

Zeolites in Soil Environments

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INTRODUCTION

"The limited occurrence of these minerals has resulted in a scant knowledge about their properties in the soils."

Zelazny and Calhoun (1977)

As pointed out by the above authors, the occurrence of natural zeolites in soils is rare and not well known, and only about 75 papers have been published describing the occurrence of zeolites in soils. These occurrences range from hot, humid soils in India to cold, arid soils in the Dry Valleys of Antarctica. Most of these reports describe residual zeolite phases that have persisted from the parent material during soil formation; however, there are reports of zeolites that have formed in soil environments. A variety of natural zeolites have been found in soils, including analcime, chabazite, clinoptilolite, gismondine, laumontite, mordenite, natrolite, phillipsite, and stilbite.

Over the past 25 years, natural zeolites have been examined for a variety of agricultural and environmental applications because of their unique cation-exchange, adsorption, and molecular sieving properties and their abundance in near-surface, sedimentary deposits. Natural zeolites have been used as soil conditioners, slow-release fertilizers, carriers for insecticides and herbicides, remediation agents in contaminated soils, and dietary supplements in animal nutrition (Ming and Allen, this volume; Pond 1995). These applications can result in direct or indirect incorporation of natural zeolites into soils. If these minerals are to be used effectively in these applications, it will be necessary to understand the long-term stability and effects of zeolites in soils or soil-like systems.

Several reviews have been published on the occurrences and properties of zeolites in soils (Zelazny and Calhoun 1977, Ming and Dixon 1987c, Ming and Dixon 1988, Ming and Mumpton 1989, Boettinger and Graham 1995). This chapter provides an overview and update on the occurrence of zeolites in soils and briefly describes methodology used for identifying and characterizing zeolites in soil environments.

OCCURRENCES IN SOIL

The zeolite group of minerals has been known for over one hundred years to exhibit the property of cation exchange, and when soils were also found to have ion-exchange properties, it was assumed that zeolites were major constituent (e.g. see Burgess and McGeorge 1926, Breazeale 1928). It was not until the introduction of modern X-ray diffraction (XRD) methods that this misconception was invalidated. However, in the past 20 years this group of minerals has indeed been reported in a variety of soils.

Ming and Mumpton (1989) first proposed a classification system for zeolites in soil

environments based on the origin of the zeolite, i.e. whether the zeolite was pedogenic (formed in the soil) or lithogenic (a residual mineral phase) from either volcanic or non-volcanic parent materials. Boettinger and Graham (1995) suggested slight modifications to the classification system, which we refine here. The types of occurrences in soil environments currently include (1) pedogenic zeolites in saline, alkaline soils of non-volcanic parent materials; (2) pedogenic zeolites in saline, alkaline soils of volcanic parent materials; (3) lithogenic zeolites inherited *in situ* from volcanic parent materials; (4) lithogenic zeolites inherited *in situ* from non-volcanic parent materials; (5) lithogenic zeolites from eolian or fluvial deposition; and (6) zeolites in other soil environments.

Most occurrences of zeolites in soils have had some influence from previous volcanic activity, e.g. tuffaceous parent materials, however, some zeolites have either been inherited into or formed in soils without previous influence by volcanic activity. Clinoptilolite is the most abundant zeolite found in soils, but, analcime, chabazite, gismondine, heulandite, laumontite, mordenite, natrolite, phillipsite, and stilbite have also been reported to occur in soils. In the following sections we briefly describe the several types of zeolite occurrences in soils.

Pedogenic zeolites in saline, alkaline soils of non-volcanic parent materials

Occurrences of pedogenic zeolites are almost always restricted to soils with saline, alkaline conditions (i.e. soils with pH > 7 and containing appreciable soluble salts). Unlike most sedimentary zeolites, volcanic parent materials are not necessary for zeolite formation in soils. Analcime appears to form most frequently in these soils, but chabazite, clinoptilolite, mordenite, natrolite, and phillipsite have also been reported to form in soils (Table 1).

Table 1. Pedogenic zeolites in saline, alkaline soils of non-volcanic parent materials.

<i>Zeolite</i>	<i>Soil locality</i>	<i>References</i>
Analcime	Burundi	Frankart & Herbillon (1970)
	California, USA	Schultz et al. (1964); Baldar & Whittig (1968); El-Nahal & Whittig (1973); Baldar (1968)
	India	Kapoor et al. (1980)
	Former U.S.S.R.	Travnikova et al. (1973)
	Kenya	Renaut (1993)
	Tanzania	Hay (1963); Hay (1976); Hay (1978)
Chabazite	Tanzania	Hay (1970); Hay (1978)
Clinoptilolite	Alberta, Canada	Goh et al. (1986); Spiers et al. (1984)
Mordenite	Chad	Maglione & Tardy (1971)
Natrolite	Kenya	Renaut (1993)
	Tanzania	Hay (1970); Hay (1978)
Phillipsite	Former U.S.S.R.	Travnikova et al. (1973)
	Tanzania	Hay (1964); Hay (1970); Hay (1978)

One of the first reported occurrences of zeolites in soils was discovered because of an unusual cation-exchange property of a soil in the San Joaquin Valley of California. The soil had an unusually high exchangeable sodium percentage (ESP) of up to 75%, but rice grown in the soil did not exhibit any sodium toxicity effects due the high ESP (Schultz et al. 1964). It became apparent that the sodium was easily removed during exchangeable-cation measurements in the laboratory but was not easily exchanged in the field. Schultz et al. (1964), Baldar and Whittig (1968), and El-Nahal and Whittig (1973) used XRD analyses to confirm that analcime was responsible for this unusual cation-exchange behavior.

