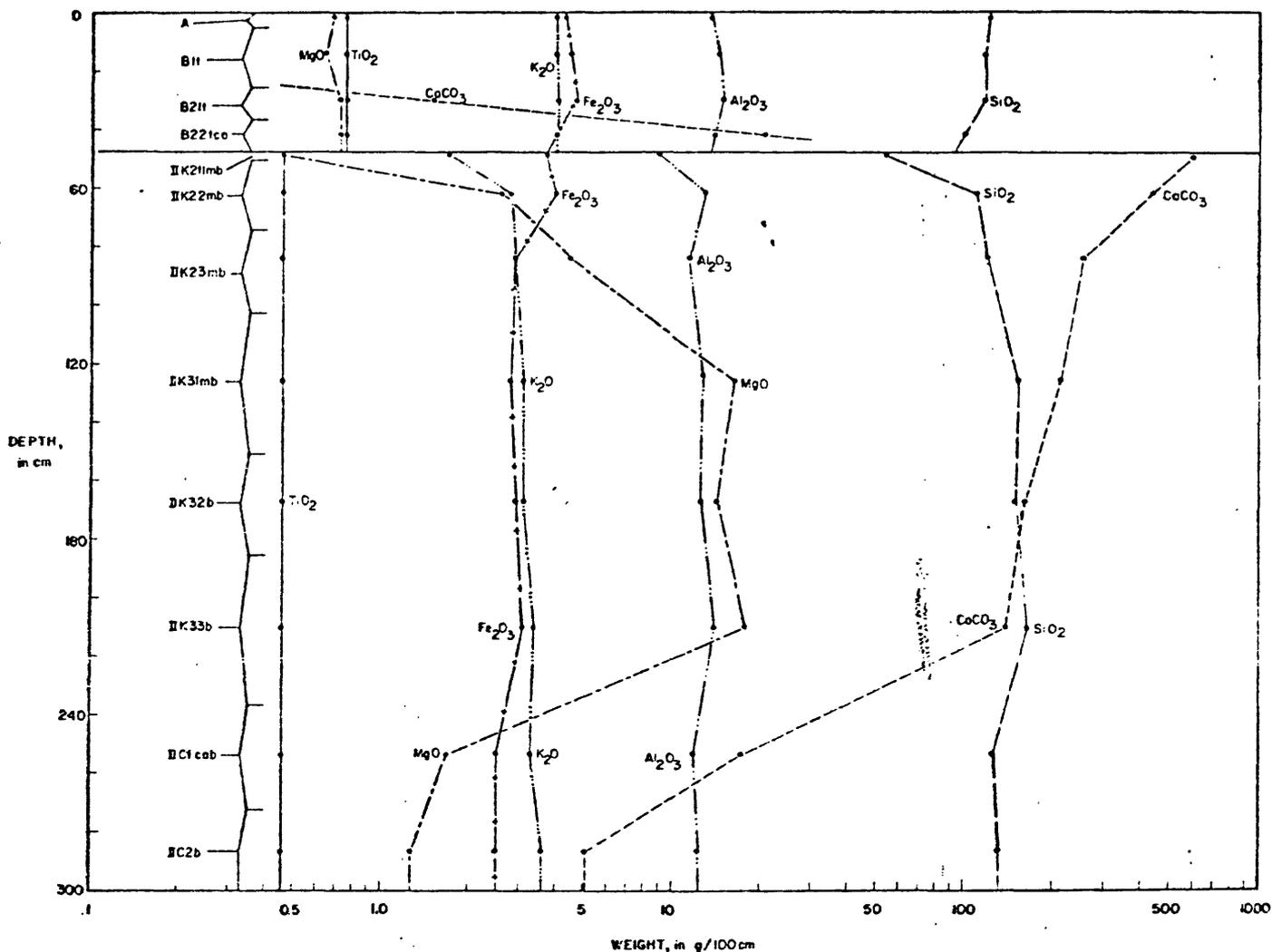
Figure 29.—Weight gain-loss diagram for the La Mesa pedogenic calcrete which has formed on a lower parent material (II), then was buried by eolian sand on which additional soil formed. The IIC2b horizon represents unaltered parent material. Oxide contents are calculated from chemical analyses (Vanden Huevel, 1966, table 1), bulk densities (Gile and others, 1971, p. A-68, and this study), and horizon thicknesses (Gile and others, 1971, p. A-69). All values are recalculated to a constant TiO_2 content of 0.46 percent (IIC2b). The oxide values in the upper parent material are based on a TiO_2 content of 0.75 percent.

reflects that thickness of parent material from which the present 224 cm-thick soil has formed. These thickness calculations correspond with similar calculations based on grain-size distribution, $CaCO_3$ content, and bulk density data.

Based on an original soil parent-material thickness of 117 cm (p. ___) a net balance for the La Mesa pedogenic calcrete (table 6) can be derived from the data in table 5.

The upper soil (A, Blt, B21t, and B22tca horizons) at Las Cruces were considered to be part of the relict La Mesa soil by Gile (1961), Vanden Heuvel (1966), and Gile, Hawley, and Grossman (1971). We consider the upper soil profile to be younger and rest unconformably on the older, buried La Mesa soil. This interpretation is based on the well-developed laminar horizon which is locally cut-and-relaminated in pipes, by the dissimilarities in chemistry between the noncalcareous phases of each soil (fig. 28), and by the differences in physical and lithologic properties of each of the soils parent materials (Gile and others, 1971, p. A-68). Additionally, the B horizon of the upper soil has a maximum of 15 percent clay, whereas the parent material (eolian sand) probably was deposited with about 3-5 percent clay. Although this is a moderately strong clay accumulation, we believe that the relict (La Mesa soil) B horizon would be more developed than it is based on a comparison of soils in the Denver area of the Colorado Piedmont (Machette and others, 1976) where the annual precipitation is from 300-450 mm. It is probable that the relict B horizon of the La Mesa soil was engulfed by $CaCO_3$ prior to burial as suggested by higher Fe_2O_3 - FeO content of the upper part of the horizon (fig. 28).

Table 6.--Net weight gains and losses for the La Mesa pedogenic calcrete

| Component | Unit weight, in grams/cm^2 soil-column | | Percent gain or loss |
	original	present	
SiO_2	154.8	163.1	+5.4
Al_2O_3	14.44	14.49	+ .4
Fe_2O_3	3.04	3.30	+8.6
TiO_2	.54	.54	constant
K_2O	4.24	3.66	-13.7
MgO	1.49	10.93	+634
CaO	1.59	[2/]1.82	[2/]+14.5
Other	2.26	10.18	350
$CaCO_3$	[1/]12.0	175.0	+1,360
Total--------	194.4	382.5	+97

[1/] Based on 3.1 percent primary $CaCO_3$.

[2/] Constant CaO value portioned to insoluble residue fraction of soil. Percent gain is not relevant.

Table 6 includes some MgO in solid solution with $CaCO_3$. The average formula for the calcium carbonate in the buried soil is $Ca_{.986}Mg_{.014}CO_3$, this results in an average Ca:Mg ratio of approximately 70. Thus, the MgO total should also include the 1.2 g of MgO in solid solution with calcite, making a net gain of 815 percent MgO. Our $CaCO_3$ and Ca:Mg analyses of the La Mesa soil were made on samples collected from Vanden Huevel's profile description of the SCS pedon locality. We have assigned a CaO content for the noncalcareous fraction of each sample in table 5, using as a model the parent material CaO content (0.87 percent).

From the analysis of both Aristarain's (1970) and Vanden Heuvel's (1966) data it appears that the main chemical attribute of these two calcic soils, and those of similar genesis, is the pervasive engulfment and eventual dilution of soil parent materials by $CaCO_3$. Associated with the accumulation of $CaCO_3$ is the formation of Mg-rich authigenic clay minerals.

The parent materials of these calcic soils do not show significant weathering. Additions of Fe_2O_3 and FeO are probably the result of accumulations of iron in the B horizon while SiO_2 is depleted in the upper soil (former B horizon) but has an overall net gain for the soil profile. These changes are masked by a strong carbonate engulfment, completely obscuring the presence of an older B horizon. Aerosolic dust may contribute iron and silica to the soil as it does for Mg and Ca. K_2O, which is lost in moderate amounts (ca. 14 percent), probably is leached during occasional deep wettings of the soil. The two other oxides, Al_2O_3 and TiO_2, are relatively stable on a total weight-volume

basis, although Al_2O_3 does move within the profile. Those changes that more fully characterize calcic soils—Ca:Mg ratio, clay mineralogy, $CaCO_3$ content, and bulk density—will be dealt with later in more detail.

Minor elements in calcic soils and pedogenic calcretes

Sixty-nine soil samples from widely spaced localities in the southwestern United States were analyzed for trace elements by semiquantitative spectrographic analysis. The purpose of these analyses was to determine if there is a distinctive association of elements in calcic soils or pedogenic calcretes as related to time, geography, or position in the soil profile.

Trace elements, which we detected, were measured in ppm (parts per million). A typical calcic soil includes Ba (200-3,000 ppm), Cu (7-20 ppm), Mn (50-150 ppm), Cr (3-30 ppm), and Sr (200-2,000 ppm). Trace elements less commonly present, or present in minute quantities, are Ni (7-10 ppm), V (7-70 ppm), Ag (rare; 5-7 ppm), and Li (rare; 200 ppm).

The suite of samples which we analyzed was not sufficiently large for meaningful statistical analysis. The high quantities of Ba and Sr in some samples appear to be anomalous and may deserve more complete study. We did not detect unusual concentrations of particular elements by geographic or stratigraphic constraints. It is probable, however, that soils on fans adjacent to areas of mineralized bedrock contain traces of anomalous metals. Such soils, in the vicinity of the old Madrid mining district near Santa Fe, New Mexico (fig. 10), contain 15 to 50 ppm Pb and lesser amounts of Y and Nb.

Ca:Mg ratio and clay minerals

The Ca:Mg molal ratio of the calcareous fraction of calcic soils and pedogenic calcretes is closely associated a the horizon's carbonate content and position in the soil profile, the clay mineralogy of the sample, and the initial Ca:Mg ratio of carbonate in both the parent material and extraneous (airborne) sources.

Ca:Mg ratios were determined by two methods, Versine titration and AAS. (See section on analytical procedures and laboratory methods.) Versine measurements reflect the total Ca and Mg contents of a sample, thus they may be considered as "whole rock" Ca:Mg ratios. Most Ca:Mg ratios computed for calcretes from published data are either whole rock (Vanden Huevel, 1966; Aristarain, 1970) or are of an unspecified type (Goudie, 1972, 1973; Gardner, 1972). AAS measurements reflect the Ca and Mg contents of the carbonate fraction of a sample. Ca:Mg ratios determined by both AAS and Versine were compared for 77 samples from calcic soils and pedogenic calcretes, which ranged from 3 to 84 percent $CaCO_3$ (fig. 30). In all cases the AAS determined ratios were higher than the Versine; this indicates that Mg is enriched relative to Ca in the noncalcareous fraction of the soil. The line of best fit indicates that Versine Ca:Mg ratios are approximately one-half of AAS determined ratios. The large scatter of the data is the result of composites of many soil profiles, differing parent material chemistry, and the formation of pedogenic clay mineral.

The Ca:Mg ratio (AAS) was plotted against combined soil carbonate content $(Ca_xMg_yCO_3)$ to determine if a relationship exists between these two variables (fig. 31). The field of 112 samples lies to the right of

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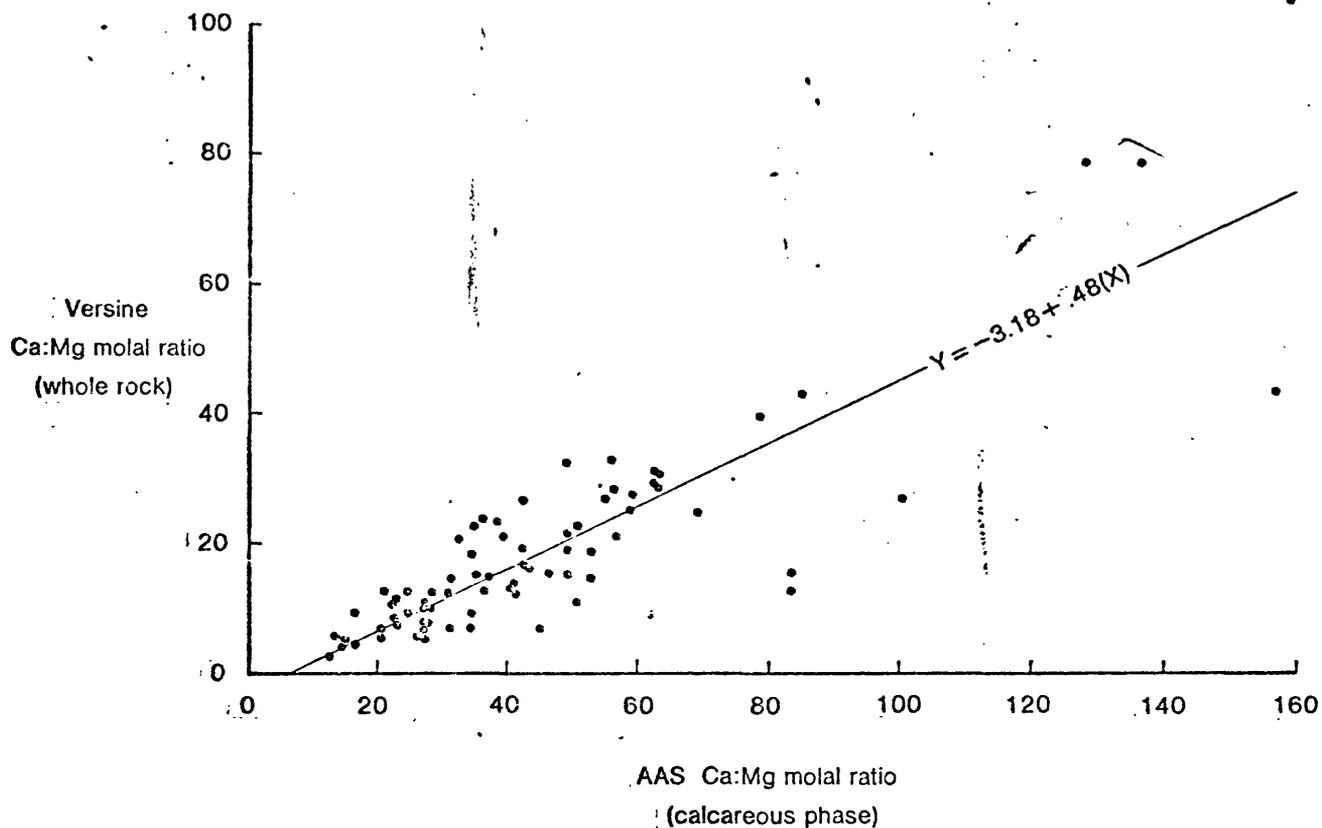
Figure 30.--Relationship of Ca:Mg molal ratios between whole rock (Versine) and calcium carbonate component (AAS) for some calcareous soils in the southwestern United States.
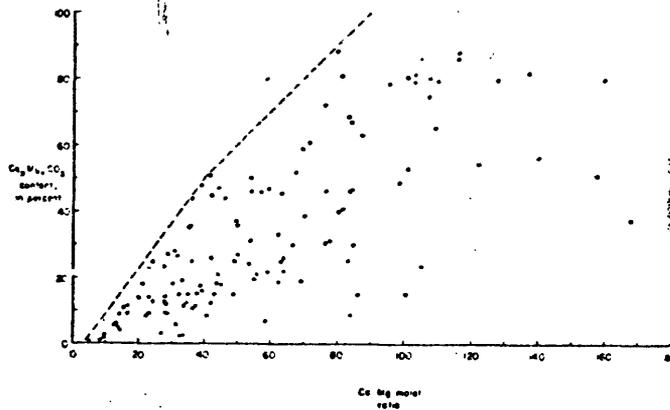
Figure 31.—General relationship between Ca:Mg molal ratio
and calcium carbonate $(Ca_xMg_yCO_3)$ content for
calcareous soils of the southwestern United States.
Both analyses are by AAS methods (see section on
analytical procedures and laboratory methods). Open
circles indicate laminated and (or) brecciated
horizons, closed circles represent all other soil
horizons.

