PERSISTENCE OF A ZEOLITE IN TUFFACEOUS SOILS OF THE
TEXAS TRANS-PECOS

by

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CHAPTER I

INTRODUCTION

Soil mineralogy is often considered to be a rather arcane discipline: mostly scholarly erudition of little practical use. The study of weathering phenomena of soil minerals would seem to be one step further removed from practicality. What is the practical use, for example, of a mineral weathering sequence?

Soil fertility has always had a claim to practicality, but so has soil mineralogy, although the practicality has not been as readily apparent. The two disciplines, though, are in fact intimately related. A knowledge of the fertility status of a soil is not complete without a knowledge of the mineralogy of that soil, because the latter controls availability of many nutrients.

C. E. Marshall (1977) stated:

The exchange complex is clearly the chief link between the geographical and chemical aspects of soil (p. v).

Mineralogy (the exchange complex), then, is the connection between the factors of soil formation and the fertility or chemical aspects of soils. If the minerals that are likely to occur in given situations are known,

i.e., a weathering sequence, then important predictions about soil chemistry and fertility, which are based on knowledge of soil forming factors (topography, parent material, etc.), can be made. This predictive ability is perhaps the most powerful use of soil mineralogy. The study reported herein was an investigation of soil mineralogy and mineral weathering of selected soils in West Texas. It will hopefully illuminate the relationships between mineralogy and soil-forming factors in the study area. It will then serve as a basis for making inferences about soil productivity and other soil properties.

The soil mineralogy of three soils from the Texas Trans-Pecos was investigated during the course of this study. The principal mineral on which the study was focused, a zeolite, has been known for some time to occur in tuffaceous sediments of the Trans-Pecos. The specific objectives of this study were to:

1. Identify the zeolite species in the soils.
2. Determine transformations, if any, the zeolites have undergone during weathering and pedogenesis.
3. Identify, if possible, soil properties related to the presence of zeolites.

CHAPTER II

LITERATURE REVIEW

Zeolites were first discovered by the Swedish mineralogist, Cronstedt, in 1756. Because of their peculiar itumescence or frothing when heated, Cronstedt called these minerals "boiling stones" (zeolite, from the Greek zein, to boil, and lithos, stone). Zeolites were soon recognized as common constituents of vugs and cavities of basalts and other extrusive igneous rocks. For the next 200 years they were rarely recognized elsewhere and were primarily considered to be a geological curiosity of minor significance (Mumpton, 1977).

Chemists began to discover interesting properties associated with zeolites, especially the molecular sieve effect, in the 1930s (Mumpton, 1977). Because of the rarity of these minerals, chemists began synthesizing zeolites for use in commercial applications. Reports began to circulate of zeolites in environments other than basaltic vugs, particularly in sedimentary rocks, during the next two decades. Spurred by the commercial interest in zeolites, geologists began to find them in more extensive, often economic quantities. Today they are considered to be common constituents of many sedimentary deposits. Both

synthetic and natural zeolites are now used in a wide variety of applications (Mumpton, 1977). These include radioactive waste treatment, sewage treatment, oxygen production, removal of nitrogen from agricultural waste waters, and use as soil amendments, among many others.

Zeolite Crystal Chemistry

Zeolites are hydrated aluminosilicates of the alkali and alkaline earth cations of the tectosilicate mineral group. They are similar to the feldspars, but have a considerably more open framework. Zeolite frameworks consist of silica and alumina tetrahedra infinitely extended in three directions. Cations and water molecules within these frameworks can easily be exchanged or removed without structural alteration, in contrast to the feldspar group, in which only surface cations can be exchanged without alteration to the framework.

Gottardi (1978) gives a general formula for zeolites:

M = Na, K, or other monovalent cations

D = Ca, Mg, or other divalent cations.

Zeolites occur in all six crystallographic systems (Hay, 1966). They have been classified several different ways. Deer et al. (1962) grouped zeolites according to their dominant direction of bonding: (1) the natrolite

group, in which tetrahedral linkages are more numerous in one crystallographic direction than in the plane at right angles, resulting in a fibrous morphology; (2) the heulandite group, with linkages more numerous in one crystallographic plane than in a direction at right angles, resulting in a platy morphology; and (3) the phillipsite group, in which the bonding strength is equal in all directions. More recently, zeolites have been classified according to type of framework based on "secondary building units" or assemblages of tetrahedral linkages, e.g., single four rings, double six rings, etc. (Breck, 1974; Gottardi, 1978). There are approximately 23 types of framework structures for all zeolites, including synthetic ones, but there are only seven main types for the natural zeolites. Gottardi (1978) provides another classification based on the ratio: $R = \text{Si}/(\text{Si} + \text{Al} + \text{Fe})$. In all zeolites $0.50 < R < 0.87$. Gottardi groups zeolites as acid, intermediate, or basic, depending on R (R smallest for basic zeolites). The more acid, siliceous zeolites are the most hydrated and most disordered, and consist mostly of the heulandite group (Hay, 1966; Gottardi, 1978).

The heulandite group is one of the more common zeolite groups. It is also the most commonly reported group in freely drained, non-sodic soils. In addition, the zeolite reported in this study is a member of the

group. Therefore, this group merits a more detailed discussion.

The heulandite group includes the minerals heulandite, clinoptilolite, brewsterite, stilbite, and barrerite (Breck, 1974; Barrer, 1978). The secondary building unit of this group is the $T_{10}O_{20}$ unit (10 tetrahedra and 20 oxygens) as shown in Fig. 1. This unit is arranged in sheet-like structures, as in heulandite, shown in Fig. 2. Bond densities between the sheets are lower than within the sheets, resulting in the characteristic lamellar habit of the heulandite-group crystals.

Heulandite and clinoptilolite, the principal minerals of the heulandite group, appear to be isostructural and apparently form a limited solid solution (Alietti, 1972). Clinoptilolite is Na or K rich, whereas heulandite is Ca rich. Differences between these two minerals have long been assumed to be due to these different cations. These minerals, however, display a different thermal stability that cannot be explained solely as a function of cation species. Clinoptilolite is stable past 700C; heulandite is destroyed at 550C. In addition, heulandite displays several temperature polymorphs below 550C. A K-exchanged heulandite is stabilized to heating. Although a Ca-exchanged clinoptilolite exhibits temperature polymorphism, it is not destroyed at 550C (Boles, 1972; Sheppard and Starkley, 1964).

Figure 1. $T_{10}O_{20}$ secondary building unit of heulandite
(from Breck, 1974).

Figure 2. Layer arrangement of heulandite
(from Breck, 1974).

The Si/Al ratio number also affects thermal stability, one of the best diagnostic tests for placing a heulandite mineral in the continuum. The higher the ratio, the higher the temperature required to destroy the crystal structure. Clinoptilolite has the higher ratio, which explains its greater stability.

The structure of heulandite, as determined by Merkle and Slaughter (1968), consists of $T_{10}O_{20}$ building blocks arranged in sheets as shown in Figs. 1 and 2. Bonding density is much greater in the ac planes, between which large, open channels occur. The principal channels in heulandite are made up of 10- and 8-member tetrahedral rings parallel to the c axis. These are linked by 6-, 5-, and 4-member rings. The 10-member ring channels comprise the principal exchange channels in this mineral; the other channels are blocked by tightly held Ca ions. Breck (1974) lists the aperture of the 10-member ring as $4.4 \times 7.2 \text{ \AA}$ ($0.44 \times .072 \text{ nm}$) and the two 8-member rings as $4.1 \times 4.7 \text{ \AA}$ ($0.41 \times 0.47 \text{ nm}$) and $4.0 \times 5.5 \text{ \AA}$ ($.40 \times 0.55 \text{ nm}$).

Charge in heulandite is derived from Al substituting for Si in the tetrahedra (Breck, 1974). Most of the substitution occurs in tetrahedra involved in interlayer bonding. Exchangeable Ca is associated with oxygens of the substituted tetrahedra. The Ca ions are in 8-fold coordination with three framework oxygens and five H_2O molecules.

Physical Properties of Zeolites

The most unusual physical properties of zeolites are the ability to continuously give off water on heating, with relative ease of rehydration (Breck, 1974). Zeolitic water is coordinated to cations within the channels, and does not occupy lattice sites within the framework. Some water, however, is bound to oxygen ions on the framework faces, especially in the laminar species; these species will exhibit some irreversible dehydration.

Particle size of synthetic zeolites ranges from 1 to 10 micrometers (μm), although natural zeolites may occur as much larger crystals, especially in cavities of igneous rocks (Breck, 1974). The surface areas of zeolites approximate $800 \text{ m}^2/\text{g}$. Hardness of crystals is 4 to 5 on Moh's scale. Particle density ranges from 1.9 to 2.3 g/cc. The density of heulandite is 2.20 g/cc. Because of labile cations, hydrated zeolites tend to behave as solid electrolyte solutions, with a high electrical conductivity.