the dashed line, which approximates equal values for Ca:Mg ratio and carbonate content. In some cases the Ca:Mg ratio may be 3-4 times that of the percent carbonate indicating that these samples are significantly depleted in Mg content. Initial Ca:Mg ratios commonly range from 10-20 in unaltered parent materials (unconsolidated surficial deposits) or in modern eolian sand, while laminated, brecciated, or pisolitic calcic horizons of 80-90 percent carbonate content have ratios that range from 100-160.

We selected six soil profiles, which range from late Pleistocene to Pliocene in age, to illustrate common trends of Ca:Mg ratios as compared with a sample's position in the soil profile and its carbonate content (fig. 32). The minimum ratio usually occurs at the base of the profile, unless the profile is a buried or part of a composite soil. Young soil profiles, which have low carbonate contents, have the least complex ratio-trends; as soils become more developed with age the young Ca:Mg trend can be modified by burial, erosion, leaching, or clay mineral authigenesis. Although considerable variation exists from one profile to another, there seems to be a systematic trend in soil Ca:Mg ratios; that is one of progressive depletion of Mg in the carbonate phase of a calcic soil. Example A (fig. 32) is a non-palygorskite bearing calcic soil; note the relatively low Ca:Mg ratios since Mg is not being extracted from the calcareous fraction at the soil.

Based on the above data, and the profile distribution of palygorskite and sepiolite (see clay mineral distribution section), it seems reasonable to postulate the following model for Ca and Mg accumulation in calcic soils. In early stages of soil development $CaCO_3$
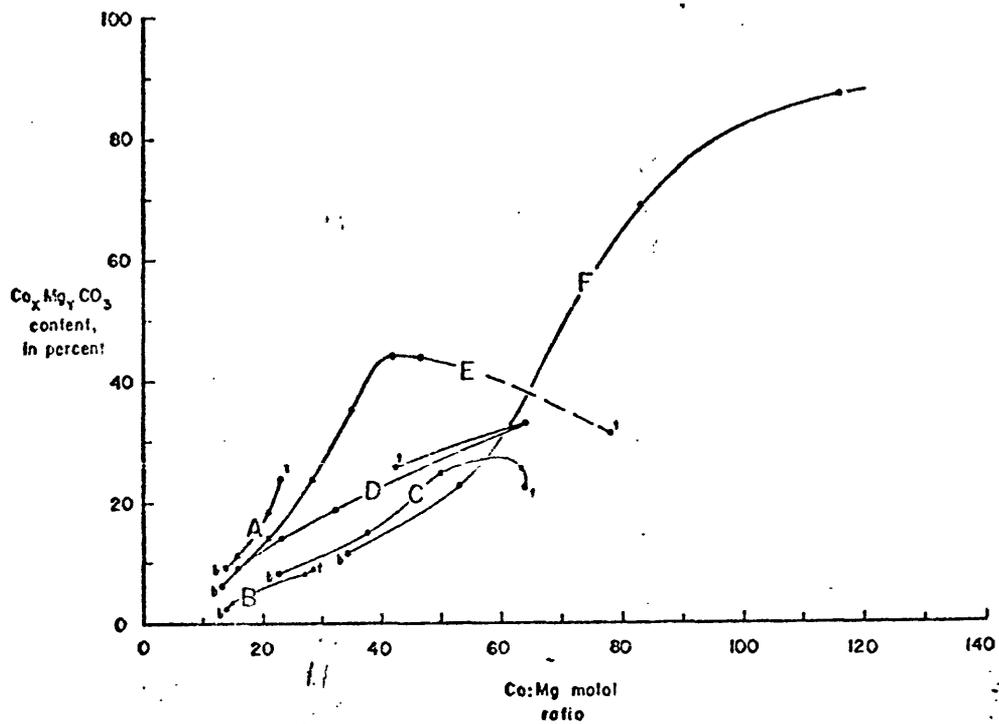
Figure 32.—Relationship between $Ca_xMg_yO_3$ content and Ca:Mg molal ratio in six soil profiles. Symbols t and b indicate top and bottom of soil profile; where no symbol is shown profile sampling is not complete. Letter symbols indicate ages of soil profiles: A, late Pleistocene; B, late Wisconsin; C, D, and E, early late Pleistocene, and F, late(?) Pliocene.

accumulates through pedogenic processes and Mg, supplied in small portions (that is, 1/10th to 1/20th of the Ca concentration), can either precipitate in solid solution with the calcite or occupy exchangeable cation positions in montmorillonite or mixed-layer montmorillonite-illite clay minerals. These two clay minerals and illite are common in semiarid and arid desert soils (Grim, 1968; Loughnan, 1969; and Birkland, 1974) and are almost always the dominant clay minerals in B horizons of Mollisols and Aridisols. Under conditions of high pH and moderate Mg supply (Weaver and Beck, 1977), Mg-saturated montmorillonite or mixed-layer montmorillonite-illite undergoes either direct precipitation (fig. 20), solid-state transformation (fig. 33), or surface-dissolution and reprecipitation (fig. 34) as palygorskite. Sepiolite, a hydrated, Mg-rich silicate clay mineral, occurs in soils only where palygorskite is dominant and montmorillonite is relatively depleted. This same association in soils has been noted by Vanden Heuvel (1966) and Frye and others (1974), and in peri-marine deposits by Weaver and Beck (1977). The occurrence of sepiolite in soils, which we consider to be a late stage product of pedogenesis, has been noted only in soils of middle Pleistocene to Pliocene age (Vanden Heuvel, 1966; Gile, 1967; Netterberg, 1969; McLean and others, 1972; Frye and others, 1974; and this report). Sepiolite in calcic soils usually occurs in a medial portion of the soil profile (that is, K3m horizon); this suggests that the occurrence of sepiolite may be a function of the depth of soil-water infiltration. Frye and others (1974) have suggested that sepiolite forms as a result of increased aridity, but this concept does not account for the absence of sepiolite in soils younger than middle

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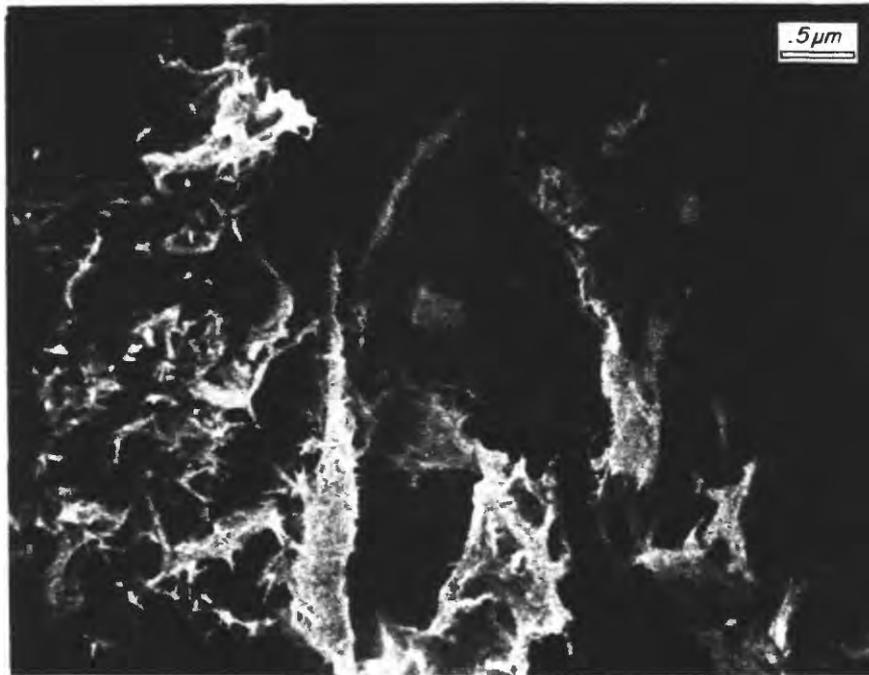
Figure 33.—SEM photograph of mixed-layer illite-montmorillonite (large sheet-like structures) undergoing transformation directly to palygorskite (fibrous and barbed structure. Photograph of <2 clay fraction of Llano de Albuquerque calcic soil, IIK3m horizon. One-half micron bar for scale.
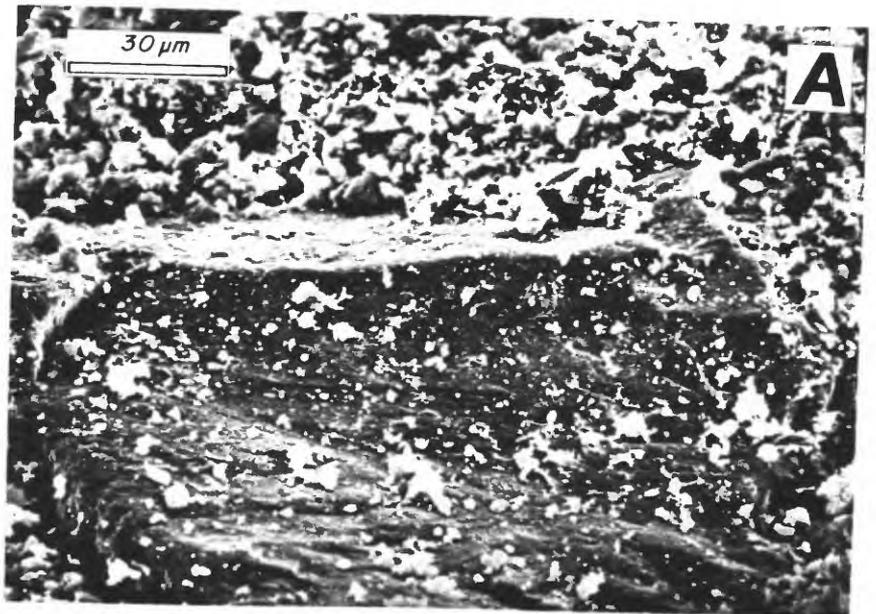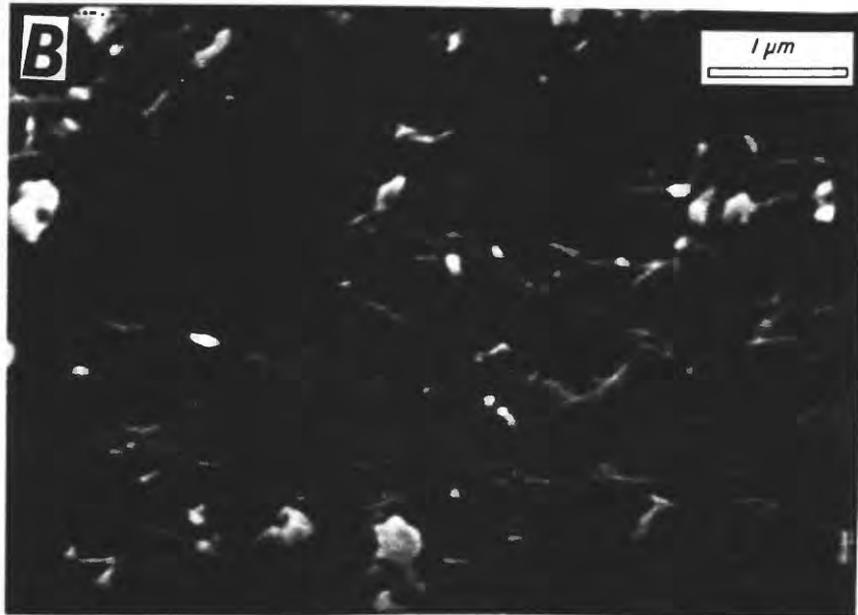
Figure 34.—A. SEM photograph of the surface of a quartz grain (upper left-hand corner) with 30 m bar for scale. Inset close-up shows surface texture of quartz grain at high magnification (one m bar for scale). Palygorskite is probably being precipitated and quartz dissolved. This texture and precipitation-dissolution scheme was first noted by Weaver and Beck (1977, p. 165, fig. 85, middle) in peri-marine palygorskite beds.

Pleistocene. The occurrence of sepiolite is probably a complex function of host mineral lithology and abundance, previous pedogenic mineral formation, Mg source and supply, and both climatic and soil water relationships.

Palygorskite and sepiolite are Mg-sinks within calcic soils and pedogenic calcretes; the $Ca_xMg_yCO_3$ phase of a soil is progressively more depleted in Mg (fig. 32), both with age and clay mineral formation. Ca:Mg ratios for the carbonate fraction of palygorskite and sepiolite-bearing calcic soils commonly exceed 100 and occasionally reach 150-160. In these cases, MgO may be a major component of the whole rock chemistry comprising up to 5 weight percent (Vanden Huevel, 1966) of some calcareous horizons (table 5).

The origin and concentration of the Mg in calcic soils raise questions. Several sources for the Mg in calcic soils exist; airborne dust, desert loess and eolian sand blown from weathered bedrock or unconsolidated surficial deposits (including older soils) and rainwater, which dissolves some of the dust, provide Mg-bearing calcium carbonate. Marine limestones, limey sandstones, gypsums, and dolomites, form a substantial portion of the Paleozoic section in the southwestern United States. Marine limestones in the southwestern United States commonly range from 0 to 10 percent dolomite-equivalent, or have Ca:Mg ratios as low as 15 (Steidtmann, 1917; Goldich and Parmalee, 1947; Chave, 1954; Pettijohn, 1957; and McKee and Gutschick, 1969). Dolomites, although not as widespread areally as limestones, provide some $MgCO_3$ which contribute to a higher Mg concentration in eolian carbonates. Rainwater contains an appreciable amount of Ca (Junge and Werby, 1958), especially

in the southwestern United States. Although Junge and Werby did not measure Mg in rainwater, it is reasonable to assume that Mg exists in solution in rainwater. Thus, Mg, like Ca, is probably being supplied to the soil from extraneous sources.

Using Vanden Huevel's (1966) data, table 5, we have calculated the total MgO in the La Mesa soil; 12.1 g/cm^2 soil-column. Using 117 cm as the original thickness of parent material where the soil is now formed, approximately 1.6 g/cm^2 of the 12.1 g/cm^2 of MgO is primary (detrital). This leaves 10.5 g/cm^2 of secondary (pedogenic) MgO. A total of 163 g/cm^2 soil-column of secondary $Ca_xMg_yCO_3$ has accumulated in the soil. Assuming an average Ca:Mg ratio of 15 (CaO:MgO ratio of 21) for the extraneous carbonate sources, 7.3 g/cm^2 of MgO would have been supplied to the soil in solid solution with $CaCO_3$ or as dolomite. This accounts for about 70 percent of the MgO in the profile. Additionally, rainwater may supply Mg to the soil in a higher proportion than Ca since Mg is a fairly soluble ion.

Geographic, stratigraphic, and pedologic

distribution of clay mineral

We have previously discussed the occurrence of palygorskite and

sepiolite in calcareous soils and their relationship to Ca:Mg ratios.

As recently as 1966, Vanden Heuvel (p. 206) stated that there were "no

reported instances in the literature where sepiolite has been thought to

form in place in soil." Previous reports of palygorskite in soils

implied ground water or lacustrine origins, or inherence (Michaud,

Cerighilli, and Dronineau, 1945; Muir, 1951; Barshad and others, 1956;

Millot, Raider, and Bonifas, 1957; Loughnan, 1960; Millot, 1964; Al Rawi

and Sys, 1967); these reports were largely prejudiced by a substantial

volume of literature on the association of palygorskite with marine,

playa, and lacustrine environments (Wiersma, 1970; Weaver and Beck,

1977), as well as hydrothermal origins. The work of Millot and others

(1969) and ourselves indicates that many of the early reported

palygorskite-sepiolite occurrences were probably of pedogenic origin.

Since 1966 pedogenic palygorskite or sepiolite have been reported in

soils from Israel, Syria, Australia, Russia, India, South Africa,

Morocco, Afghanistan, and the United States. Thus, what appeared to be

local occurrences, is now known to be a widespread association of

palygorskite or sepiolite in calcareous soils. In the United States,

soil-palygorskite and sepiolite have been reported by Vanden Huevel

(1966), Gile (1967), Gardner (1972), McLean, Allen, and Craig (1972),

Glass, Frye, and Leonard (1973), Frye and others (1974), Goolsby and Lee

(1975), and Lee and Goolsby (1975).

Our x-ray diffraction and SEM studies indicate that palygorskite is

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widespread in calcareous soils of the southwestern United States, first occurring in upper Pleistocene soils and becoming the predominant clay mineral in middle Pleistocene and older soils.

Palygorskite shows a progressive development in calcareous soils near Albuquerque, New Mexico (fig. 35). X-ray diffraction patterns were chosen to reflect the maximum palygorskite occurrence in each soil. The oldest soil (A, fig. 35) is on the Llano de Albuquerque, a geomorphic surface of about 500,000 yrs age. Soil B, developed on the Llano de Manzano, is moderately well developed and may be about 280,000 yrs old (Bachman and Machette, 1977). Soil C, the youngest palygorskite-bearing soil we have found, is present on an upper Pleistocene terrace of the Rio Grande which may be about 120,000 yrs old. In calcic soils older than 300,000 yrs palygorskite is the predomimant clay mineral. Expandable clay minerals (randomly interlayared illite-montmorillonite, and montmorillonite) show a progressive depletion as palygorskite develops; this relationship supports the proposed transformation of expandable clays to palygorskite. Illite, kaolinite, and chlorite are of detrital origin and although diluted by authigenic mineral growth, seem to persist in most soil profiles.

Palygorskite shows a vertical distribution within soil profiles (fig. 36) which suggests that its maximum concentration may be largely influenced by soil-water distribution within the profile. In figure 36 palygorskite is most abundant, relative to the expandable clays, in the IIK3mb horizon, at a depth of 64-100 cm. Two patterns are shown for the parent material (IICnb horizon), a weakly calcareous, occasionally nodular, sand. Field relationships prove that the nodules are pedogenic
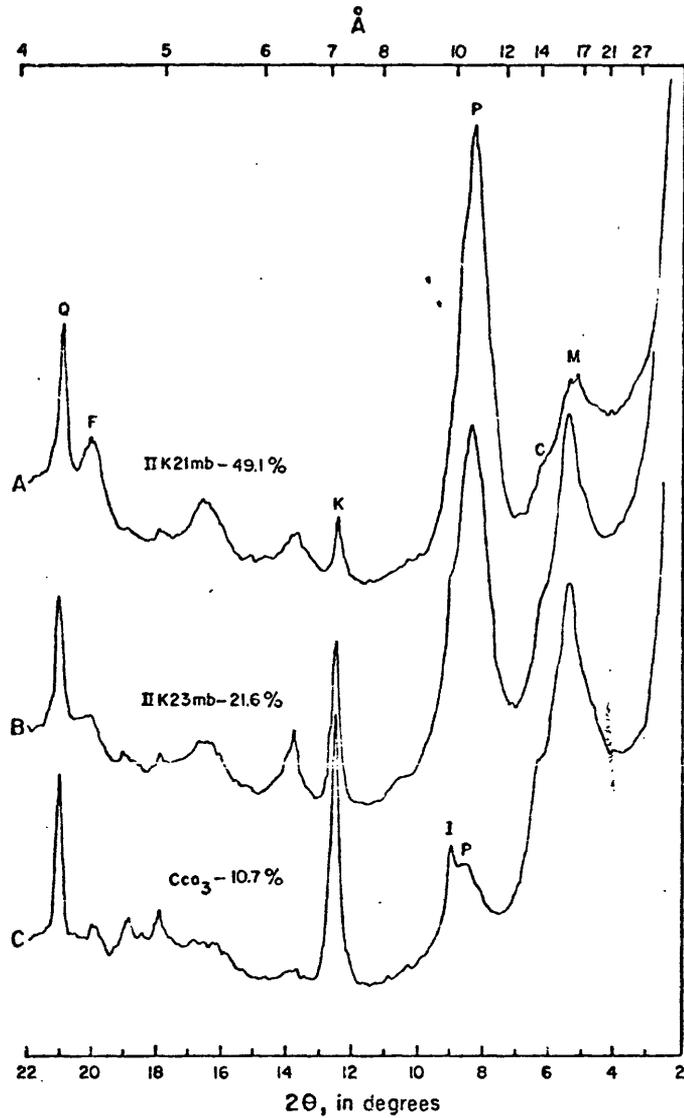
Figure 35.--Comparison of clay minerals present in three
palygorskite-bearing soils near Albuquerque, New
Mexico. Soil "A" is developed on the Llano de
Albuquerque (middle Pleistocene), soil "B" is
developed on the Llano de Manzano, and soil "C" is
developed on an upper Pleistocene terrace of the Rio
Grande. Soil "C" is the youngest palygorskite-bearing
soil in the Albuquerque-Belen Basin.
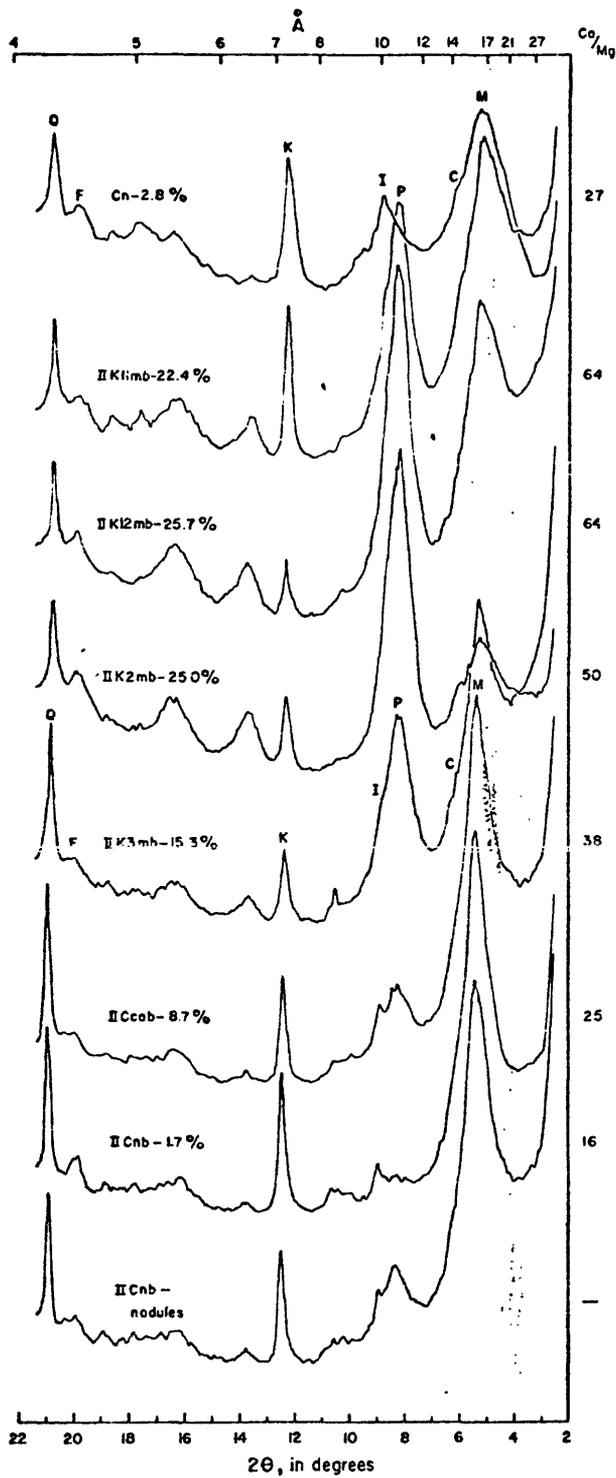
Figure 36.—Clay mineral distribution in a moderately well developed soil near Socorro, New Mexico. Soil horizonation is shown, on the left, with representative soil carbonate contents (in percent) and Ca:Mg molal ratios. M = randomly interlayered illite-montmorillonite or montmorillonite, C = chlorite, P = palygorskite, I = illite, K = kaolinite, F = feldspar, Q = quartz.

and not reworked from older soils. The noncalcareous fraction is composed of randomly interlayered illite-montmorillonite (about 25 percent illite interlayers; Reynolds and Hower, 1970), kaolinite, and minor amounts of illite and chlorite which were identified by heat treatment. The nodules (bottom pattern, fig. 36) show a clay mineral assemblage similar to the parent material, except for the presence of some palygorskite. The interlayered illite-mon orillonite within nodules is more illitic (that is, 30 percent); this may reflect a loss of montmorillonite layers as palygorskite is formed.

The occurrence of void filling is restricted to cases of lateral flow such as surface impregnation and ground-water cementation. Calcretes which have formed from these two processes have grain-to-grain contact and grossly different physical properties than calcic soils or pedogenic calcretes. An example of void-filling is illustrated in case G (fig. 38) and shows the anticipated physical properties based on the same parent material as examples A through F. The resultant bulk density is 2.76 g/cm^3 with a car^L nate content of 48 pϵ ent.

In comparison, pedogenic calcretes (columns D, E, and F; fig. 38) have higher carbonate contents and porosities and lower bulk densities than the void filling example. The grain size distribution of a soil's parent material has a profound effect on bulk density, especially in soils which are not well developed. Gravelly parent materials become impregnated much sooner than sandy parent materials, and the inherently lower porosity of gravelly parent materials results in a higher initial bulk density. Thus, a large scatter occurs when plotting carbonate content versus bulk density for some soils. In later stages of calcic

soil development (IV, V, and VI) the strong cementation, and rejection of larger clasts, results in a more homogeneous field for bulk density and carbonate plots (fig. 37). The fields for indurated horizons of the Mescalero, Ogallala, and Mormon Mesa pedogenic calcretes are well defined and form separate fields. The soil on the Mormon Mesa is generally thinner than that on the Ogallala and has a higher bulk density. Calcic soils from New Mexico partly reflect the effects of initial (parent material) bulk density and would plot as a wide field in the lower left-hand corner below the Mesa-Jornada del Muerto field.