Chemical Properties of Zeolites

. The most notable chemical property of zeolites is their extraordinary capacity for cation exchange (Barrer, 1978; Breck, 1974). They do not, however, follow the usual rules of ion exchangers, i.e., the lyotropic series. The result is a phenomenon known as molecular sieving:

zeolites can differentially exchange for some cations to the total exclusion of others, usually without regard to the position of these cations in the lyotropic series. This differential sieving is principally due to the steric effects of channels in the zeolite framework and to the hydration energies of the exchanging cations, i.e., the size of the cation prohibits its access to exchange sites in the framework.

The cation exchange capacity (CEC) of these minerals arises from a charge imbalance created by Al substitution for Si in the tetrahedra; consequently, the lower the Si/Al ratio, the higher the CEC. CEC in zeolites can range from 200 to 600 meq/100 g (Breck, 1974).

The unusual chemical and physical properties listed above enable zeolites to be useful as industrial catalysts, sorbents, etc. (Barrer, 1978).

Geologic Occurrence and Genesis

Zeolites occur in a wide variety of sedimentary rocks, but most commonly occur in rocks of volcanic origin (Sheppard, 1973). Sheppard (1973) classifies the geologic environments in which zeolites form as: (1) hydrothermal, (2) burial metamorphic, (3) weathering, (4) open systems, and (5) closed systems. Hydrothermal zeolites are associated with hot springs deposits. Burial metamorphic zeolites occur in thick deposits and exhibit vertical

zonation of species with depth. Weathering zeolites are those which form in alkaline soils. Open and closed type zeolites are the most common and are found extensively in tuffaceous deposits. These zeolites are formed by the reaction of pore waters with tuffaceous materials. Open systems are freely drained while closed systems occur in saline lake deposits.

The conditions for zeolite formation in open and closed sedimentary deposits include high pH, high Si(OH)_4 activity, and high base activity (Hay, 1978). Given these conditions, zeolites can form from almost any aluminosilicate mineral, although volcanic glass is the most common starting material. According to Hay (1966), the zeolitic alteration of volcanic glass is a solution phenomenon rather than a devitrification or hydration process in the solid state.

Although zeolites are common reaction products of volcanic glass, they are far from being the most stable products expected. Dibble and Tiller (1981) propose to account for their common occurrence with a model they term "non-equilibrium authigenesis." Because glass is much more soluble than more stable reaction products such as feldspars, the system becomes supersaturated with respect to these products. A large difference in solubility products between reactants and products facilitates many

metastable reactions. Metastable products can precipitate before stable species because their growth rates are faster and they can thus lower the overall free energy of the system sooner.

Early in this process when supersaturation is highest, smectites, and occasionally amorphous gels, form around glass shards. Zeolites form after the formation of clay minerals has lowered the free energy of the system. Attainment of equilibrium may be delayed drastically by the formation of these metastable products. They may dominate the system for tens of millions of years.

Occurrence and Genesis of Zeolites in Soils

Reports of zeolites in soils were rare until the early 1960's. Many early workers began by investigating anomalous cation exchange behavior in certain salt-affected soils. Mineralogical examination led them to zeolites as the source of the strange behavior. Shulz et al. (1964), for example, found exchangeable sodium percentages (ESP's) in the Fresno soil of California of 63 to 75 percent, using standard methods of analysis; yet this soil supported excellent rice crops. Where crops were sparse, they found seemingly impossible values of 130 percent. Various extractants were used to observe exchange for Na. Low ESP values were observed when Ca was used as the extractant, while high values were observed when K was the

extractant. No explanation for this behavior was available until the zeolite, analcime, was found in the soil by X-ray diffraction.

Baldar and Whittig (1968) were the first to make a fairly extensive survey of zeolites in soils. They looked at several salt-affected soils of the San Joaquin Valley in California and found analcime concentrated in sodic soils. Since then, the bulk of soil zeolite investigations have been done on salt-affected soils (Hay, 1964; El-Nahal and Whittig, 1973; Frankart and Herbillon, 1970), with a few reports of zeolites in freely drained, non-sodic soils (Portegies Zwart et al., 1975; Southard and Kolesar, 1978; Asvadurov et al., 1978).

All reports of pedogenic zeolites are restricted to salt-affected soils. For zeolites to form in the soil, pH must be greater than 9, and base activity, Na and K in particular, must also be high (Hay, 1964).

Analcime is the most commonly reported zeolite in salt-affected soils. Presence of Na_2CO_3 is required in addition to high pH (Baldar and Whittig, 1968; Frankart and Herbillon, 1970, 1971). Baldar and Whittig (1968) considered the presence of analcime in the Pond soil of California to be pedogenic because the mineral was most concentrated near the surface and its concentration decreased with depth. In addition, the analcime was detected in the fine clay fraction ($<0.2 \text{ } \mu\text{m}$). Frankart

and Herbillon (1971) studied sodic soils of the Rusizi Plain of Burundi, Africa. The soils were developed in ancient lacustrine alluvium. The authors showed that montmorillonite (present in the parent material) was progressively disappearing in the upper profile and being replaced by analcime. The authors considered that the montmorillonite supplied sufficient Al and Si for the formation of analcime.

Hay (1964) found phillipsite, higher in K than analcime, in salt-affected soils of the Olduvai Gorge, Tanzania. He considered the phillipsite to be of pedogenic origin.

Zeolites in non salt-affected soils occur in a wide range of parent materials, but volcanic ash and tuff appear to be the most common. Zeolites in such soils are for the most part assumed to be inherited from the parent material. The stability of inherited zeolites is dependent, of course, on equilibrium conditions in the soil: no zeolites have been reported in acidic, leached soils of humid regions. Analcime has been reported in acid soils of the crater of Mt. Baker in Washington, but these are hydrothermal soils (Bockheim and Ballard, 1975).

Portegies Zwart et al. (1975) reported inherited analcime and calcic zeolites in soils developed in lacustrine sediments, but influenced by volcanic ash, in the Valle Latina of Italy. The analcime was deemed to be

unstable in the current soil environment, and the calcic zeolites stable because of high Ca activities of the drainage waters. Southard and Kolesar (1978) noted high extractable K in the Blackrock soil of Utah, developed in tuff, and determined the source to be clinoptilolite, presumably inherited from the tuff. Asvadurov et al. (1978) also noticed high extractable K in Romanian soils developed in tuff, and also determined the source to be clinoptilolite.

Zeolites of the clinoptilolite-heulandite group were found to predominate in the 0.3- to 5.0- μ m fraction of the Harwell soil in England developed from a glauconitic clay (Talibudeen and Weir, 1972). The soil was high in extractable K.

An interesting occurrence of the zeolite, mordenite (high Na), was observed in the Rotomahana soil of New Zealand (Kirkman, 1976). The dominant clay mineral was interstratified montmorillonite/mica, with a fair amount of allophane in the A horizon. The mordenite was thought to be a product of hydrothermal alteration, inherited from the parent material.

Effects of Zeolites on Soil Behavior

As described above, anomalous ion exchange characterizes zeolitic soils. Aside from this property, little research has been done on effects on other properties, e.g., bulk density, water relations, rheology, etc.

El-Nahal and Whittig (1973) speculated that gypsum reclamation procedures on soils high in analcime would have little effect because the Na in analcime shows little or no exchange for divalent cations. However, no research has been carried out to test this hypothesis. It should be remembered that although zeolitic soils have an excessively high base exchange status, these values represent cations in the zeolite framework which may, or may not, be easily exchanged into the soil (Shulz et al., 1964; El-Nahal and Whittig, 1973).

Geologic Setting of Study Area

The study was located in an outcrop area of the Tascotal Formation of the Texas Trans-Pecos Volcanic Field (Fig. 3). The field covers most of Jeff Davis and Presidio Counties and part of western Brewster County. The field extends into the northern parts of the Mexican states of Chihuahua and Coahuila. Centers of volcanic activity are spread throughout the field. Almost all forms of volcanic ejecta are present, including ash flow tuffs, welded tuffs, ignimbrites, lava flows, etc. Most of the activity occurred from about 45 to 20 million years B.P. (Wilson, 1980).

The Tascotal Formation crops out in the Alamito Creek Valley in the south-central part of the volcanic field (Fig. 3). The Tascotal is defined by its boundaries

Figure 3. Location of Tascotal Formation outcrop in Presidio County, Texas (adapted from Walton, 1979).

rather than by its lithology: the Rawls Formation above and the Mitchell Mesa Ignimbrite below. The Mitchell Mesa is Oligocene in age and the Rawls, although not definitively dated, may be late Oligocene or early Miocene. No dates have been determined for the Tascotal (Walton, 1979).

The upper members of the Tascotal Formation consist of pumice-rich sandstones, mudrocks, and conglomerates. The lower members consist of volcanic apron sediments comprised of tuffs and ash-flows (Walton, 1979). Most of the tuffs in the lower members have been reworked by water; Walton uses the term "volcanic arenites" to describe their lithology. These lower members form the parent material for the soils of the study area.

Walton (1979) describes the Tascotal as a progradational-aggradational volcanic apron sequence. The progradational phase represents the active phase of the Chinati Mountains volcanic center. The progradational apron was constructed in a manner similar to marine deltas or fans, with finer sediments distal to the source. The aggradational sequence represents the inactive phase of the Chinatis. As the Chinatis became quiescent, the volcanic peaks began to erode and coarser sediment aggraded to the east. The coarser sediments comprise the upper members of the Tascotal Formation. The Perdiz Conglomerate is the most conspicuous upper member.

CHAPTER III

MATERIALS AND METHODS

Field Studies

A toposequence of three soils overlying the Tascotal Formation was selected for the study (Fig. 4). Each pedon was described in detail. Two to 3-kg samples were taken from each horizon of the three pedons described.

Laboratory Analyses

Pretreatment consisted of light rolling and crushing. The samples were passed through a 2-mm sieve. Only the fine-earth fraction (<2 mm) was saved for analysis. Determination of coarse fragment (>2 mm) percentages is described below. The samples were stored in cardboard containers.

Chemical Analyses

Soil Reaction

Soil pH was determined for all samples on a saturated paste as described in USDA Handbook 60 (U.S. Soil Salinity Laboratory Staff, 1954). An Orion model 601A pH meter was used for the measurement. Saturated water content was also determined from these pastes.

Figure 4. Cross-sectional view of study area (drawing by Vance Holliday).

Electrical Conductivity (EC)

The EC of the samples was measured on the extract of saturated pastes according to USDA Handbook 60 (U.S. Soil Salinity Laboratory Staff, 1954). A Beckman Solu-Bridge was used for the determination.

Soluble Cations

Soluble cations were determined on saturated paste extracts according to USDA Handbook 60 (U.S. Soil Salinity Laboratory Staff, 1954). K and Na were analyzed by flame emission on a Coleman Model 21 flame photometer. Ca and Mg were determined by atomic absorption on a Perkin-Elmer 290B atomic absorption spectrophotometer.

Calcium Carbonate Equivalent

CaCO_3 was determined by acid neutralization as described in USDA Handbook 60 (U.S. Soil Salinity Laboratory Staff, 1954).

Organic Carbon

Organic Carbon percentage was determined by the Walkley-Black method (Allison, 1965).

Extractable Cations and Cation Exchange Capacity

Exchangeable cations and cation exchange capacity were determined on ammonium acetate extracts as described in USDA Handbook 60 (U.S. Soil Salinity Laboratory Staff,

1954). In addition, extractable Ca and Na were determined on magnesium acetate and lithium chloride extracts. Differential exchange for one of these cations of Mg or Li is indicative of zeolite presence (El-Nahal and Whittig, 1973).

Physical Analyses

Particle Size Distribution

Percentage of coarse fragments (>2 mm) was determined on 1-kg representative subsamples. The subsamples were weighed and passed through a 2-mm sieve. The fraction retained by the sieve was transferred to 1-l plastic jars with 10 ml of 10% sodium metaphosphate and 750 ml water. The jars were shaken for 12 hours and the contents again passed through a 2-mm sieve. The >2 mm portion was oven dried and weighed. Density measurements were made on bulk samples and on coarse fragments. Percentages were then calculated on a volume basis.

The particle size distribution (PSD) of the <2 mm portion was determined by the Simplified Day Procedure (Gee and Bauder, 1979). Dispersion was effected by placing 50 g soil in 250-ml screw-top plastic bottles with 100 ml 5% sodium metaphosphate. The bottles were shaken for 12 hours on a reciprocating shaker. The contents were transferred to 1000-ml cylinders and analyzed according to the procedure outlined. In addition, the Bouyoucos method

(Bouyoucos, 1951), as modified by the SCS in Texas (6-hour reading for clay versus 2 hours as recommended in the original procedure), was also used. A blank sample with dispersant was used in both cases to account for the density increase caused by the addition of the dispersant to the samples.

The sand fraction (0.05-2.0 mm) was obtained by wet sieving the dispersed sample through a 45- μ m sieve and weighing the fraction not passing the sieve.

Sand subfractions (very coarse, coarse, medium, fine, and very fine) were obtained by dry-sieving the bulk sand fraction through 1.0-mm, 0.5-mm, 0.25-mm, 0.10-mm, and 0.05-mm sieves, corresponding to the respective sand fractions listed above. The sieves were mounted in tandem on a Janette sand fractionator (Janette Electric Mfg. Co., Morton Grove, Ill.) and shaken for 15 minutes.

Water Retention

Water retention was determined on a pressure membrane apparatus on 0.033 megapascals (MPa) and 1.5 MPa (U.S. Soil Salinity Laboratory Staff, 1954).

Bulk Density

Bulk density was determined according to the paraffin-clod method described by Blake (1965).

Particle Density

Particle density was determined under suction according to the method described in USDA Handbook 60 (U.S. Soil Salinity Laboratory Staff, 1954).

Mineralogical Analyses

Sample Pretreatment

The samples were not pretreated prior to dispersion for fractionation to avoid possible decomposition of the zeolites. After the samples were fractionated it was found that H_2O_2 treatment for organic matter destruction did not decompose or alter the zeolites, but actually aided in their identification.

Sample Fractionation

Five ml of 10% sodium metaphosphate were added to approximately 75 g of whole soil (<2 mm) in 200 ml of water. The samples were shaken for 12 hours on a reciprocating shaker. The sand fraction was separated by passing the sample through a 45- μm sieve. That retained by the sieve was discarded, since sand fractions obtained from PSD were retained for mineralogical examination. The clay fraction (<2 μm) was separated from the silt fraction (2-50 μm) by gravity sedimentation in 1000-ml cylinders. The clay fraction from selected horizons was separated into fine (<0.2 μm) and coarse clay (0.2-2.0 μm) fractions by centrifugal sedimentation (Jackson, 1959).

X-ray Diffraction (XRD)

All samples were examined on a General Electric SPG-5 diffractometer at $2^\circ 2\theta$ per minute, with a time constant of two and scale factor of 1000 counts per second. Scale factor was increased on several samples with off-scale XRD peaks. The reduced intensity peaks were inset under the off-scale peaks in the diffractogram figures.

Random powder-mounts were prepared for XRD analysis of sand- and silt-size fractions. The samples were ground to pass a 60-mesh sieve.

Clay specimens were prepared by the filter-membrane peel technique developed by Drever (1973). The optimum amount of clay on a slide was found to be 25 mg. Larger amounts developed cracking and did not appreciably improve diffraction patterns.

Identification of phyllosilicate clay minerals was determined by differential XRD. Aliquots containing 25 mg of clay were transferred to 15-ml centrifuge tubes. One tube was filled with a 0.3N CaCl_2 solution and another tube with 0.3N KCl. The tubes were centrifuged and the supernatant liquid discarded. This process was repeated twice. The Ca saturated samples were then washed and centrifuged at least twice with a 30% glycerol solution. The K saturated samples were washed at least twice with deionized water (until beginning of dispersion). The clays were then filtered onto a 0.45- μm filter membrane and

transferred onto petrographic quality glass slides, as recommended by Drever (1973). The Ca saturated samples were then examined by XRD. The K saturated samples were heated to 250C for four hours and X-rayed. The same samples were further heated to 550C for four hours and X-rayed again.

Total Potassium

Total K on selected fine-clay fractions was determined by a modification of the method of Webber and Shivas (1953). One ml of 1:5 H_2SO_4 was added to a platinum crucible containing a weighed oven-dry sample. Samples of 0.1 to 0.2 g were used. The crucible was swirled to mix the acid and the clay. Five ml concentrated HF were then added and the suspension was gently boiled on a hot plate until a gel-like residue resulted. The crucible was then immersed in a 1:20 solution of HNO_3 , and heated to near boiling. The crucible was removed and quantitatively rinsed. The HNO_3 was evaporated to a gel-like consistency and the residue taken up in 0.1N HCl. No insoluble fraction remained. Standard solutions of 5, 10, 20, 30, and 40 ppm K in 0.1N HCl were prepared and the K determined on a Coleman model 21 flame photometer.

Differential Heating

Silt fractions of selected horizons were heat treated to 400C and 550C for 12 hours to differentiate

clinoptilolite from heulandite and to detect any temperature polymorphs of these minerals (Alietti, 1972).