In the New Mexico-Texas area we have found sepiolite only in middle Pleistocene or older soils. Sepiolite occurs in association with palygorskite, palygorskite being the host mineral for sepiolite formation. Aristarain (1970) studied the clay mineralogy of the Ogallala "caprock" (pedogenic calcrete) in eastern New Mexico and reported that illite ($10\overset{o}{A}$ basal spacing) was the predominant clay mineral in the soil. We resampled Aristarain's soil profile no. 1 and found the two major clay minerals to be palygorskite and sepiolite. Since then, Frye and others (1974) have reported similar clay mineral assemblages for pedogenic calcretes on the Ogallala Formation in the southern High Plains. They believe that palygorskite and sepiolite are alteration products of montmorillonite, while Vanden Heuvel (1966) believes these minerals precipitated from solutions. Based on our studies we propose the following clay mineral authigenesis for calcic soils:
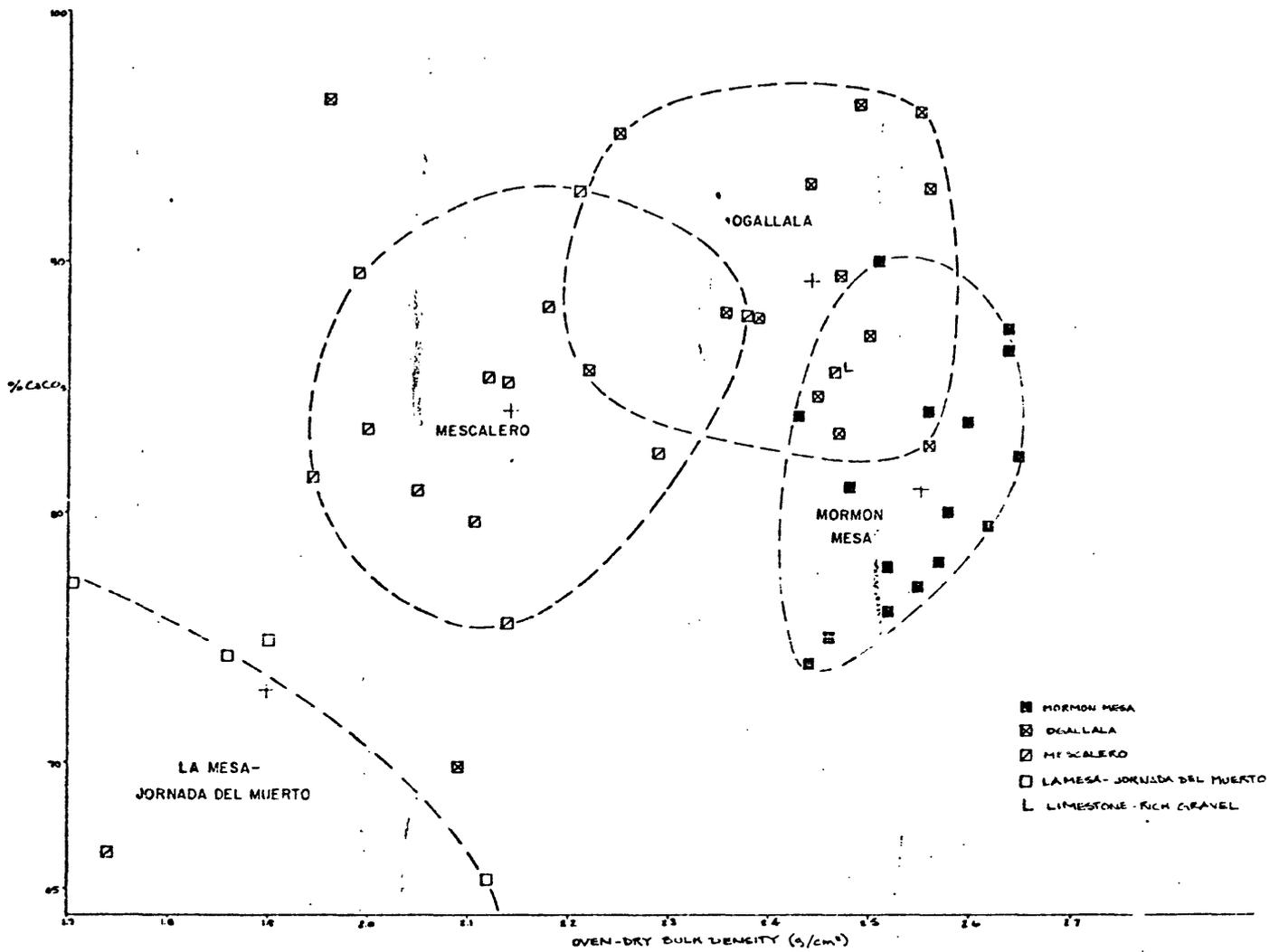
Figure 37.--Percent CaCO$_3$ versus bulk density for
    indurated horizons of calcic soils and pedogenic
    calcretes of the southwestern United States. Fields
    for soils developed on each surface are out_ined by
    dashed lines; the mean of each field is indicated by a
    cross.

---increasing total calcium carbonate--->

montmorillonite or
random interlayered ------> palygorskite ------> sepiolite
illite-montmorillonite

This scheme is similar to one proposed by Loughnan (1960) for clay

minerals in some Tertiary lake beds of Australia.

The transformation from palygorskite to sepiolite occurs in soils

of middle Pleistocene age or older in southern and central New Mexico;

sepiolite has not been noted in soils from either central and northern

New Mexico or from southern Nevada (Gardner, 1972.) Where present

sepiolites distribution follows that of $CaCO_3$ concentration in soils,

sepiolite occurring in areas of high calcium calcium carbonate

accumulation.

A common geochemical environment is necessary to explain both the

diversity of environments in which palygorskite and sepiolite form and

their widespread occurrence in calcic soils. In calcic soils, the

environment is one of moderately high pH (8-9), expandable clay mineral

hosts, abundant $(Ca,Mg)CO_3$ that supplies Mg, and a well-drained site in

an arid to semiarid climate. Watts (1976) utilized the palygorskite-

pedogenic calcrete association to postulate a semiarid climate for a

Permian-Triassic paleosol in southwest Scotland. In Morocco, Paquet and

Millot (1973) have shown that palygorskite is stable in soils which have

less than 300 mm of annual precipitation. Millot, Paquet, and Ruellan

(1969) have also shown that detrital palygorskite is being destroyed

within soils in wetter semiarid environments of Morocco. Additional

study of the distribution and abundance of palygorskite and sepiolite in

relict, buried, or exhumed soils may help to further decipher the pedo-

genic, climatic, and geologic histories of deposits and soils in an

area.

Physical properties of calcic soils

and pedogenic calcretes

Calcium carbonate is the primary chemical component of calcic soils and calcretes, and as such contributes to their physical properties. Perhaps the most apparent effect of carbonate accumulation is the increase in bulk density and induration of calcic soils ultimately resulting in pedogenic calcretes. These two features are largely dependent on the carbonate content of a soil. Other physical properties that are of primary geologic and engineering importance are the thickness, porosity, infiltration rate, and compressive strength of calcic soils and calcretes.

Carbonate content, bulk density, and porosity

Carbonate contents, bulk densities, and porosities of calcic soils are interdependent and are discussed together. Carbonate accumulations result largely in the filling of soil-pore space with semiporous carbonate matrix. This accumulation is accompanied by an increase in the soil bulk density, but complete impregnation of calcic soils does not occur as a result of pedogenesis. Laboratory and thin section data suggest that initially grain surfaces are coated with carbonat nd a semiporous matrix forms in the soil-pore space. Subsequent cementation forces framework grains apart as $CaCO_3$ crystallizes. Sand- to pebble-size clasts are forced from the zone of carbonate accumulation and as the clastic content decreases, the bulk density increases. The soil eventually becomes relatively impermeable to downward infiltrating soil water. This developmental scheme is portrayed in table 7, and uses s

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Table 7.—Calculated values of soil porosity, volume, and density based on laboratory data for soils of various ages in southern and southeastern New Mexico

[Column G illustrates the void-filling hypothesis. (See similar calculations by Gardner, 1972, and Yaalon and Singer, 1974.) Parent material for all examples is a medium-sorted, fine-grained noncalcareous alluvium (column A). Carbonate (c) is schematically shown as either coatings (black layers) or matrix cement (stipple). Symbols m and f in diagrams represent matrix (pore space) and framework grains respectively]
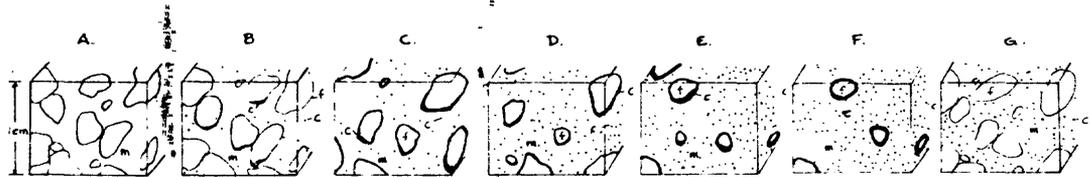
Parameter	Symbol	Units	Present clay parent material	Isaacks' Ranch: late Pleistocene	Pichaco: late Pleistocene	La Mesa: middle Pleistocene	Mescalero: middle Pleistocene	Ogalala late Pliocene	void-filling (hypothetical)
$CaCO_3$ content	Cc	%	0	.15	.30	.60	.75	.85	.42 (Wc÷Ds)
framework content	Cf		1.00	.85	.70	.40	.25	.15	.58 (Wf÷Ds)
bulk density of soil	Ds	g/cm³	1.6	1.65	1.7	1.85	2.10	2.40	2.76 (Wc+Wf)
specific gravity of $CaCO_3$	Dc	g/cm³	2.7	2.7	2.7	2.7	2.7	2.7	2.7
specific gravity of framework	Df	g/cm³	2.8	2.8	2.8	2.8	2.8	2.8	2.8
density of framework	Wf	g/cm³	1.6 (Cf·Ds)	1.40	1.19	74	.53	.36	1.60 (Vf·Df)
density of $CaCO_3$	Wc	g/cm³	0 (Cc·Ds)	.25	.51	1.11	1.58	2.04	1.16 (Vc·Dc)
volume of framework	Vf	cm³	.57 (Wf÷Df)	.50	.43	.26	.19	.1	.57 (from A)
volume of $CaCO_3$	Vc	cm³	0 (Wc÷Dc)	.09	.19	.41	.59	.16	.43 (from A)
volume of air	Va	cm³	.43 [1-(Vf+Vc)]	.41	.38	.33	.22	.11	0
porosity of soil	Ps	per cent	43 (Va×100)	41	38	33	22	11	0
porosity of matrix	Pm	per cent	100 ($\frac{Va}{Va+Vc}$×100)	82	61	45	27	13	0
specific gravity of matrix	Dm	g/cm³	0 ($\frac{Wc}{Va+Vc}$)	.50	.82	1.50	1.95	2.34	2.7

1/ measured value
2/ estimated value
3/ hypothetical value

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an example a soil-alluvium sequence from southern and southeastern New Mexico.

Gardner (1972) argued that calcic soils and pedogenic calcretes do not form strictly by accumulation of calcium carbonate in soil-pore space (that is, void filling) but by an expansion process. Data of Gile (1961), Gile, Hawley, and Gros an (1971), and this study confirm Gardner's argument. Goudie (1973, p. 25) recognized the same process of calcrete accumulation, a "tendency for the growth of $CaCO_3$ concentrations to lead to a dispersal of coarse grains," the result being "floating" grains (Brown, 1956). In calcretes from Libya (unknown origin) and Cyprus the silt and clay fraction comprise greater than 70 percent of the insoluble residue in samples with more than 80 percent $CaCO_3$ (Goudie, 1972). Unless the parent materials for these calcretes were silts and clays, the net result of their formation is a distinct decrease in grain size for the detrital grains. Grain size data for a calcic soil on the La Mesa surface are provided by Gile (1961, table 1, soil profile 1). The silt and clay fractions are greatest in the most calcareous horizons (table 8). Part of the clay and silt is authigenic, but the majority of the increase is due to a dilution of framework grains and upward movement of the coarser clasts.

Grain size, bulk density, and soil horizon thickness for the La Mesa pedogenic calcrete (Gile and others, 1971, p. A-68, 69) were used to calculate the original parent material thickness in which the soil was formed. If no framework grains are lost in the expansion process, the present content of framework grains (that is, insoluble residue 202.5 g; fig. 39) can be redistributed at its original concentration

Table 8.--Grain size (in percent) and calcium carbonate data for a middle Pleistocene soil in southern New Mexico

[Data from Gile, 1961, table 1, soil no. 1. Soil horizons modified to conform to modern nomenclature (Gile and others, 1965). Grain size listed in mm]

DEPTH (cm)	HORIZON	SAND					SILT	CLAY	SAND	CaCO$_3$ %
		vc	c	m	f	vf				
30 - 63	IIK21lm	-	0.4	0.8	6.8	20.2	39.0	32.8	28.2	93
30 - 63	IIK22m	1.3	6.4	10.1	32.6	18.3	14.2	17.1	68.4	65
63 - 102	IIK23m	1.9	8.6	13.8	35.9	9.3	17.3	13.2	69.5	62
102 - 178	IIK31	1.4	8.4	14.0	34.7	12.8	20.5	8.2	71.3	54
178 - 229	IIK32	1.0	7.5	15.1	35.8	5.6	26.8	8.3	64.9	32
229 - 315	IIC33ca	1.2	8.6	17.6	45.2	15.9	7.7	3.8	88.5	6
315 - 356	IICn	2.7	22.7	31.5	31.9	5.9	3.9	1.4	94.7	1

1/ Laminar part of K2lm horizon
2/ Blocky part of K2m horizon
3/ Recomputed from matrix and nodule components. Computation based on 15 percent nodules and 15 percent matrix.

(0.97 g/1.0 g soil and 1.60 g/cm^3). Thus computed, the original soil

parent   terial thickness is about 127 cm (table 9). Based on TiO$_2$

content   ? p. __) the computed thickness was 117 cm. The similarity

of both   ιculations suggest that the buried La Mesa pedogenic calcrete,

which is about 224 cm thick, has expanded about 1 m since the formation

of the La Mesa surface about one-half m.y. ago.

.Bulk densities of calcretes range from 1.2 to 2.7 g/cm^3 (table 10).

Undoubtedly, the wide range in values reported in the literature reflect

samples from different soil horizons, the maximum values being from

laminar and brecciated horizons. In Israel, Yaalon and Singer (1974)

showed that a nari (pedogenic calcrete formed on chalk) developed almost

entirely by compaction, the bulk density changing from 1.3 to

2.2-2.5 g/cm^3. Indurated horizons of calcic soils and pedogenic

calcretes in the southwestern United States range from 1.4 (anomalously

low due to dissolution channels in sample) to 2.65 g/cm^3; but the

majority of pedogenic calcretes are greater than 2.0 g/cm^3. Dense

limestones usually range from 2.54 to 2.72 g/cm^3 (Krynine and Judd,

1957), thus many calcretes approach limestones both in bulk density and

carbonate content (table 4).