Scanning Electrical Microscopy

A brief examination of selected bulk samples of soil and tuff was carried out on a JEOL JEM-100CX electron microscope. All samples were gold coated. Energy dispersive spectra (EDS) of the samples were analyzed for elemental composition.

CHAPTER IV

RESULTS

Field Studies

Pedon Descriptions

All three pedons were located on the Hays Mitchell Ranch (Alamito Ranch) in the Alamito Draw of Presidio County, Texas (see photographs in appendix). The ranch entrance is approximately 20 miles south of Marfa on U.S. 67 and FM 149. The pedons were approximately 300 m to the east of the eastern leg of a landing strip. Pedon 1 was on a small mesa-like structure about 150 m to the north of the road extending to the east of the landing strip. Pedon 2 was about 60 m to the southwest of pedon 1 on the sloping segment with a western aspect. Pedon 3 was approximately 100 m to the south of pedon 2 in the swale. (All colors listed in the descriptions are moist colors.)

Profile 1

Classification: Ustollic Calciorthid, fine-loamy,
mixed, thermic.

Vegetation: Creosotebush (Larrea tridentata), broom-
weed (Xanthocephalum sarothrae), bush muhley
(Muhlenbergia porteri), fluffgrass (Erioneuron

pulchellum), whitethorn acacia (Acacia con-
stricta), tasajillo (Opuntia leptocaulis).

Site Position: Alluvial fan remnant. Slope was less than 1%. A desert pavement covered approximately 90% of the surface.

- A1 0 to 11 cm; dark brown (10YR 4/3) clay loam; mixed weak platy and granular structure; soft; common fine and very fine roots; 10% coarse fragments; strongly effervescent; clear smooth boundary.
- Bw 11 to 32 cm; dark yellowish brown (10YR 4/4) gravelly clay loam; weak medium subangular blocky structure; slightly hard; common fine and very fine roots; 20% coarse fragments; strongly effervescent; clear wavy boundary.
- Bk1 32 to 52 cm; dark yellowish brown (10YR 4/4) gravelly clay loam; 20% brown (7.5YR 4/4) clay loam bodies; 20% very pale brown (10YR 7/4) carbonate bodies; weak medium subangular blocky structure; hard; few fine and very fine roots; 15% coarse fragments; strongly effervescent; gradual wavy boundary.
- Bk2 52 to 75 cm; yellowish brown (10YR 5/4) gravelly clay loam; 20% brown (7.5YR 4/4) bodies; 25% very pale brown (10YR 7/3) carbonate bodies, weak medium subangular blocky structure; hard and slightly hard; few fine roots; 15% coarse

fragments; strongly effervescent; gradual wavy boundary.

Bk3 75 to 102 cm; dark yellowish brown (10YR 4/4) clay loam; 25% very pale brown (10YR 7/3) carbonate bodies; weak medium subangular blocky structure; slightly hard and hard; few fine roots; 10% coarse fragments; strongly effervescent; abrupt wavy boundary.

Cr/B 102 to 112 cm; pale olive (5Y 6/3) tuff and dark yellowish brown (10YR 4/4) loam; tuff fragments comprise greater than 60% of mass; weak medium subangular blocky structure; slightly hard and hard; few fine roots; less than 5% coarse fragments; strongly effervescent; abrupt wavy boundary.

Cr 112+ cm; pale olive (5Y 6/3) tuff; non-calcareous; pronounced horizontal fractures; few weakly developed vertical fractures.

Profile 2

Classification: Lithic Torriorthent, fine-loamy, mixed, thermic.

Vegetation: Creosotebush (Larrea tridentata), broomweed (Xanthocephalum sarothrae), fluffgrass (Erioneuron pulchellum), three-awn grass (Aristida species), burrograss (Sceleropogon brevifolius), bush muhley (Muhlenbergia porteri).

Site Position: Main slope. A desert pavement covered about 90% of the surface. Slope was 2-3 percent.

A1 0 to 9 cm; brown (10YR 5/3) loam; weak medium subangular blocky and weak fine granular structure; soft; common fine segregations of carbonates; strongly effervescent; common fine roots; clear smooth boundary.

A2/Cr 9 to 21 cm; brown (10YR 5/3) silt loam; 40% carbonate-coated olive gray (5Y 6/2) tuff fragments; weak medium subangular blocky structure; common fine segregations of carbonates; common fine roots; strongly effervescent; abrupt wavy boundary.

Cr1 21 to 32 cm; light gray (5Y 7/1) tuff; pronounced horizontal fracturing; common carbonate coatings in fractures; violently effervescent in fractures; few fine roots; gradual smooth boundary.

Cr2 32 to 55 cm; light gray (5Y 7/1) tuff; gradual smooth boundary.

Cr3 55+ cm; light gray (5Y 7/1) tuff.

Remarks: upper few centimeters of solum showed platy structure; horizon boundaries in tuff were chosen on apparent bedding planes.

Profile 3

Classification: Aridic Argiustoll, clayey, smectitic, thermic.

Vegetation: Creosotebush (Larrea tridentata), mesquite (Prosopis glandulosa), broomweed (Xanthocephalum sarothrae), fluffgrass (Erioneuron pulchellum), mariola (Parthenium incanum), javelinabush (Microrhamnus ericoides), blue grama (Bouteloua gracilis), whitethorn acacia (Acacia constricta), catclaw acacia (Acacia greggii), tobosagrass (Hilaria mutica), burrograss (Sceleropogon brevifolius), tarbush (Flourensia cernua), bush muhley (Muhlenbergia porteri).

Site Position: Topographic swale; no desert pavement.

- A1 0 to 5 cm; very dark grayish brown (10YR 3/2) clay loam; weak medium platy structure; hard; common fine and medium roots; weakly effervescent in upper few centimeters; peds are non-calcareous; abrupt smooth boundary.
- A2 5 to 13 cm; very dark brown (10YR 2/2) silty clay loam; moderate medium subangular blocky structure; very hard; common fine and medium roots; non-calcareous; clear smooth boundary.

- Bt 13 to 30 cm; very dark brown (10YR 2/2) silty clay; moderate coarse and medium subangular blocky structure; very hard; common fine and medium roots; non-calcareous; abrupt wavy boundary;
- Bw 30 to 46 cm; very dark grayish brown (10YR 3/2) clay loam; moderate medium subangular blocky structure; very hard; few medium roots; few angular pebbles; strongly effervescent; clear wavy boundary.
- 2Bk1 46 to 67 cm; dark brown (10YR 3/2) clay loam; very weak medium subangular blocky structure; very hard; few medium roots; 10% rounded and angular coarse fragments; violently effervescent; smooth gradual boundary.
- 2Bk2 67 to 90 cm; dark yellowish brown (10YR 4/4) clay loam; very weak medium subangular blocky structure; very hard; few medium roots; violently effervescent; clear wavy boundary.
- 3Bk/Cr 90 to 110 cm; olive (5Y 5/3) clay loam; 40% olive (5Y 5/3) tuff fragments; weak medium subangular blocky structure; hard; violently effervescent; clear wavy boundary.
- Cr 110+ cm; olive (5Y 5/3) tuff; pronounced horizontal fracturing.

Soil--Geomorphic Relationships

The study area was on an old erosional surface, possibly a pediment, sloping slightly to the east. Pediment forming processes are no longer active, since the surface has been dissected. Micro-geomorphic processes now predominate, and these processes will be the focus of the following discussion of soil morphology with respect to geomorphology. The discussion follows Carson and Kirkby (1972).

The more arid a climate, the more pronounced the geomorphic thresholds (Cooke and Warren, 1973). The soil sequence under study reflects this principle. A small change in slope angle results in a large change in soil morphology. The study area is on a slope sequence consisting of three principal segments: a convex upslope, a straight main slope, and a concave base (Fig. 4). The first two segments are essentially erosional surfaces, while the base is depositional.

Two processes are important for hillslope form: weathering and transportation. On a stable surface, weathering will predominate over transportation (erosion), and a well developed soil will result. On an unstable surface, transportation processes predominate and only a shallow soil will develop. The first surface is referred to as a transport-limited surface; the second surface is a weathering-limited surface.

Pedon 1, on the upslope convexity, is on a transport-limited surface. The profile of this pedon displays a classic horization sequence for an Aridisol on a relatively stable surface. The accumulation of carbonates (in the Bk horizons) is characteristic of well developed Aridisols. This soil is in stage III of the carbonate accumulation sequence of Gile et al. (1966) and the profile, therefore, is probably older than 5000 years, but younger than latest Pleistocene. Since the parent materials in which this soil has developed date approximately to the Oligocene, the surface must be erosional. However, this surface has reached a steady state, and the equilibrium is tipped in favor of profile development.

Pedon 2 is on the main slope of the sequence. Although the slope is gentle (slope = 3%), the morphology differs greatly from that of pedon 1. It is very weakly developed, as evidenced by its thin profile and lack of diagnostic subsurface horizons. Only a slight change in slope angle was necessary to effect this profound morphological change, confirming the thesis that arid geomorphic thresholds are quite pronounced relative to more humid environments. Moreover, critical angles for change are well defined over a small range of values. On this slope, then, transport phenomena predominate over weathering processes, and the soil is perpetually "young" or weakly developed (surface age is probably no more than a few

hundreds of years). Weathering occurs, of course, but erosion removes weathering products faster than they can accumulate.

A relatively well developed desert pavement overlies pedons 1 and 2. The coarse fragments (>2 mm) of the pavement are probably derived from the Perdiz Conglomerate, as lag gravels. Pedon 1 contains a significant amount of coarse fragments (>2 mm) in the profile. The fragments are similar in lithology to the pavement. The pavement, then, could have formed either by deflation or by pedoturbation forcing the fragments upward, or by a combination of the two. However, the quantity of coarse fragments decreases with depth, suggesting a lag gravel origin.

Pedon 3, on a depositional surface formed in a topographic swale, shows both the effects of depositional phenomena and weathering in place. Lithological discontinuities in the profile attest to different sequences of deposition. The horizons of accumulation of silicate clays and carbonates reflect the stability of the site. A greater influx of water occurs due to the topographic position, hence the development of an argillic horizon.

The calcic horizon has formed below the argillic horizon, which is the usual sequence where both horizons occur together (Soil Survey Staff, 1975). With the greater influx of water, carbonates are leached to a moderate depth within the soil. Silicate clays are

mobilized in the resulting non-calcareous part of the solum and are translocated to a lesser depth than the carbonates.

The soil sequence of this study area can be explained with the concepts of modern process geomorphology theory, especially as they relate to hillslope form and process. Pronounced desert geomorphic thresholds define the nature of the soils on each slope segment.

Chemical Analyses

Soluble Cations

Pedons 1 and 3 present an interesting contrast in terms of soluble cations (Table 1). Na is the dominant cation in the subsurface horizons of pedon 1 while Ca dominates the subsurface of pedon 3. The topographic positions of these pedons would suggest the opposite situation. Pedon 2 exhibits a high Na/Ca ratio, but total amounts of soluble cations are much less than pedons 1 and 3. One would expect a higher soluble Na in pedon 3, both because of a lower topographic position and the presence of a restricting Bt horizon. The source of the sodium was not identified.

Electrical Conductivity

Electrical conductivity (EC) values correspond well with total amounts of soluble cations (Table 1). EC values are highest in the B horizons, indicative of salt

TABLE 1. Chemical properties: soluble cations and electrical conductivity (E.C.)

Horizon	Soluble Cations				E.C.
	Na	K	Ca	Mg	
	- - - meq/l - - -				ds/m
	<u>Profile 1</u>				
A1	1.6	0.3	5.0	0.8	0.8
Bw	6.3	0.3	0.4	0.8	0.9
Bk1	24.0	0.3	3.3	3.3	3.4
Bk2	75.0	0.4	11.5	3.5	9.0
Bk3	110.0	0.7	10.5	4.0	10.0
Cr/B	85.0	0.6	8.0	3.0	9.0
	<u>Profile 2</u>				
A1	3.5	0.1	0.4	0.3	0.5
A2/Cr	8.8	0.8	0.2	0.3	0.9
	<u>Profile 3</u>				
A1	1.6	0.6	3.0	1.3	0.9
A2	3.0	0.7	7.0	1.3	1.5
Bt	3.2	0.9	45.8	5.5	5.0
Bw	2.6	0.8	32.5	4.5	3.8
2Bk1	1.5	0.4	7.5	1.5	1.8
2Bk2	1.5	0.3	0.9	0.6	0.5
3Bk/Cr	1.0	0.2	2.0	0.5	0.5

lessivation. Capillary rise of solutes is not evident in any of the profiles.

Soil Reaction

Pedons 2 and 3 show maximum pH values at the surface with a slight decrease downward in the profile (Table 2). Pedon 2 does not show a significant pH depth trend. The relatively high pH's are within the range expected for calcareous soils.

Calcium Carbonate Equivalent

Values for CaCO_3 correspond to trends observed for field and microscopic morphology (Table 2). Calcic horizons have significantly higher CaCO_3 values than other horizons.

Comparing values between pedons, however, reveals an interesting phenomenon. A B horizon labeled with a k in one pedon has less CaCO_3 than a Bw in another pedon. This may be due to simple observational bias or to more complex carbonate-soil matrix interactions.

The 2Bk1 horizon of pedon 3 has less of CaCO_3 than the Bw horizon of pedon 1 (15.2 vs. 18.8%). This latter horizon apparently did not have the same amount of observable secondary carbonate bodies as the 2Bk1. Differential manifestations of CaCO_3 accumulation have been observed in southern New Mexico in a study comparing gravelly and nongravelly soils (Gile and Grossman, 1979). In that

TABLE 2. Chemical properties: calcium carbonate (CaCO_3), organic matter (O.C.), and pH

Horizon	CaCO_3	O.C.	pH
	- - - percent - - -		
	<u>Profile 1</u>		
A1	8.2	1.1	8.2
Bw	18.8	1.2	8.0
Bk1	23.5	0.6	8.0
Bk2	22.0	0.3	7.7
Bk3	18.9	0.5	7.7
Cr/B	15.1	0.2	7.8
Cr	3.5		
	<u>Profile 2</u>		
A1	17.6	1.0	8.1
A2/Cr	23.0	1.0	8.2
	<u>Profile 3</u>		
A1	3.0	1.6	8.1
A2	3.2	1.7	7.5
Bt	4.2	0.7	7.3
Bw	12.7	1.0	7.6
2Bk1	15.2	0.8	7.8
2Bk2	22.3	0.7	7.9
3Bk/Cr			8.0
Cr	13.1		

study it was found that less CaCO_3 was required to produce observable films in gravelly soils. In this study, however, the Bw horizon of pedon 1 has both more carbonate and more gravel than the 2Bk1 horizon of pedon 3. Texture was the same (clay loams) in both horizons. The observable manifestations of carbonate in these soils, then, cannot be explained by texture and/or coarse fragment content.

Organic Carbon

Organic carbon (O.C.) values (Table 2) are somewhat high for an arid environment, possibly due to CaCO_3 acting as a complexing agent to preserve the organic matter. The high O.C. values in the surface of pedon 3 may reflect depositional inputs. Also, the slight topographic concavity in which pedon 3 is located is a somewhat more moist environment; thus, more vegetative growth would result.

Cation Exchange Capacity and Extractable Cations

Cation exchange capacity (CEC) is relatively high in these soils and reflects the presence of smectites and probably zeolites as well (Table 3). However, CEC does not follow clay distribution trends in any of the profiles. (Particle size distribution will be discussed later.) The high CEC values of the sand and silt

TABLE 3. Cation exchange capacities*

Horizon	Whole Soil	Fine Sand	Silt	Clay
- - - - - meg/100g - - - - -				
<u>Profile 1</u>				
A1	22.2	6.9	23.0	76.4
Bw	25.0	7.8	18.2	82.8
Bk1	26.0	12.7	13.0	71.0
Bk2	28.5	19.1	19.9	80.4
Bk3	32.1	13.8	22.2	95.2
Cr/B	42.6	41.6	23.6	84.7
Cr	59.1	52.3	72.9	103.7
<u>Profile 2</u>				
A1	29.0		31.2	77.5
A2/Cr	37.9		32.3	83.2
Cr1	75.8			
Cr2	90.8			
Cr3	70.1			
<u>Profile 3</u>				
A1	35.4		30.9	73.1
A2	35.5		28.8	51.4
Bt	43.3		27.0	68.7
Bw	30.6		20.8	77.1
2Bk1	23.7		17.5	73.4
2Bk2	26.9		20.0	63.7
3Bk/Cr	21.4		18.7	64.7
Cr	22.9			

*NH₄OAc method (U.S. Soil Salinity Laboratory Staff, 1954).

fractions are unusual. Zeolites were identified in these fractions and undoubtedly account for most of the CEC. In addition, CaCO_3 accounts for some of the clay percentage, i.e., silicate clay is actually lower than PSD percentages indicate. The CEC of CaCO_3 is negligible, and its presence would also account for lack of percent clay/CEC correlation.