Compressive strength and infiltration rate
of calcic soils and calcretes

Goudie (1973) lists some examples of the engineering properties of

calcretes, but their general nature and undistinguished origin prevents

us from drawing conclusions as to their relationship with degree of soil

development. Most calcretes and well-developed calcic soils tend to be

Table 9.—Original thickness of soil parent-material

[Soil parent-material assumed to be similar to Cn horizon: original bulk density = 1.65 g/cm³, and original CaCO₃ content = 0.03; then original insoluble residue concentration = 1.60 g/cm². Total weight of insoluble residue is 202.5 g/cm² (fig. 40). Original thickness is as follows:

$$\frac{202.5 \text{ g/cm}^2}{1.60 \text{ g/cm}^3} = 126.6 \text{ cm}]$$

Horizon	Depth cm	Thickness cm	Carbonate content	[1]I.R. content	Bulk density g/cm³	Total [1]I.R. content g/cm²	[1]I.R. conc. g/cm³	Initial [1]I.R conc. g/cm³	Expansion of [1]I.R. percent
IIK211mb	48–50	2	0.89	0.11	2.20	0.5	0.24	1.60	561
IIK22mb	50–74	24	0.76	0.24	1.90	10.9	0.46	1.60	251
IIK23mb	74–102	28	0.63	0.37	1.70	17.6	0.63	1.60	154
IIK31mb	102–150	48	0.52	0.48	1.65	38.0	0.79	1.60	102
IIK32b	150–185	35	0.46	0.54	1.65	31.2	0.89	1.60	80
IIK33b	185–236	51	0.40	0.60	1.70	52.0	1.02	1.60	57
IICtcab	236–272	36	0.12	0.86	1.65	52.3	1.45	1.60	10
IIC2b	272+	0	0.03	0.97	1.65	0	1.60	1.60	0
Total						202.5 g/cm3			

[1] Insoluble residue.

Table 10.—Bulk densities of pedogenic calcretes and calcic soils

[Symbol 1 of soil horizon designates laminar horizon, m designates indurated horizon]

| Author | Locality | Bulk density | | | Soil horizons |
		Range	No. of samples	Mean	
Netterberg, 1967	South Africa, calcrete	1.2 -2.7	10	--	Unknown
Goudie, 1973	Kalahari, calcrete	1.71-2.61	45	--	Unknown
Goudie, 1973	Libya, calcrete	1.81-2.50	7	--	Unknown
Yaalon and Singer, 1974	Israel, pedogenic calcrete	1.3 -2.5	20	--	Unknown
Gile, 1961	La Mesa, pedogenic calcrete	1.3 -2.22	14	--	K21m - Cca
Gardner, 1972	Mormon Mesa, pedogenic calcrete	2.52-2.65	6	2.62	K22m
Gardner, 1972	Mormon Mesa, pedogenic calcrete	2.46-2.58	8	2.53	K2m
This study	Ogallala, pedogenic calcrete	2.20-2.57	13	2.40	K21m, K2m
This study	Mescalero, pedogenic calcrete	1.97-2.38	13	2.12	K22m
This study	Llano de Albuquerque and La Mesa, calcic soils and pedogenic calcretes	1.40-2.20	115	1.71	K21m, K2m

nonplastic or slightly plastic (Gile, 1961; Goudie, 1973), hard, and fairly competent in compressive and shear tests.

Singer and Yaalon (1974) reported on the strength and porosity of nari (pedogenic calcrete developed on chalk). The main feature of this soil is a compaction of the chalk, a loss of porosity, and an increase in the dry unconfined compressive strength. Maximum strength ranged from 35-56 kg/cm^2 for upper indurated horizons and about 1.4 kg/cm^2 for the chalk. They also reported a strong negative correlation between porosity and strength.

Very little data is published on the strength of calcic soils or calcretes in the United States although we suspect a considerable body of data exists in files of local, state, and federal highway departments. Gile (1961) reported unconfined air-dry compressive strengths as much as 555 kg/cm^2 for very strongly indurated horizons (stage IV, La Mesa pedogenic calcrete); based on their bulk densities and carbonate contents the soils developed on the Mescalero and Mormon Mesa surfaces, and on the Ogallala Formation probably equal or exceed this value. Wet indurated samples averaged about 1/2 of their dry strength and wet nonindurated about 1/12 their dry strength (Gile, 1961). Post (1966, in Yaalon and Singer, 1974) reports compressive strengths of 10-250 kg/cm^2 for calcretes (probably ground-water type) near Tucson, Arizona.

Limestones generally exceed calcic soils in compressive strength (768 kg/cm^2; average of 12; Obert and others, 1946), while many of the blocky and laminar horizons of calcic soils are comparable in strength to concrete (U.S. Bureau of Reclamation, 1975).

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As a result of the dense cementation which leads to high strengths, permeability is greatly reduced, especially in near-surface horizons. Gile reported in situ infiltration rates of less than 1.3 mm/hr for laminar horizons to about 13 mm/hr for nonindurated calcic (Cca) horizons. In a more comprehensive study Cooley and others (1973) conducted surface and shallow bore-hole infiltration tests to investigate the effects that calcretes (largely ground water type) have on surface runoff in the Las Vegas area, Nevada. Infiltration rates for surface laminated horizons were as little as 1/100th of the underlying, less-well indurated horizons. They found that the runoff potential is largely controlled by calcrete development (cementation) and depth to the impervious barrier.

Our field observations lead us to conclude that, for calcic soils and pedogenic calcretes, infiltration rate and runoff potential are related to surface-material properties (that is, eolian sand versus indurated calcic horizons) and soil development. As in most cases, slope and vegetation are additional factors. Gully-bed cementation, case hardening, and petrocalcic (pervasively cemented) horizons all cause marked reductions in surface infiltration rates. Case hardening is known to occur relatively quickly, and Lattman and Simonberg (1971) reports examples of case hardened roadcuts. Pouquet (1966) mentions the formation of a thin but hard crust forming in Algeria during the war years 1939-45. Likewise, we have seen laminar layers in manmade drainage ditches on limestone-rich fan gravels in southeastern New Mexico. Thus it appears that some forms of calcretes may form quickly on landforms of most any age and as such may result in local to

widespread areas where surface water infiltration is greatly reduced. These areas pose severe environmental limitations to urban growth and development.

Thickness of calcic soil

The thickness of a calcic soil is partly a function of age, although various factors may affect this relationship. Generally, thicknesses of young soils of late Pleistocene or Holocene age reflect the zone in which carbonate precipitates after occasional wettings. In older soils, aggradation occurs both in response to expansion and blockage of infiltrating soil waters and to cementation of overlying material. Incorporation of younger materials into calcic soils, slow continual burial, or shallow episodic burial may result in attenuated carbonate distribution within soil profiles; the result is a poorly defined carbonate bulge and lack of an associated vertical zonation in soil morphology. Climate also influences the thickness of a calcic soil. Near the pedocal-pedalfer boundary in the midwestern part of the United States (Jenny, 1941) the top of calcium carbonate accumulation is deeper and the carbonate is less concentrated in the soil than in more arid areas; this is largely in response to increased annual precipitation. Thus, the comparison of depth of carbonate accumulation or thickness of accumulation should not be correlated with age in regional studies.

Calcium carbonate content

Due to differences in parent material such as soil permeability, porosity, and grain-size, as well as other soil-forming factors, carbonate content and thickness cannot be used solely to make quantitative comparisons of soils or for estimates of ages of soil.

A quantitative measure that is useful is the pedogenic calcium carbonate content of a calcic soil or pedogenic calcrete. The total amount of carbonate in a soil profile is not influenced by vertical carbonate distribution or by parent material characteristics (with the exception of consolidated or calcareous deposits). The total carbonate content of a calcic soil is the sum of the products of each calcareous horizon's thickness, bulk density, and carbonate content. Our calculations are in grams for a one square centimeter column through the soil profile, although similar calculations by Gile and others (1971) are expressed in kilograms per square meter. The pedogenic carbonate content of a soil is the difference between the total content and the primary (detrital) carbonate that was present in the parent material of the soil. Thus, when using pedogenic carbonate as a quantitative measure of calcic soil development the sampled soil profile must penetrate uncalcified parent material (Cn horizon). Layered parent materials also create problems because soil processes can completely mask the original characteristics of a parent material.

Use of calcic soils and pedogenic calcretes in

Quaternary geomorphologic, stratigraphic, and tectonic studies

Soils are an important aspect of Quaternary, geomorphologic, stratigraphic, and tectonic studies, but until recently have been used mainly in the context of relative age criteria. With the advent of radiometric dating, more precise control has been established for much of the Quaternary record. Soils continue to be widely used since they are commonly the most widespread chronostratigraphic tool. Although a substantial research effort has been made on "dating" soils, most efforts still rely on some type of radiometrically dated stratigraphic unit (volcanic flows and ashes or diagnostic fossils) associated with a soil or geomorphic surface.

Methods of dating geomorphic surfaces and soils

Various methods have been used to date Quaternary alluvial deposits and their geomorphic surfaces, the most often used being stratigraphic sequence, correlation by physical properties and geomorphic position, and soil development (Colman and Pierce, 1977). Methods used less often or those used under special circumstances, include historical and dendrochronological records (very young deposits), radiocarbon (deposits less than 40,000 yrs old), fossils and artifacts, rock and mineral weathering, and landform modification. Additionally, numerical methods such as Uranium-series, K-Ar, fission track, obsidian hydration, tephra hydration, thermoluminescence, or amino-acid racemization may be used if the appropriate material is associated with the deposit.

In the southwestern United States, geomorphic studies have typically utilized some combination of soil development, geomorphic position, and stratigraphic sequence; often these techniques are used to correlate alluvial deposits with glacial deposits.

Several methods have been used or are currently under development for directly dating calcic soils, the most widely used being radiocarbon (^{14}C). Williams and Polach (1971) were abl to date soil carbonate in young soils, while Gile, Hawley, and Grossman (1971) have had moderate success with Holocene soils. Older soils yield dates that tend to reflect late stage pedogenesis because new and old carbonate can be interchanged in the soil. Birkeland (1974) discusses the problems associated with ^{14}C dates in inorganic carbon.

Recently some workers have experimented with the Uranium-series disequilibrium method (Szabo, 1969) (which has been used mostly to date coral, molluscs, or bone) in dating calcrete and travertine. Ku (1974) reported U-Th dates for calcium carbonate in Holocene and Pleistocene soils of the Vidal Junction area, southeastern California (fig. 1). As used in calcic soils, the method measures Th^{230}/U^{234} ratios; ages are determined from decayed isotopic ratios, and covers a time span of about 300,000 yrs (Ku, 1974, p. G-B-1). Problems arise in the assumption of closed system conditions for the carbonate. Much of the data we have presented here suggests a continual process of carbonate accumulation, no doubt involving some partial solution and reprecipitation of existing soil carbonate. Many of Ku's samples, which from soil development and relative geomorphic position were thought to be 0.5 to 1.5 m.y. old, have U-Th ages of <300,000 yrs. Replicate analyses were run on

7 samples by Ku (1974, Amendment 1, p. G-A-13) to measure the reproducibility of U-Th ages from soils developed on alluvial unit Q2a. The estimated age of the alluvium, based on soil development (qualitative) is 50,000 to 200,000 yrs (Bull, 1974, Amendment 1, p. G-A-16). The U-Th ages for soils developed on Q2a range from 73,000 to 93,000 yrs, and average about 81,000 yrs for carbonate crusts on pebbles. Although it is difficult to assess the accuracy of the U-Th dates on soil carbonate, inasmuch as the analyzed samples have not been calibrated with other radiometric methods, U-Th ages on corals and gastropods generally are young if closed-system conditions have not been sustained.

Other radiometric or quantitative methods currently being investigated involve U-trend dating of soils (John Rosholt, U.S. Geol. Survey, written commun., 1977) maghemite-hematite conversion (Steve Mabey, Colorado Univ., written commun., 1977) and thermoluminescence (Rodd May, U.S. Geol. Survey, written commun., 1977). Laboratory analyses are still being performed using these methods. In each case some independent means of cross-reference will be necessary to assess the potential of the methods for dating calcic soils or pedogenic calcretes.

Methods of determining rates of calcic soil formation

Calcic soils and pedogenic calcretes are widespread on upper Pliocene and Pleistocene unconsolidated deposits in semiarid and arid parts of the southwestern United States. These soils are often associated with relict landforms and could be particularly useful for

analyzing amounts and timing of faulting, landform stability, and Pliocene-Pleistocene stratigraphic and geomorphic history.

The main purpose of this study is to develop methods of dating Quaternary fault movements in the southwestern United States. Preliminary work in central New Mexico (Bachman, 1976) led us to recognize the importance and potential widespread application calcic soils could have in our problem. As previously mentioned, efforts to date soils have been of limited success. If rates of calcic soil formation could be established by using radiometric calibration, soil ages could be estimated from the quantity of carbonate in the soil. Quantification of calcic soil and calcrete properties was necessary to provide a basis for evaluating soil development.

Numerous studies have been devoted to estimating rates of accumulation of carbonate in calcic soils. Jenny and Leonard (1934) observed that in the central United States the depth to calcic horizons in pedocals (calcic soils) increases with increasing rainfall. Empirically, they developed a formula

$$D = 2.5 \ (P-12),$$

where D is the depth to the upper surface of the carbonate horizon and P is the average annual precipitation. They believed this equation to be valid where P>12 and <40.

These observations were examined by Arkley (1963) who found them to be invalid for areas of the west coast and the southcentral part of the United States. He derived a similar formula with different constants:

$$D = 1.63 \ (P-0.45).$$

From this approach Arkley attempted to establish the rate of carbonate

translocation using climatic and soil-textural data. He empirically determined a calcium carbonate solubility in water and estimated the quantity of carbonate leached from the upper part and precipitated in the lower part, using an originally uniform distribution of carbonate throughout the soil. The calculated original carbonate content was compared with the present content to determine the amount of carbonate that moved. "Finally, the total carbonate translocated past any depth, divided by the rate of water movement past that depth [determined experimentally] and by the solubility of the carbonates, gives the minimum time required" to form the carbonate horizon (Arkley, 1963, p. 245-246).

Arkley was aware that this procedure has deficiencies. It does not correct for chemical unconformities in soil parent materials, and no allowance was made for either the effects of surface runoff, the possibility that carbonates were added to the surface as dust, or the role of plants. In addition, he did not consider the role of evaporation in the vadose zone or the fact that very few relict calcic horizons are overlain by their original profile.

In order to relate soil formation to age (time) it is necessary to control other soil-forming factors (Jenny, 1941). Throughout the course of our study, this aspect of the analysis was of paramount importance. Within New Mexico, sample sites were selected to minimize the effects of parent material, topography, climate, and biotic factors.

Soil sampling sites normally were located on stable upland surfaces, within similar ecozones in semiarid climates, and on unconsolidated noncalcareous alluvium. Additionally, soils developed on

fine-grained parent materials enabled bulk density measurements to be made more easily than on gravelly parent materials. Thus, the majority of our soil samples are fine grained.

When Jenny (1941) outlined his concept of soil formation, the importance of extraneous sources for some soil constituents (calcium carbonate and clay) was not recognized. In the southwestern United States the influx rate of calcium carbonate (dustfall) and time are primary factors in the development of calcic soils on stable sites. Other factors may become dominant but these cases are usually easily recognized from geomorphic or topographic relations.

The carbonate in a calcic soil is composed of two phases: 1) primary (detrital) carbonate deposited in, or with, the parent material, and 2) secondary (pedogenic and authigenic) carbonate that has accumulated since deposition of the parent material. Inasmuch as we want to relate soil age to degree of soil development, in terms of pedogenic carbonate content, accumulations of nonpedogenic carbonate, such as those in ground-water calcretes, are not considered.

Gardner (1972) was the first to calculate the pedogenic carbonate content of a soil on a weight-volume basis and to relate this measurement to soil age. Using the present rainfall (11.4 cm) in Overton, Nevada, (fig. 1) and the solubility of calcium (0.0160 g/L), he estimated the minimum time necessary to form the Mormon Mesa "caliche" (pedogenic calcrete), 890,000 yrs. Based on regional stratigraphic correlations the calcrete may be as old as 2.5 m.y.

Goudie (1973, p. 88) cites two rates of calcrete formation. The first, 360,000 yrs/m, is derived from Gardner's (1972) 890,000-yr-old

age for the Mormon Mesa. The second, 300,000 yrs/m is based on dust deposition rates, in Texas of 24 g/cm/kyr ·with 25 percent carbonate content in the dust. Goudie's calcrete formation rates are expressed in years of time necessary to form a meter of calcrete. As previously discussed, soil thickness is a function of. many variables. Likewise, the total carbonate content of a calcrete is a function of thickness, carbonate content, and bulk density of individual samples in a soil profile. By using Gardner's (1972) and Goudie's (1973) we have recalculated Goudie's cited rates in terms of grams of calcium carbonate accumulated on a one-cm^2 area per million years.

These two rates are about 460 (pedogenic) and 500 (total) $g/cm^2/m.y.$ for the Mormon Mesa and Texas sites, respectively. Based on our studies these rates are rapid; they compare with the most rapid rates we have established in New Mexico, although Goudie (1973, p. 85) states that the rate (500 $g/cm^2/m.y.$) from Texas dust fall data is "a rather low value."

Our method of establishing rates of calcic soil formation does not rely on annual precipitation (Gardner, 1972), soil texture (Arkley, 1963), or dust-fall rates (Goudie, 1973), but is based on the total amount of pedogenic calcium carbonate that has accumulated in a relict soil. The calculated rates are based on three assumptions:

1. The carbonate present in a soil is a cumulative product of soil processes since the time of deposition of the soil parent material. No material has been lost by leaching or erosion.

2. The calculated rate of accumulation is an average due to cyclic fluctuations in climates and carbonate influx rates. This

rate is applicable to soils of other ages (within the Quaternary in the region). Noticeable deficiencies in this assumption are young soils of Holocene or late Pleistocene age which may largely reflect one extreme of a cycle.

3. The rate is based on a soil of known age the age being determined by radiometric or paleontologic control and stratigraphic relations.

As previously discussed, careful sample site selection helps control some soil forming functions. Climatic changes in low-land areas of New Mexico were probably not severe enough to cause leaching of calcic soils. Sites at higher elevations (above 2,000-2,500 m altitude) may have experienced periods of deep soil-water penetration, and as such, may not be suitable for quantitative calcic soil studies. We are fortunate to have a well established soil datum in New Mexico. Other areas we have studied (fig. 18) do not have as much control and thus their rates should be considered less reliable.

Certain qualifications must be met in order to apply pedogenic carbonate content for estimates of calcic soil age. They are:

1. The soil parent material should be relatively noncalcareous; that is, <10 percent $CaCO_3$. Primary (detrital) and secondary (pedogenic or authigenic) carbonates are difficult to differentiate in soils developed on calcareous parent materials.

2. Paleoclimates under which relict calcic soils formed must have been either semiarid or arid. Excess moisture of wetter climates may have leached carbonate from the soil. For example, certain calcic soils withi pedalfer regions on the Colorado

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Piedmont or along the Arkansas River Valley near Buena Vista, Colo. (fig. 19) reflect cyclic episodes of carbonate accumulation and leaching (Machette and others, 1976).

3. Relict soils are most useful for soil age estimates. Buried soils can be used, but the soil age calculated represents only that time the surface was exposed to pedogenic processes. Carbonate content of eroded soils is useful to indicate minimum ages.

The total content of calcium carbonate in a soil is calculated from bulk density, carbonate content, and soil-horizon thickness data. The resultant value is the sum of two soil components; primary and secondary carbonate. Primary carbonate content is based on the concentration in the parent material (Cn horizon). Secondary carbonate is the difference between the total and the primary carbonate contents. In the case of pedogenic calcretes and calcic soils, the secondary carbonate component is pedogenic. All three values (total, secondary, and primary) are expressed in grams per unit area (1 cm^2) for a column through the soil profile.

For a more detailed explanation of the method of calculating carbonate contents the reader may refer to Gardner (1972) or Machette (1978).

Rate of calcic soil formation in

areas of the southwestern United States

There exists in New Mexico a series of widespread geomorphic surfaces which we think are broadly equivalent in age. These surfaces, the Mescalero, La Mesa and Jornada del Muerto, and Llano de Albuquerque (fig. 19) were formed about 500,000 years ago (see discussion, p.   ).

By controlling the effects of parent material, topography vegetation, and climate, any statistically significant changes in the development of relict calcic soils or pedogenic calcretes on these surfaces would reflect differences in rates of formation or ages of soils (table 11).

The rate of calcic soil formation in the Roswell-Carlsbad area of southeastern New Mexico exceeds all other areas we have studied in New Mexico, and is more than twice as rapid as in the Albuquerque-Belen Basin (table 11). We believe that the rate of dust influx and, more importantly, the $CaCO_3$ content of that dust is the prime determinant in the rate of calcic soil formation in regions of low rainfall. Carbonate contents of dust are determined by the amount of calcareous parent material and local climate (leaching-nonleaching) of the dust source area. The Roswell-Carlsbad area has an annual precipitation of about 330-355 mm (table 1), noticeably moister than the 205 mm of precipitation at Albuquerque. The increased precipitation in southeastern New Mexico (and western Texas) allows more effective downward movement of $CaCO_3$ into the soils; the net result is a rapid rate of accumulation of pedogenic carbonate (0.5 $g/cm^2/kyr$). Mean annual temperature of the study areas vary from about 13°-17^oC, the Albuquerque area being topographically highest and coolest (table 1).

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Table 11.--Pedogenic carbonate contents (C_s) and rates of calcium carbonate accumulation determined

for relict calcic soils of about one-half million years age in three areas of New Mexico

Area	Geomorphic surface	C_s, in g/cm^2 $\bar{x}\pm s$ (range)		Rate, in g/cm^2/kyr $\bar{x}\pm s$ (range)	
Albuquerque-Belen Basin	Llano de Albuquerque	110±11	(98-124)	0.22±0.02	(0.20-0.25)
Las Cruces	La Mesa-Jornada del Muerto	159±14	(150-188)	.32±.03	(.30-.38)
Roswell-Carlsbad area	Mescalero	257±30	(229-307)	.51±.06	(.46-.61)

How do these rates compare with other areas in the southwestern United States? Near Vidal Junction in southeastern California (fig. 10), calcic soils and various types of calcretes are developed on alluvium of many ages. Recent mapping by Wilfred Carr and Del Dickey of the U.S. Geological Survey (written commun., 1977) and soils investigations by Woodward-McNeil and Associates (1974) enabled us to sample a suite of soils. As previously discussed, the ages of the alluviums are not well known and individual alluvial units may represent fairly long intervals of deposition. Based on Ku's (1974) U-Th ages for soil carbonates and the development of both the argillic and calcic horizons, we have assigned an age of 200,000 years to the outlier of Q2a alluvium which Ku dated in replicate. The morphology and structure of soils on Q2a alluvium are not as well developed as those on some younger deposits (fig. 18) in the Las Cruces area such as the Picacho Alluvium of Gile and others (1971). Maximum carbonate buildup is stage III, although thick pebble coatings and some carbonate, which occurs preferentially along alluvial bedding planes, are present in the K21m horizon at a depth of 36-55 cm. The pedogenic carbonate content of one soil we sampled on Q2a (Woodward-McNeill and Associates, 1974, amendment 1, p. G-A-13, U-Th sample site 51) is 19 g/cm^2. Assuming an age of 200,000 yrs for the deposits the average rate of calcic soil formation in this area is about 0.095 $g/cm^2/kyr$ or about 30 percent of the Las Cruces rate. The age of many of the alluvial units in the Parker area were based on the soil morphological sequence established by Gile, Hawley, and Grossman (1971). Based on our age and ratio estimates soil morphology and total carbonate in soils of the Vidal Junction area

develops more slowly than in Las Cruces (fig. 18 and table 11). The above example illustrates the inadaquecies of regional soil correlations based on qualitative studies inasmuch as soil morphology and total carbonate develop at significantly different rates in response to local source, parent material, and climatic factors.

The Colorado Piedmont near Denver (fig. 19) is another area in which comparisons of rates of carbonate accumulation may be made with some degree of confidence. The Verdos Alluvium, a widespread pediment deposit, has Pearlette type O ash interbedded in the basal part of the deposit. At other localities the ash has been dated at about 0.6 m.y. (Naesar, Izett, and Wilcox, 1973). Thus the Verdos Alluvium is thought to be just slightly younger than 600,000 years old (Machette and others, 1976).

In some places a younger deposit (younger Verdos Alluvium) is inset into and graded to a slightly lower level than the (type) Verdos Alluvium. Near Broomfield, Colorado, about 30 km north of Denver, a well-developed calcic soil is present on the younger Verdos Alluvium. The soil is much more developed than that on the next younger depcsit, the Slocum Alluvium. Based on geomorphic position and degree of soil development, we estimate the age of the younger Verdos Alluvium to be about 450,000 years. The total carbonate content of the soil is about 40 g/cm^2; thus the average rate is about 0.09 g/cm^2/kyr or about one-quarter of the Las Cruces rate and comparable to that of the Vidal Junction area. The sampled soil near Broomfield is representative of those on the younger Verdos deposit (Machette, 1977a), although its position is within 10 km of the pedocal-pedalfer boundary as shown by

Malde (1955). Some loss of carbonate from excessive leaching may have occurred during times of moister climates. Main controlling factors of carbonate accumulation in pedocal soils of the Colorado Piedmont is the low calcium carbonate content of the dust and the relatively low concentration of Ca^{++} in rainwater (Junge and Werby, 1958); near the mountains annual precipitation becomes more important as a limiting factor by leaching soils of their carbonate.

Rates of carbonate accumulation are largely influenced by the climate and $CaCO_3$ source. For areas we have studied in the southwestern United States where calcic soils are now present, those soils may have formed at rates of from 0.09 to 0.51 g/cm/kyr. Soil correlations based on total soil carbonate contents or soil morphology can be erroneous without the establishment of a known soil datum for the rate of soil development.

Changes in rate of pedogenic carbonate accumulation

There are substantial differences in rates of calcic soil formation, at least on a regional basis, but what effects have climatic changes had on the rate of formation of calcic soils?

Soils of various ages, from Holocene to middle Pleistocene, are developed on alluvial deposits near Las Cruces, New Mexico. Detailed pedologic and geomorphologic studies by the SCS (Hawley, 1975) has generated a wide suite of soil profiles which are accompanied by thorough laboratory analyses. We have either calculated the pedogenic carbonate content or used published values from Gile, Hawley, and Grossman, (1971) to plot the rate of formation versus soil age (fig. 38). The wide range in rates is the result of using age ranges for each alluvium: for example, 50,000-75,000 yrs for a late phase of the Picacho Alluvium. Soils that are older than 50,000 years plot with rates of 0.2-0.4 g/cm^2/kyr, while the average rate for soils on the La Mesa surface are 0.32 g/cm^2/kyr. Soils of late Pleistocene and Holocene age appear to have higher rates although uncertainities in the age result in large differences in the calculated rates. If the age ranges for these soils are correct there seems to have been an increase in the rate of calcic soil formation during Holocene time. Warmer and (or) drier climates would support a less extensive vegetational cover and increase the potential amount of calcareous dust available to the soil surface.

Annual precipitation is a critical soil forming factor for calcic only either when the supply of CaCO$_3$ exceeds the leaching potential of the annual precipitation or when the annual precipitation is so great

Fillmore alluvium   Isaacks' Ranch   Picacho and   La Mesa
                      alluvium   Jornada II   alluvium
                                        alluviums

0.9

0.8   Picacho   Jornada I
                                        alluvium   and La Mesa II
0.7   (late phase)   alluviums

0.6
Rate, in
0.5
g/cm²/kyr
0.4   59-7   59-16   61-8   61-7
                                   59-6   60-21
0.3   68-4   61-9   60-2
         62-3   68-9
0.2   59-13   59-6   65-7
              66-16
0.1
         1   2   .3   5   10   20   50 75 100   200 300 500 700 1000

Time, in 10³yrs (log₁₀ base)
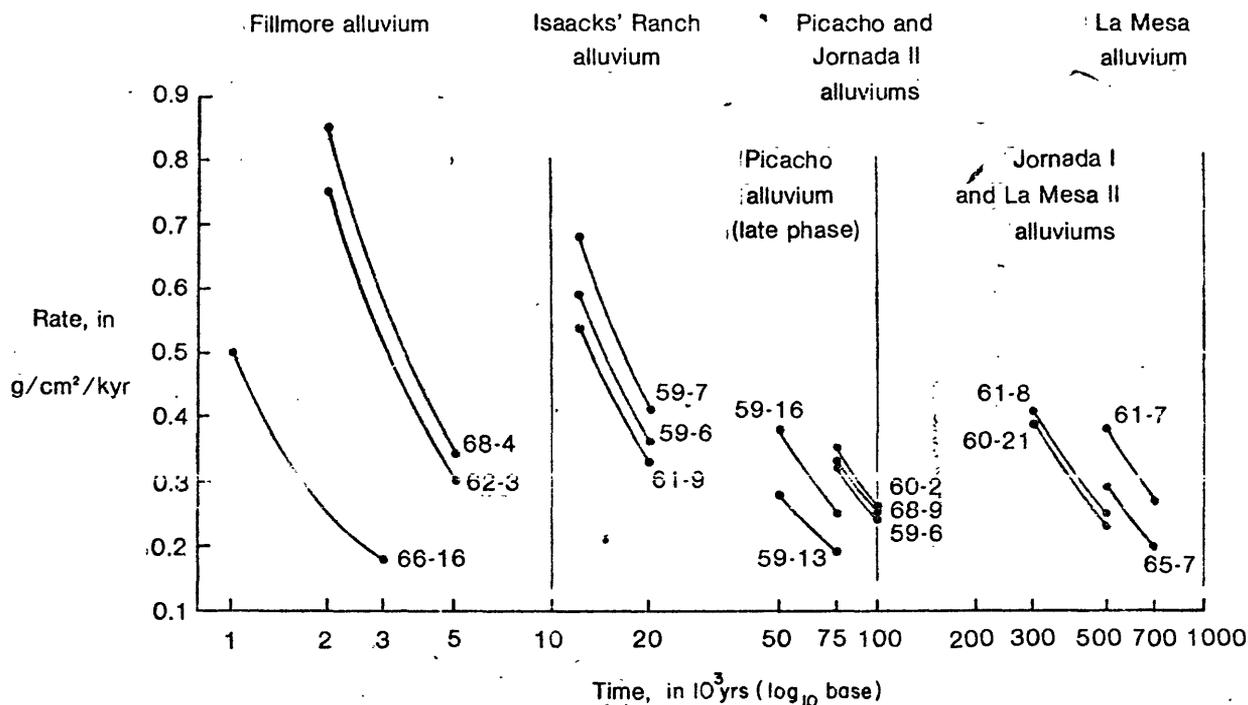
Figure 38.--Rates of pedogenic calcium carbonate accumulation in soils
near Las Cruces, New Mexico. Age and total CaCO₃ for Fillmore
Alluvium from Gile, Hawley, and Grossman (1971, p. 58). Ages for
other alluviums estimated from Hawley and others (1976, p. 244).
Pedogenic CaCO₃ for all other soils is calculated from laboratory
data of Gile (1971). Arrows on bars indicate CaCO₃ values
considered to be minimum due to erosion or burial of soil. Soil
sites are indicated by SCS pedon numbers (Gile and others, 1971).