Cation exchange experiments did not serve to conclusively identify zeolite species, as had been hoped. Exchange experiments could not distinguish between zeolitic and carbonatic Ca. It was originally thought that the predominant zeolites were Na rich because of the high soluble Na in pedon 1. Electron microscopy and energy dispersive spectra revealed few, if any, Na zeolites. Most were Ca-rich, and a few were K-rich.

Some zeolitic Na was evident in the tuff (Cr horizon). LiCl-extractable Na was greater than either MgOAc- or NH_4OAc -extractable Na (Table 4), indicating differential exchange. NH_4OAc -extractable Ca was greatest in all horizons, but this may be due to increased solubility of CaCO_3 in NH_4OAc . For exchange experiments to provide meaningful information, CaCO_3 would have to be removed from the system without altering the zeolites.

TABLE 4. Extractable cations (whole soil) with NH_4OAc , MgOAc , and LiCl

Horizon	NH_4OAc				MgOAc		LiCl	
	Ca	Mg	K	Na	Ca	Na	Ca	Na
- - - - - meg/100g - - - - -								
<u>Profile 1</u>								
A1	71.8	1.6	2.6	0.5	56.7	0.7		
Bw	164.7			3.3				
Bk1	201.0			8.5	54.0	6.9	41.8	7.1
Bk2	150.6			14.5				
Bk3	184.0			16.6	54.6	15.6	31.3	24.9
Cr/B	184.0			22.5				
Cr.	81.5	2.6	7.0	32.0	12.5	32.0	28.5	55.9
<u>Profile 2</u>								
A1	81.4	1.6	3.8	3.8				
A2/Cr								
<u>Profile 3</u>								
A1	59.5	2.0	6.6	0.4				
A2	22.0	2.3	5.5	0.3				
Bw	31.4	3.7	4.4	0.4				
Bt	72.0	3.5	4.3	0.4				
2Bk1								
2Bk2								
Bk/Cr								
Cr	81.5	2.7	3.6	0.7				

Physical Analyses

Particle Size Distribution

Coarse fragment distribution in pedon 1 decreases linearly from the surface downward, suggesting lag gravel as the origin for these fragments (Table 5).

Particle size ratios indicate relative uniformity of parent materials in pedons 1 and 2 (Table 6). The ratios indicate a lithological discontinuity at the Bw-2Bk1 boundary in pedon 3. Sand/silt, very fine sand/silt, and fine sand/very fine sand ratios all show a striking increase at this boundary. (Actually some change is evident between the Bt and Bw horizon.) A discontinuity described in the field between the 2Bk2 and 3Bk/Cr horizons of pedon 3 was not indicated by the ratios. Laboratory textures of the fine earth fraction (Table 5) correspond well with field textures, with a few exceptions.

Water Retention

Water retention values at 0.033 MPa and 1.5 MPa (Table 7) are in the range of values for those of similar soils in Texas (Soil Survey Staff, 1976; Hallmark, 1972). The ratio of water held at 1.5 MPa to percent clay is always less than one, so substantial evidence of amorphous colloids is not indicated (Soil Survey Staff, 1975). However, the ratio in these soils was considerably higher than the ratios obtained for similar, smectitic soils in

TABLE 5. Particle size distribution

Horizon	Sand	Silt	Day*	Boy.†	Coarse Fragments	Texture‡
			Clay			
		weight percent			volume percent	
<u>Profile 1</u>						
A1	58.7	19.8	21.5	22.9	50.4	VGSCl
Bw	39.0	22.8	38.2	38.4	41.4	VGCL
Bk1	26.5	32.7	40.8	45.6	26.6	GC
Bk2	28.5	41.2	30.3	33.9	8.3	CL
Bk3	34.7	38.8	25.5	30.0	10.1	CL
Cr/Bk	46.4	28.2	25.4	28.8		CL
<u>Profile 2</u>						
A1	47.4	27.2	25.4	27.3		L
A2/Cr	38.2	34.1	27.7	31.6		CL
<u>Profile 3</u>						
A1	18.9	57.5	23.6	25.5		SiL
A2	14.9	55.3	29.8	32.5		SiCL
Bt	9.4	48.8	41.8	45.8		SiC
Bw	23.4	38.7	37.9	41.5		CL
2Bk1	41.8	25.2	33.0	36.7	11.0	CL
2Bk2	32.5	28.4	39.1	45.4		CL
3Bk/Cr	40.0	29.2	30.8	35.4		CL

*Simplified Day Method

†Boyucos Method. Clay was determined by a 6-hour reading.

‡Texture class was determined using the clay reading obtained by the Modified Day Method. VGSCl = very gravelly sandy clay loam; VGCL = very gravelly clay loam; gravelly clay; CL = clay loam; L = loam; SiL = silt loam; SiCL = silty clay loam; SiC = silty clay.

TABLE 6. Particle size ratios

Horizon	Sand/Silt	Fine Sand/ Very Fine Sand	Very Fine Sand/ Silt
<u>Profile 1</u>			
A1	3.0	0.4	1.3
Bw	1.7	0.5	0.7
Bk1	0.8	0.4	0.4
Bk2	0.7	0.2	0.4
Bk3	0.9	< 0.1	0.6
Cr/B	1.6	0.1	0.9
<u>Profile 2</u>			
A1	1.7	0.2	1.3
A2/Cr	1.1	0.2	0.9
<u>Profile 3</u>			
A1	0.3	< 0.1	0.2
A2	0.3	< 0.1	0.2
Bt	0.2	0.1	0.2
Bw	0.6	< 0.1	0.5
2Bk1	1.7	0.2	0.9
2Bk2	1.1	0.2	0.9
3Bk/Cr	1.4	0.1	0.7

TABLE 7. Physical properties

Horizon	Water Retention 1.5MPa	Water Retention .033Mpa	Saturated Water Content	1.5MPa/ %Clay	Particle Density	Bulk Density
- - weight percent - -			- - Mg/m ₃ - -			
<u>Profile 1</u>						
A1	9.5	11.6	30.4	0.44	2.68	
Bw	15.3	26.3	46.9	0.40	2.59	1.35
Bk1	16.5	33.8	45.1	0.40	2.63	1.33
Bk2	14.3	30.6	41.7	0.47		1.25
Bk3	13.8	28.2	37.3	0.52	2.66	1.31
Cr/Bk	15.7	30.3	38.7	0.61	2.66	1.23
Cr						1.61
<u>Profile 2</u>						
A1	13.8	25.1	39.0	0.54	2.62	1.06
A2/Cr	8.7	27.7	43.1	0.31		1.15
Cr1						1.52
Cr2						1.48
Cr3						1.58
<u>Profile 3</u>						
A1	15.9	34.0	43.1	0.67	2.54	
A2	17.7	31.4	47.8	0.59	2.55	1.31
Bt	20.1	31.5	53.3	0.48	2.31	1.52
Bw	16.8	28.6		0.44		1.46
2Bk1	14.2	26.9	41.5	0.43	2.75	1.43
2Bk2	16.3	27.3	43.1	0.50	2.71	1.42
3Bk/Cr			40.1		2.62	1.33/ 1.64

Hallmark's (1972) study. The ratios for the soils of this study was never less than 0.40, with one exception, whereas the ratios in similar soils studied by Hallmark were never greater than 0.40. Zeolites may account for the extra water-holding capacity.

Bulk Density

Bulk densities (Table 7) are within the range of values obtained for Calciorthids and similar Aridisols in Texas (Soil Survey Staff, 1976). Bulk densities for the tuff (Cr horizons) are consistently higher than bulk densities for the soil, which would be expected in view of the lithified nature of the tuff.

Particle Density

Values are in the range 2.50 - 2.75 g/ml (Table 7), with the exception of the Bt horizon of pedon 3. This value is probably erroneous.

Mineralogical Analyses

Principal minerals identified in the clay fraction were smectite, illite (probably interstratified with smectite), and zeolite of the heulandite group. Minerals identified in both the silt and sand fractions were quartz, plagioclase feldspar, and zeolite.

Smectite identification by XRD when using the membrane-peel technique presented a few problems since a

1% glycerol solution would not fully expand the smectite. Several soil smectites of known composition were solvated with glycerol. It was found that when using the membrane-peel technique a 1% glycerol solution would not fully expand these minerals. Perhaps excess glycerol is lost through filtration. A 30% solution was sufficiently concentrated to expand all the soil smectites investigated.

Selected clays from this study were also subjected to the conventional treatment for clay orientation carried out in the soil laboratories at Texas Tech University. The treatment consists of the saturation procedures described in the methods section, except with the use of a 1% glycerol solution. The clay suspensions are dried on a glass slide.

The smectite in the clays of these samples did not expand past 1.5 nm when the 1% glycerol solution was used. Saturation with Mg instead of Ca, and/or solvation with ethylene glycol also failed to fully expand these smectites.