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that carbonates are leached from the soil profile. For example, the $CaCO_3$ supply/annual precipitation ratios are highest for two of our study areas; Vidal Junction, California, and southeastern New Mexico. In both cases the annual precipitation probably limits the amount of $CaCO_3$ that will be precipitated in the soil. The two other areas in New Mexico (table 11) probably have experienced limited $CaCO_3$ supply relative to annual precipitation, a condition that exists in most areas of the southwestern United States.

Multicyclic climatic changes probably cause flucuations of rate and the results of figure 38 suggest that interpluvial (interglacial) climates may be most favorable to maximum accumulation rates for calcic soils.

Correlation of Quaternary deposits using calcic soils data

A series of Quaternary alluvial deposits are present along the Rio Grande in New Mexico, some or all being present at different localities. Previous attempts to correlate these deposits (Ruhe, 1967) were based almost entirely upon height above stream level. This criteria is valid in certain cases and has been used successfully in stable tectonic areas such as the Colorado Piedmont (Scott, 1963; Machette and others, 1976). On the other hand, Quaternary stratigraphic correlations based on topographic position can result in gross miscorrelations in actively tectonic areas such as the Rio Grande rift of New Mexico.

We have made some tentative correlations for Quaternary alluviums, their geomorphic surfaces and soils which are present along the Rio Grande (fig. 39). These correlations are based primarily upon pedogenic
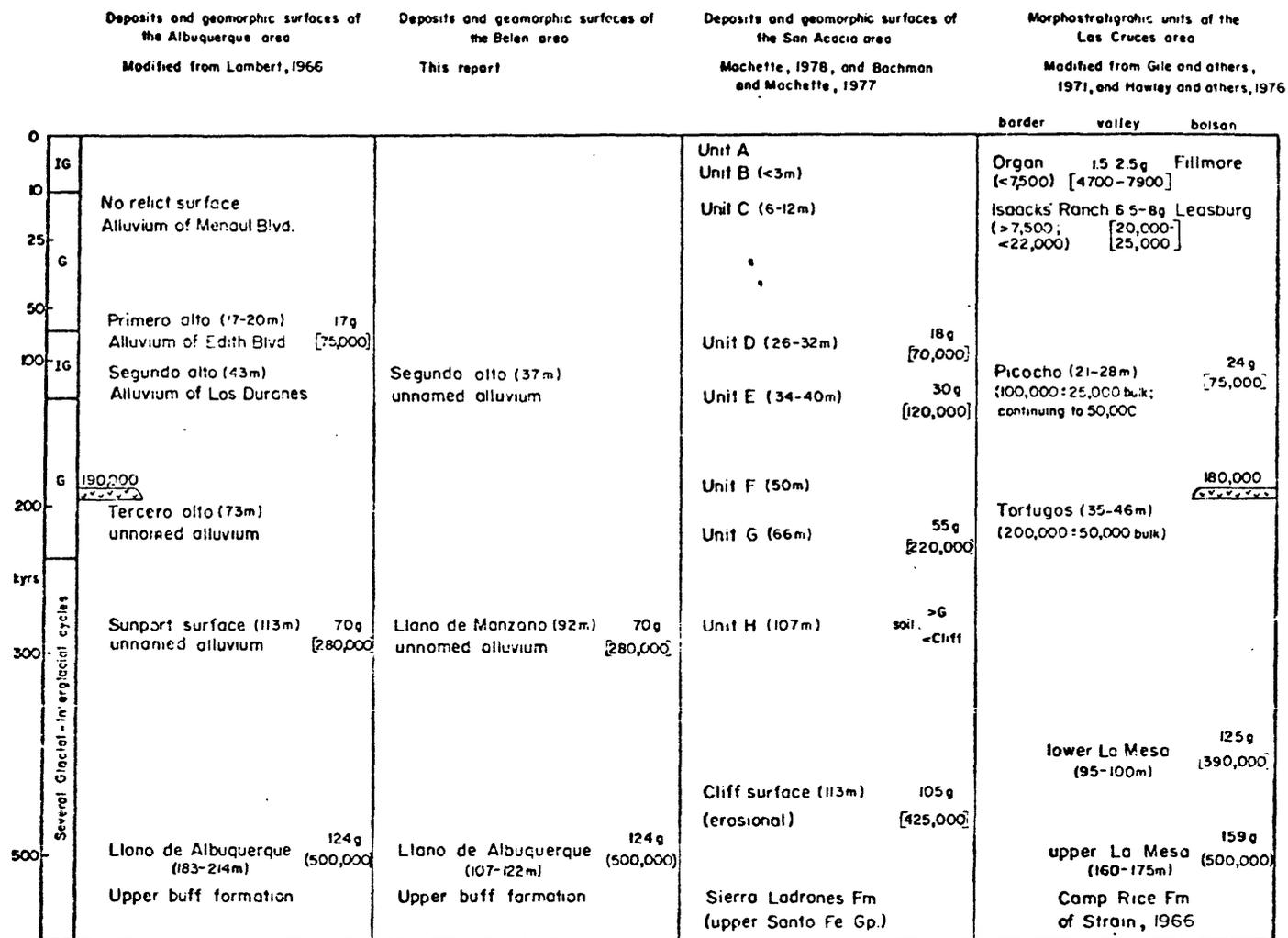
Deposits and geomorphic surfaces of the Albuquerque area Modified from Lambert, 1966	Deposits and geomorphic surfaces of the Belen area This report	Deposits and geomorphic surfaces of the San Acacia area Machette, 1978, and Bachman and Machette, 1977	Morphostratigraphic units of the Las Cruces area Modified from Gile and others, 1971, and Hawley and others, 1976		
			border	valley	bolson
No relict surface Alluvium of Menaul Blvd.		Unit A Unit B (<3m) Unit C (6-12m)	Organ 1.5 2.5g Fillmore (<7,500) [4700-7900] Isaacks' Ranch 6 5-8g Leasburg (>7,500; [20,000] <22,000) [25,000]		
Primero alto ('7-20m) 17g Alluvium of Edith Blvd [75,000] Segundo alto (43m) Alluvium of Los Durcnes	Segundo alto (37m) unnamed alluvium	Unit D (26-32m) 18g [70,000] Unit E (34-40m) 30g [120,000]	Picocho (21-28m) 24g [75,000] (100,000±25,000 bulk; continuing to 50,000		
190,000 Tercero alto (73m) unnamed alluvium		Unit F (50m) Unit G (66m) 55g [220,000]	180,000 Tortugos (35-46m) (200,000±50,000 bulk)		
Sunport surface (113m) 70g unnamed alluvium [280,000]	Llano de Manzano (92m) 70g unnamed alluvium [280,000]	Unit H (107m) soil. >G <Cliff			
		Cliff surface (113m) 105g (erosional) [425,000]	lower La Mesa 125g [390,000] (95-100m)		
Llano de Albuquerque 124g (183-214m) (500,000)	Llano de Albuquerque 124g (107-122m) (500,000)	Sierra Ladrones Fm (upper Santa Fe Gp.)	upper La Mesa 159g [500,000] (160-175m)		
Upper buff formation	Upper buff formation		Camp Rice Fm of Strain, 1966		

Figure 39.—Tentative correlation of Quaternary alluvial deposits and geomorphic surfaces along the Rio Grande in New Mexico. Correlations are based upon pedogenic soil carbonate content, soil morphology, height above stream level (shown in parentheses), and configuration of alluvial deposits (for example cut-and-fill terraces, strath terraces, and so on). Estimated soil ages (shown in brackets) are based on pedogenic carbonate content in relict soils of 0.5 m.y. age. Maximum values of carbonate contents for relict soils are used for age estimates, not average values. Chronologic age control for alluvial units shown in parentheses. Two K-Ar dated basalt flows are shown in their stratigraphic position.

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carbonate content, soil morphology (see fig. 18) and configuration of alluvial units (that is, cut-and-fill terraces, strath terraces, and so on). Topographic position is included for comparison.

Two surfaces which have not been previously discussed either here, or in the literature, are the tercera alto and Sunport. The tercero alto is a surface which Lambert (1966, p. 37) designated as the "surface underlain by Albuquerque volcanoes basalt." The basalt flowed on a former terrace level of the Rio Grande and is partly equivalent to old terrace gravels recently mapped at the north end of the Llano de Albuquerque (Bachman and Machette, 1977). The oldest of the basalt flows of the Albuquerque volcanoes rests on the tercero alto and has been dated by the K-Ar method at 190,000±40,000 years (Bachman and others, 1975).

The Sunport surface (fig. 39), an informal term, is equivalent to Lambert's (1966, p. 29) higher part of "the Sandia piedmont plain" and is best considered as an isolated section of the Llano de Manzano, a widespread piedmont slope surface.

Based on our correlations, the topographic position of correlative alluvial deposits is generally higher in the northern (upstream) part of each geographic basin but are at different heights in separate basins. This topographic relationship may reflect a lack of major integration of depositional basins in late Santa Fe time (pre-0.5 m.y.), as each basin continued to aggrade. The oldest surface which reflects a continuously-integrated drainage course for the Rio Grande is the Llano de Manzano, about 280,000 years old. This surface is not recognized in the Las Cruces area.

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If our preliminary correlations are correct, expansion of the active magma-chamber underlying the Socorro area (Sanford and others, 1976; Oliver and Kaufman, 1976), which has been detected in releveling studies (Reilinger and Oliver, 1976), has not had a profound effect on the late Quaternary geomorphology of that area. More importantly, these correlations may indicate that an atypical stress-stat exists at present in that area. More detailed studies of the Quaternary geology of this area is highly warranted in conjunction with ongoing geophysical studies.

Based on soil age estimates (figs 18, 39), the following alluvial deposits are broadly correlative in the Denver (Machette and others, 1976) and Las Cruces (Hawley and others, 1976) areas:

a) Piney Creek and post-Piney Creek: Organ-Fillmore

b) Broadway: Isaack's Ranch-Leasburg

c) Louviers: Picacho

d) Slocum: Tortugas

e) Verdos: La Mesa (upper)

Deposition of the lower La Mesa surface was controlled largely by faulting and represents a total geomorphic surface. Units equivalent to the Rocky Flats and Nussbaum Alluviums are not preserved as relict surfaces in New Mexico but are present as parts of the Camp Rice Formation of Strain (1966), a basin-fill deposit.

Other uses of pedogenic carbonate content of calcic soils

The use of pedogenic carbonate content for making soil age estimates, stratigraphic correlations, and analyses of soil-formation rates has been discussed previously. Two other applications that we have developed are the use of calcic soils in evaluating the occurrence of displaced and deformed geomorphic surfaces and in evaluating the history of fault movements where buried sections containing calcic paleosols. These two applications are the subjects of recent papers (Bachman and Machette, 1977; Machette, 1978).

Under certain topographic and geomorphic conditions the analysis of surface and subsurface configuration of calcic soils can resolve the positions of Quaternary faults and magnitudes of fault displacement. For one example near Albuquerque, New Mexico, we have been to demonstrate repeated episodic-faulting by analyzing carbonate contents of buried calcic paleosols and relict calcic soils. Both the magnitude of displacement a history of four discrete episodes of movement occurred during the past 400,000 years, the most recent activity occurring about 20,000 years B.P. (Machette, 1978). Recurrence intervals between episodes of faulting vary from 90,000 to 190,000 yrs, although each episode may consist of more closely spaced fault movements which are not discernable in the soils-sediment record.

Analytical procedures and laboratory methods

Calcium carbonate content

Calcic soils were routinely analyzed for calcium carbonate content by the Chittick (gasometric) method (Assoc. Official Agr. Chemists, 1945; Dreimanis, 1962). A known weight of calcareous soil is dissolved with 6N HCl and the volume of CO_2 evolved is measured. Corrections are applied to standardize both temperature and atmospheric pressure. Dreimanis (1962) provides a careful outline of both the analytical procedures and errors inherent in making calcite and dolomite analyses with the Chittick apparatus.

In this study certain modifications were made to expedite the analyses or to increase the precision of the method. Magnetic stirring devices help to promote rapid and complete dissolution of calcite grains. Mechanically splitting pulverized (<2 mm) samples reduces sample inhomogeneity and the use of maximum sample size increases the volume of CO_2 produced. Sample weights, which produce small CO_2 volumes, and sample inhomogeneity were found to be the primary source of laboratory error.

The Chittick apparatus has a 200-ml capacity, graduated manometer tube in which the evolved CO_2 is collected. Although the tube is graduated in 1-ml volumes, careful reading allows volume estimates of ± 0.5 ml. The resultant error is a function of CO_2 volume (fig. 40). The minimum reading error will occur with maximum (200 ml) CO_2 volume. Thus, it is advantageous to maximize CO_2 volume by adjusting, proportionately, sample size. Samples that contain low carbonate content (<10 percent) usually require more than 4 g to produce 100 ml of
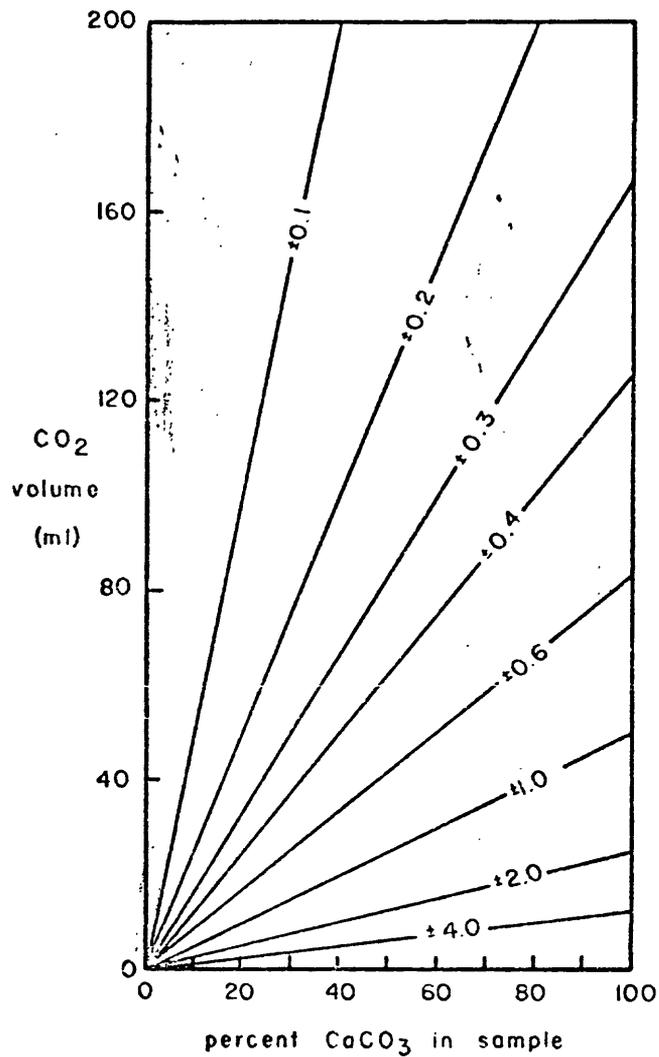
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Figure 40.--Expected error in $CaCO_3$ content as a function of evolved CO_2 volume with an assumed manometer reading error of ± 0.5 ml.
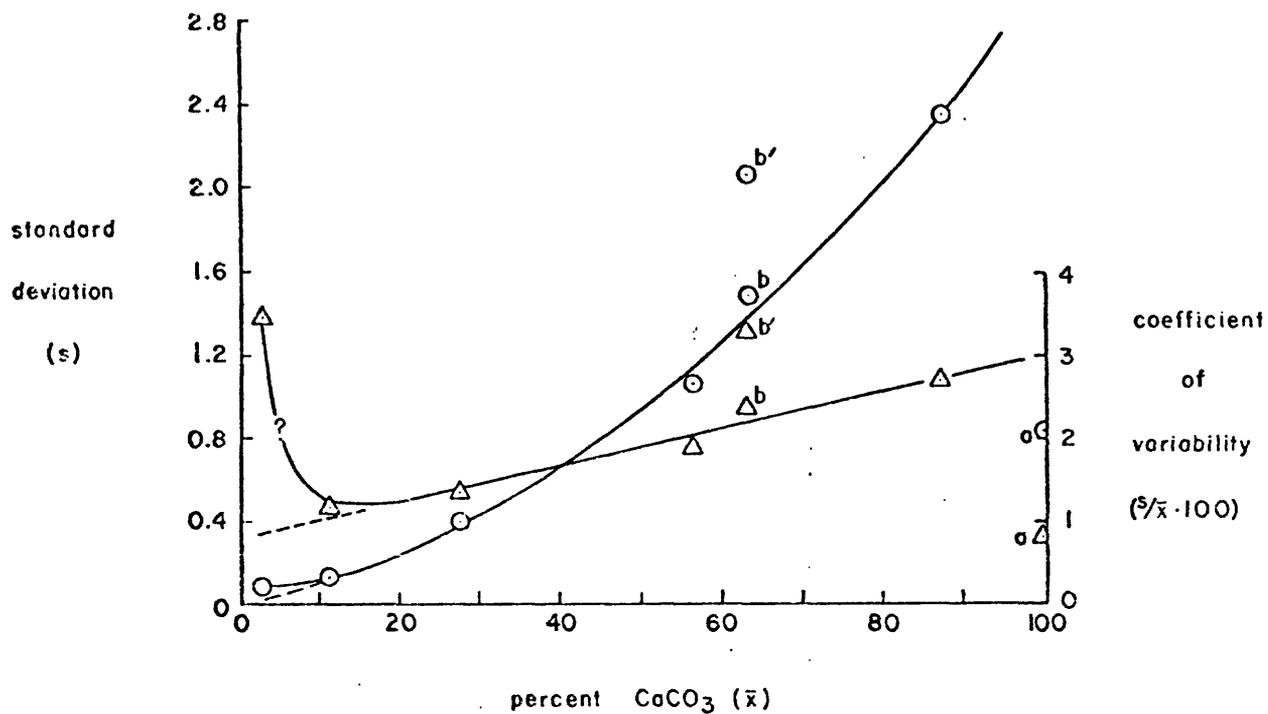
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Figure 41.—Standard deviation (open circles) and coefficient of
variability (triangles) for replicate analyses of CaCO$_3$
content. Sample "a" is reagent grade CaCO$_3$ (100.01 percent);
samples b and b' are ground to <2 mm and <200 micron
respectively.

CO_2, while pure $CaCO_3$ yields 200 ml of CO_2 from approximately 1/3 g of sample. (Both examples are for analyses. made in Denver, 1,610 m altitude; analyses at sea level require slightly more sample.)

Replicate analyses of carbonate content were performed to determine how much variation might be expected as a result of sample inhomogeneity and instrument error. Bag samples were ground to <2 mm-size and seven subsamples were mechanically split from each. Six subsets of samples were analyzed for carbonate contents, yielding a range of 2.6 to 87 percent carbonate. The mean ($\bar{x}$) and population standard deviation (s) were computed for each subset (fig. 41). The coefficient of variability ($s \div \bar{x} \cdot 100$), a commonly used index of precision (Murphy, 1961), increases linearly with increasing $CaCO_3$ content; at 90 percent $CaCO_3$, 2/3 of all subsamples should fall in the range of 87.3-92.7 ($\pm s$: 2.7 percent) $CaCO_3$.

To evaluate the effect of sample coarseness one subset was tested both in the <200 micron size and the <2 mm size (b and b' respectively, fig. 41). The coarse subset had 1.4 times the fine subset's standard deviation, thus grinding samples to finer mesh sizes helps reduce sample inhomogeneity.

Reagent-grade $CaCO_3$ (100.01 percent) was tested, in replicate, to analyze the precision and accuracy of the Chittick apparatus (fig. 41). The mean ($\bar{x}$ = 99.8) shows that the apparatus and technique yield accurate measurements and the standard deviation (s = 0.88) verifies the precision (reproducability) of measurements. Thus, it appears that the major source of error in Chittick analyses lies in sample inhomogeneity, and this error can be reduced by pulverizing samples to <200 micron size.

The Chittick method was also compared to CaO analyses made by atomic absorption spectrographic (AAS) methods. A special leaching procedure (see Ca:Mg analyses) was used to prepare calcareous samples. $CaCO_3$ values for Chittick and AAS analyses were compared for splits of the same sample (fig. 42). Although sample inhomogeneity is inherent in this comparison, the plot of values shows a strong positive correlation (coefficient of determination = 0.99) between the two methods. The line of best fit indicates that $CaCO_3$ values for Chittick analyses are slightly higher than those of AAS (line formula: AAS = 2.15 + 0.94 Chittick) above 40 percent $CaCO_3$ and vice versa below 40 percent $CaCO_3$. The t-test was used to compare differences between paired data for the two $CaCO_3$ methods. Using the null hypothesis that the mean of differences between paired-samples is not significant, the t-test provides a critical value (t-value) at a specific significance level. The AAS and Chittick population did not differ at the 0.005 percent level of significance. Thus, the above statistical tests and laboratory experiments show that the Chittick apparatus yields $CaCO_3$ measurements comparable to the more expensive AAS analysis. Additionally, the Chittick is relatively quick, easy, and inexpensive to operate.

Comparison of AAS and Chittick results with those of the Versine titration method (see Ca:Mg analyses) proved to be the least correlative. Both comparisons (AAS versus Versine and Chittick versus Versine) reject the above null hypothesis at the 0.005 percent confidence level. Poorer correlation is due to the fact that the Versine method measures total CaO in the sample, rather than Ca^{++} in the carbonate fraction of the sample.
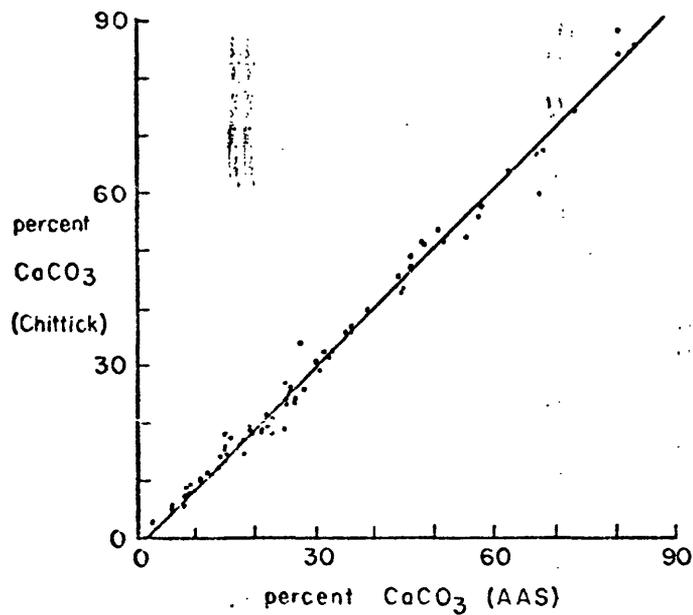
Figure 42.—Percent CaCO$_3$ for two methods of analyses:
Chittick and AAS (atomic absorption spectrography).

Calcium oxide and magnesium oxide contents of acid soluble fractions of calcareous soils were determined both by the Versine titration (Shapiro and Bannock, 1956; Shapiro, 1962) and AAS methods (Shapiro, 1975). The Versine (disodium ethylenediamine tetraacetate) method allows measurement of calcium oxide by titration using murexide (ammonium purpurate) as an indicator and magnesium oxide by titration using Eriochrome Black T as an indicator. Iron and aluminum are complexed with sodium potassium tartrate and do not interfere. The titration is carried out visually for carbonate rocks (or soils). Results from the Versine titration method reflect total CaO and MgO in samples since the sample is totally dissolved.

The AAS method used here was developed in cooperation with Wayne Mountjoy (U.S. Geol. Survey) and is designed to measure CaO and MgO contents of the calcareous fraction of soils. The less than 2 mm fraction is pulverized to pass a 80-mesh size. A representative subsample (0.500 g) is dissolved in a 1N buffered solution of glacial acetic acid and sodium acetate (pH = 5.0). The sample is placed in a steam bath (80-90°C) for 0.5 hr, stirred 3-4 times, then the supernatant liquid is centrifuged and decanted. The insoluble residue is leached again, decanted, and washed. An alloquot of the combined decantant volume is then diluted for CaO and MgO determination by AAS.

The special leaching procedure described above was used because many calcareous soils have substantial quantities of palygorskite and (or) sepiolite (see clay mineralogy section), two clay minerals which are susceptible to dissolution in various acids (Vanden Heuvel, 1966;

Nathan, 1968; Abdul-Latif and Weaver, 1969; Jackson, 1969; and Mendelovici, 1973). Their dissolution is thought to release Mg, thus any analysis (that is, Versine) using unbuffered acidic solutions will reflect anomalously low Ca:Mg ratios for the calcareous fraction of soils.

X-ray diffraction patterns of clay minerals from leached soil samples show the same crystallinity and relative abundance as in unleached samples, thus we believe that the leaching procedure is not affecting the clay minerals or framework grains. Thus, the CaO and MgO contents, as determined by AAS, reflect the chemistry of the calcareous fraction of calcic soils.

Bulk density

Bulk density (g/cm^3) determinations were made for most soil samples by one of two methods. The paraffin-coated clod method (Am. Soc. Testing Materials, 1974; Chleborad and others, 1975) was used on moderately to well-indurated samples. The other method involves driving a volume-calibrated sampling tube into a vertical face of a soil. The resulting volume (100 or 200 cm^3) is then oven-dried and weighed and direct computation of the oven-dry bulk density is made. For A, Bs, Cca, or Cn soil horizons the sampling tube is the only practical method to obtain bulk-density measurements. Compaction and inaccuracies in measurement probably result in a ±10 percent error; Chleborad and others (1975) have shown that the clod method yields a coefficient of variability ($s \div \bar{x} \cdot 100$) of less than 0.3 percent.

X-ray diffraction

X-ray diffraction patterns were made of clay mineral fractions from 10 soil profiles (45 horizon samples) in central and southern New Mexico. We followed the preparatory techniques of Vanden Heuvel (1966) for leaching and Jackson (1969) for clay mineral segregation and mounting. Clay-size fractions ($<2\mu$) were suctioned onto ceramic tiles. Air-dry, glycolated, and $550^{o}C$ heat-treated tiles were routinely run for clay mineralogy. Both Picker-Nuclear and Phillips-Norelco x-ray diffractometers were used. For the x-ray diffraction pattern shown in the text the following settings apply: 35 Kv, 20 mA, copper-K radiation ($1.5418\overset{o}{A}$) time count of 3, 1000 count-full scale deflection, 1 degree/minute scan speed.

Scanning electron microscopy

Numerous soil samples as well as ground-water cement, limestone, and calcareous crusts on limestone pebbles were examined under a Cambridge Stereoscan 180 scanning electron microscope and a Kevex energy-dispersive spectrometer. Most samples were mounted without any special chemical or physical preparation so as to preserve soil-matrix texture and fabric as well as carbonate and clay-mineral morphology. The Kevex system enabled semiquantitative spectral analysis during high-power scanning.

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