The smectites in these samples appear to be approaching beidellite in composition and charge distribution, with more substitution tetrahedrally than model montmorillonite (Carrol, 1970). A 30% glycerol solution, as noted above, expands all smectites when used with the membrane-peel technique. Perhaps a lower concentration exists which would differentiate smectites when using this

technique; however, no trials were made using the lower concentrations.

Identification of zeolite species also posed some difficulty. The zeolites, clinoptilolite and heulandite, both give X-ray diffractograms similar to the patterns given by the zeolites in the soils of this study (Table 8). X-ray diffraction alone, then, cannot distinguish these two minerals. Additional methods (scanning electron microscopy, cation exchange, and differential heating) were employed. Heulandite was tentatively identified as the principal zeolite in the soil. The two minerals are quite similar, and in the text that follows, the zeolitic mineral will simply be referred to as "zeolite."

X-ray Diffraction (XRD)

The mineralogy of the Cr horizon of pedon 1, assumed to be representative of the parent tuff of all three pedons, will be discussed first. The mineralogy of each profile overlying the tuff will then be discussed. Only diagnostic X-ray peaks will be discussed. More complete listing of peaks and their respective hkl indices are given in Tables 8 and 9.

Parent Material

The zeolite was present in all fractions of the tuff from fine clay through medium sand. The diagnostic

TABLE 8. XRD powder data: zeolites

d (nm)		hkl		I/I ₀	
Clinop.*	Heul.†	Clinop.	Heul.	Clinop.	Heul.
0.895	0.891	020		100	80
0.797	0.795	002	200	3	70
0.678		101		2	
	0.666		001		60
0.512	0.510	112	310	7	70
0.465	0.464	130	131	14	60
0.398		132		55	
0.396		004		55	
0.390	0.392	042	421	57	100
0.373	0.373	141	241	7	20
	0.343		222		70
0.297	0.296	044	350	80	90
0.280	0.280	035	530	15	70
	0.253		152	20	
	0.243		261	30	
	0.227		603	10	

*Clinop. = clinoptilolite. Data from Wise et al. (1969).

†Heul. = heulandite. Data from Merkle and Slaughter (1968).

TABLE 9. XRD powder data: selected minerals

Mineral	d(nm)	hkl	I/I _o
Calcite*	0.303	104	100
Quartz [†]	0.426	100	35
	0.334	101	100
Andesine [#]	0.641	001	50
	0.404	201	80
	0.376	111	70
	0.337	112	60
	0.321	040	100
	0.318	002	90
	0.300	131	60
	0.293	041	70
	0.253	241	70
	0.249	241	60

*ASTM powder diffraction file 5-586

[†]ASTM powder diffraction file 5-490

[#]ASTM powder diffraction file 10-359

0.89-nm 040 peak is well defined in each of the fractions (Figs. 5, 6, and 7).

The 1.77-nm XRD smectite peak is well defined in the fine clay (Fig. 5) of the tuff. The sharpness of this peak indicates the virtual absence of an interlayer component. The small 1.00-nm peak in the fine clay diffractogram of the Ca-glycerol (Ca-Gly) treatment (Fig. 5) results from a small amount of discrete illite.

The coarse clay (Fig. 6) has a similar suite of minerals with the addition of quartz (0.426 and 0.334 nm). Kaolinite was not detected in any part of the clay extracted from the tuff.

Plagioclase (0.316 nm) and quartz (0.334 nm) comprise most of the sand, but zeolite probably comprises as much as 40 to 50% of the silt. The silt of the tuff appears to contain somewhat more zeolite than any other fraction (Fig. 7). The zeolite occurring in the sands and silts (Fig. 7) does not occur as discrete crystals, but rather as micro-domains within glass shards.

Pedon 1

The three principal clay minerals of the tuff are also present in the clay of all the horizons overlying the tuff. But kaolinite (0.71 nm), which is not in the tuff, is present in the clay of the solum (Fig. 8). There is not a clear depth trend of the kaolinite in the clay. The

Figure 5. X-ray diffractograms of the fine clay from the pedon 1 Cr horizon.

Figure 6. X-ray diffractograms of the total clay (top) and coarse clay (bottom) from the pedon 1 Cr horizon.

Figure 7. X-ray diffractograms of the fine sand (top), very fine sand (middle), and silt (bottom) from the pedon 1 Cr horizon.

usual explanation for the presence of this mineral is by an eolian addition, but if this were the case, one would expect an increase upwards in the profile. Perhaps this mineral occurs as a weathering product of plagioclase feldspar. Tardy et al. (1973) found evidence of plagioclase weathering to kaolinite in a variety of climates.

Smectite is present in the total and fine clays of this pedon (Figs. 8 and 9). A depth trend is readily apparent in the diffractograms of the total clay. The 1.80-nm peak is fairly sharp in the Cr/B horizon and then gradually becomes less intense and more diffuse with proximity to the surface. Smectite is only detected by a very broad peak or "shoulder" on the A1 horizon diffractogram.

A 1.00-nm illite peak is evident in the total clay of all the horizons of this pedon. This peak becomes slightly more pronounced upwards in this profile. However, the trend of interstratification of smectite, suggested by the broadening of the 1.80-nm peak, is also increasing towards the surface. This trend is also evident in the diffractograms of the fine clays (Fig. 9).

Zeolite is present in all the fine earth fractions of each horizon in this pedon, except the fine clay. X-ray diffractograms of the total clay (Fig. 8) do not manifest a marked depth trend for the zeolite (0.89 nm). However, a trend is evident in the fine clay (Fig. 9); the zeolite is detected in the Bk2, but there is little or no

Figure 8. X-ray diffractograms of the total clay from pedon 1.

Figure 9. X-ray diffractograms of fine clays from selected horizons of pedon 1.

XRD evidence for zeolite in the Bw or Al horizons. The coarse clays (Fig. 10) contain well crystallized smectite, illite, kaolinite, and zeolite (sharp peaks at 1.77, 1.00, 0.71, and 0.89 nm, respectively). Smectite decreases with proximity to the surface, but no other depth trends are apparent from the coarse clay diffractograms.

Zeolite is present in silt- and sand-size aggregates (Figs. 11 and 12). The silt contains considerable zeolite (an estimated 10 to 30 percent). In addition to the zeolite, the silt fraction contains plagioclase feldspar (0.320 nm) and quartz (0.334 nm). Calcite (0.303 nm) is indicated from the Bw horizon downward. The zeolite peaks at 0.89 and 0.397 nm show a decrease in intensity upward in the profile.

The very fine sand has a similar mineral suite (Fig. 12). However, plagioclase feldspar and quartz are present in greater quantities compared to the silt fraction.

Pedon 2

Although pedon 2 has undergone little pedogenesis, as compared with pedon 1, the same weathering trends are evident. X-ray diffractograms of the total clay (Figs. 13 and 14) show a decrease in the intensity of the 0.89-nm zeolite peak toward the surface. Illite (1.00 nm) and smectite (1.77 nm) are also present in the whole clay. The illite peak is weak, prior to K saturation, in

Figure 10. X-ray diffractograms of the coarse clay from the Bw and Bk2 horizons of pedon 1, A2/Cr horizon of pedon 2, and Bw horizon of pedon 3, from top to bottom, respectively.

Figure 11. X-ray diffractograms of the silt from pedon 1.

Figure 12. X-ray diffractograms of the very fine sand from pedon 1.

Figure 13. X-ray diffractograms of the total clay from the pedon 2 Al horizon.

Figure 14. X-ray diffractograms of the total clay from the pedon 2 A2/Cr horizon.

diffractograms of both horizons, and no real depth trend is discernable. Smectite, on the other hand, is much better defined in the A2/Cr than in the A1 diffractogram. Interstratification, manifested by broadening of the 1.77-nm peak, is barely detectable in the A2/Cr horizon, whereas the A1 diffractogram shows a definite interstratified smectite-illite component. This is the same trend described for pedon 1.

The fine clay of the A2/Cr horizon contains well crystallized smectite and zeolite, and a small amount of discrete illite (Fig. 15). The weathering status of this horizon differs little from that of the tuff.

Sand and silt mineralogies in this pedon (Figs. 16 and 17) are very similar to those in pedon 1. Mineralogical changes with depth are not readily apparent in either of these fractions, reflecting the immaturity of the soil.

Pedon 3

Pedon 3 is in a depositional position and represents a somewhat different weathering sequence than do pedons 1 and 2. The mineral suite of the total clay is the same as in the first two pedons. Total clay XRD analyses (Fig. 18) indicate that the most obvious difference is the distinct alteration of smectite with proximity to the surface. The 1.80-nm smectite peak is relatively sharp in the 3Bk/Cr horizon, but becomes diffuse in the overlying

Figure 15. X-ray diffractogram of the pedon 2 A2/Cr horizon fine clay.

Figure 16. X-ray diffractograms of the silt from pedon 2.

Figure 17. X-ray diffractograms of the very fine sand from pedon 2.

Figure 18. X-ray diffractograms of the total clay from pedon 3.

2Bk2 horizon. No detectable differences in the smectite peak upwards from the 2Bk1 horizon in the profile are indicated. The diffractograms of the fine clay of horizons above the 3Bk/Cr (Fig. 19) show a weakly crystallized smectite. A somewhat sharper peak for smectite is present in the coarse clay diffractogram of the Bw horizon (Fig. 10). The coarse clay, as expected, is less susceptible to weathering, so well-crystallized smectite is able to persist in this horizon.

A lithological discontinuity at the 2Bk2-3Bk/Cr boundary, described in the field, was not confirmed by particle size ratios, but smectite trends in this profile would seem to confirm the discontinuity. The material above the 3Bk/Cr is apparently depositional. Since this material would already have been subjected to some weathering before deposition, a gradual weathering trend of smectite upwards in the profile would not be expected.

Zeolite and illite do not show recognizable depth trends in the total clays (Fig. 18). The fine clay diffractograms (Fig. 19), however, show little if any indication of zeolite in the 2BK2 or overlying horizons. The coarse clay of the Bw horizon (Fig. 10) does show a well defined 0.89-nm zeolite peak and the coarse clay of the Al horizon (not examined) would undoubtedly show a similar peak, since the zeolite is in the total clay but is not in the fine clay. As in pedon 1, the zeolite is not in the

Figure 19. X-ray diffractograms of the Ca-glycerated fine clay from selected horizons of pedon 3.

more weathered, i.e., surficial, fine clays, but has persisted in surficial coarse clays.

The illite peak of the fine clays shows a slight increase upwards in the profile (Fig. 19). Silt and sand mineralogies (Fig. 20 and 21) are not significantly different from pedons 1 and 2. Depth trends for the zeolite are not apparent in these fractions. However, plagioclase (0.319 and 0.321 nm) and quartz (0.334 nm) give somewhat more intense reflections in the upper horizons.

Thermal Treatments

Prolonged heating was conducted on the silt-size fraction of pedon 1. Silt in the solum of this pedon responded differently to heating in comparison to the silt separated from the tuff. Heating to 500°C for 12 hours destroyed the zeolite in the silt of all horizons above the tuff as indicated by the disappearance of the diagnostic peak at 0.89 nm. The zeolite in the silt from the tuff was not completely destroyed with this treatment, although peak intensity was very much decreased. According to the criteria of Alietti (1972), then, zeolite in the tuff is at least partly composed of a clinoptilolite-like mineral, manifested by slight persistence of the 0.89-nm peak after heating. This mineral does not persist in the soil, nor does it appear to be a significant component of the tuff. Since most of the zeolite is decomposed

Figure 21. X-ray diffractograms of the very fine sand from pedon 3.

on heating, both in the soil and in the tuff, it may be considered as heulandite.

Scanning Electron Microscopy

Composition of the tuff is shown in Figure 22. The coffin-shaped crystals are calcium-rich, and are presumably heulandite. The lath-shaped crystals as well as the thin bladed crystals are potassium-rich and are assumed to be zeolites. These crystals have formed inside the glass shard. Well crystallized smectite has formed around the outside of the shard.

Total Potassium

The total potassium of pedon 1 was determined to ascertain its relationship to illite trends with depth. Concentration of K is evident in the A1 horizon (Fig. 23). The Bw and Bk horizons are relatively depleted in K compared to both the A1 and the Cr/B horizons. Potassium values obtained by horizon were as follows: A, 1.65% K (1.93% K_2O); Bw, 1.23% K (1.45% K_2O); Bk2, 1.18% K (1.38% K_2O); Cr/B, 1.31% K (1.53% K_2O); Cr, 1.40% K (1.64% K_2O). Concentration of K by plant uptake in the root zone and decay on the surface could explain this distribution (Nettleton et al., 1973). It cannot be determined for certain whether or not this signifies a pedogenic origin for the illite. If the origin were strictly

Figure 22. Electron micrograph of parent tuff. Coffin shaped species in center of picture are heulandite crystals. Smectite is seen in the upper right hand corner.

Figure 23. Distribution of percent potassium in the fine clay of pedon 1.

eolian, a linear decrease in concentration of K (and, by extension, illite) with depth in the profile would be expected.

CHAPTER V

WEATHERING TRENDS

The weathering trends of each mineral, both within and among profiles, will be discussed below. The general weathering trend of this system is presented in Figure 24.

Zeolite

The predominant zeolite of both the tuff and soil was identified as heulandite. Other zeolites were detected in the tuff by means of electron microscopy, but these apparently do not persist in the soil. The zeolite is considered here as a primary mineral since it is part of the original mineral suite in which the soils were formed. It is present in all fractions of the tuff underlying the soils and is found hundreds of feet below the surface (Walton, 1975). The absence of zeolites in the fine clays of all the A horizons, together with a gradual decrease in the fine clays upwards in pedons 1 and 2, suggests that it is only moderately stable. Zeolite had been appreciably weathered in the entire solum of pedon 3, with little or no zeolite detected in the fine clay of the solum. The zeolite has weathered in situ in pedons 1 and 2. Pedon 3, on the other hand, has undergone one or

Figure 24. Weathering trends. Direction of arrow indicates direction of maximum concentrations.

more depositional sequences. The zeolites in the fine clays did not survive the transportation-deposition process, or had already been weathered out of the soils from which the sediments were derived.

The zeolite is present in the coarse clay and coarser fractions of all horizons analyzed. This mineral, therefore, is not markedly unstable in the pedogenic environment of the study area. Zeolite is in the coarse clay of the A horizon of pedon 3, which was apparently formed mostly in reworked material, indicating moderate stability. This mineral is not being synthesized in the soil, yet it is relatively stable as suggested by its slow weathering in this soil environment.

Dibble and Tillier (1981), as discussed earlier, consider zeolites in sedimentary, tuffaceous rocks to be metastable reaction products. How can metastable products persist for long periods in soils? The stability of these minerals is due, at least in part, to the arid environment in which these soils have formed. Particles coarser than fine clay weather very slowly in this environment. Only the finest fractions are affected by the relatively small amounts of meteoric water passing through the system. Zeolites may persist in larger fragments indefinitely, as long as the fragments remain intact, since chemical equilibria within the fragments is not significantly different from that of the tuff. In a more humid environment, where

even coarser particles are subject to more intense weathering, zeolites would not be expected to persist in soils.

Smectite

Smectite shows a readily discernible depth trend in pedons 1 and 2. Smectite is progressively degraded upwards in the profiles. Smectite is also unstable in pedon 3, but there is no linear depth trend. Smectite is degraded in the entire solum, which is consistent with the depositional model of this soil, as discussed earlier.

Smectite is often thought to be a stable soil mineral in arid environments. However, it apparently is not a stable mineral in this particular environment. Perhaps Mg activity is too low for smectite stability. The weathering mean (Jackson, 1964) of these soils would have to be placed near smectite, but the direction of weathering, at least according to Jackson's sequence, is going in the reverse direction, which Jackson recognizes as a possibility.

Illite

Illite is the only clay mineral in this study to show an increase in both crystallinity and quantity with proximity to the surface. The trends are only discernable in the fine clays. Whether this increase is caused by an eolian influx or whether illite is actually a pedogenic mineral in this case could not be ascertained in this

study. The upward increase in crystallinity suggests a pedogenic origin. The increased K content in the surface horizon (Fig. 15) could supply considerable K for illite synthesis. Enough Al and Si would also be available from zeolite decomposition for illite synthesis. Smectite peak broadening also suggests increased illite-smectite interstratification with proximity to the surface.

CHAPTER VI

CONCLUSIONS

The mineral suite in the soils studied indicate a relatively low weathering status. Although these minerals are somewhat unweathered, it should not be assumed that mineralogical changes have not occurred. Dynamic weathering processes have occurred in the soil, albeit slowly. Unstable minerals are weathering, and more stable species are either being synthesized from solution or are increasing in a relative sense because of attrition of the more unstable species. Because of the slowness of weathering in this pedogenic environment, it was necessary to examine the fine clays to elucidate mineralogical responses to the current pedochemical environment. Zeolites are unstable, but perhaps only in a geological sense. They are very slow to weather in the soil. Smectite appears to weather somewhat more rapidly and seems to be decreased at the expense of illite formation.

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APPENDIX

Figure 25. Profile of pedon 1.

Figure 26. Profile of pedon 2.

Figure 27. Landscape of pedons 1 and 2.

Figure 28. Profile of pedon 3.

Figure 29. Landscape of pedon 3.