The occurrence of analcime in the San Joaquin Valley was restricted to soils containing Na_2CO_3 with a pH above 9, and the zeolite was concentrated near the soil surface in the fine silt (2 to 5 μm) and coarse clay fractions (0.2 to 2 μm). Baldar and Whittig (1968) were able to effectively destroy the analcime in the soil with 0.5 M HCl treatments and then reprecipitate analcime by titrating the system above pH 9 with NaOH, followed by mild heating to 95°C for 14 days. The occurrence, distribution, and relative ease of synthesizing analcime led Baldar and Whittig (1968) to the conclusion that the zeolite was of pedogenic origin with no apparent influence from volcanic parent materials. Similar occurrences of analcime in soils have been reported in Burundi, India, the former U.S.S.R., Kenya, and Tanzania (see Table 1).

Renaut (1993) found up to 40% analcime and minor amounts of natrolite in exhumed paleosols on the former margin of saline, alkaline Lake Bogoria in the Kenya Rift Valley. The zeolitic sediments are up to 1 meter thick and occur in Late Quaternary fluviolacustrine siltstones, mudstones, and claystones. The sediment has many pedogenic features similar to those found in current soils, including prismatic soil structure and vertical to subvertical rootmarks. Fossilized root mats, calcareous rhizoliths, Fe-Mn concretions, and secondary concentrations of opaline silica further indicate that these sediments were pedogenically altered. The amount of analcime decreases with increasing paleosol depth, and decreases with increasing distance from the lake. The analcime occurred as subhedral and euhedral crystals (0.5 to 2.5 μm) filling former root channels. Renaut (1993) concluded that analcime probably formed from reaction of detrital silicates with Na_2CO_3 -rich pore waters, which moved upward in response to evapotranspiration near the land surface. Analcime persists in these paleosols under the present hot and semi-arid climate and may be currently forming along the margins of the lake.

Phillipsite, chabazite, and natrolite have been reported to occur in relatively minor amounts in saline, alkaline soils, which have developed in non-volcanic parent materials (Hay, 1964, 1970, 1978). Their occurrence in these soils is likely due to the saline, alkaline nature of the soil environment and the low intensity of weathering and leaching.

Highly-siliceous zeolites (e.g. clinoptilolite, mordenite) have rarely been reported to form in soils. Spiers et al. (1984) reported the occurrence of clinoptilolite in a solodized solonetz (i.e. slightly leached sodic [high ESP] soil) that had developed on loam till in Alberta, Canada. These authors suggested that the weathering of smectites supplied Si into solution necessary for the formation of clinoptilolite. The chemistry of extracted soil solution was similar to that of pore waters associated with sedimentary clinoptilolite deposits. Thermodynamic modeling of the soil solution by SOLMNEQ predicted precipitation of clinoptilolite. Clinoptilolite occurred only in the zone of active leaching of Na and salts in the top 40 cm of the soil. No zeolites were detected in the deeper soil horizons. Clinoptilolite was concentrated in the coarse clay (1 to 2 μm) and silt (2 to 20 μm) fractions. Another highly siliceous zeolite, mordenite, has been reported to form in saline, alkaline sediments and soils at the edge of Lake Chad (Maglione and Tardy 1971).

Pedogenic zeolites in saline, alkaline soils of volcanic parent materials

As described by Hay and Sheppard (This volume), zeolites are widespread in geologic deposits as alteration products (i.e. authigenic minerals) of volcanic glass subjected to saline, alkaline conditions. For example, volcanic materials (e.g. glass) near the land surface in closed hydrologic basins (i.e. saline, alkaline lake deposits) will undergo dissolution, releasing Si, Al, and alkali and alkaline earth cations into solution. Precipitation occurs when the solution becomes saturated with respect to the zeolite. The type of zeolite that will form depends on a number of factors (Surdam and Sheppard, 1978; Chipera and Apps, this volume), including (1) cation ratios, (2) pH, (3) Si/Al atomic ratios, (4) activity of silica, (5) activity of water, and (6) salinity. Therefore, it is expected that zeolites will form in soils derived from volcanic sediments under saline, alkaline conditions (Table 2).

Table 2. Pedogenic zeolites in saline, alkaline soils of volcanic parent materials.

<i>Zeolite</i>	<i>Soil locality</i>	<i>References</i>
Analcime	Tanzania	Hay (1963); Hay (1976); Hay (1978)
Chabazite	Antarctica	Gibson et al. (1983)
	Tanzania	Hay (1970); Hay (1978)
Natrolite	Tanzania	Hay (1970); Hay (1978)
Phillipsite	California, U.S.A.	McFadden et al. (1987)
	Mississippi, U.S.A.	Raybon (1982)
	Tanzania	Hay (1964); Hay (1970); Hay (1978)

Analcime, phillipsite, natrolite, and chabazite are found in the saline, alkaline soils in the vicinity of Olduvai Gorge, Tanzania (Hay 1963 1970 1976 1978). These zeolites formed during the alteration of tuffaceous sediments near the land surface under saline-sodic conditions and they have persisted in a hot, semi-arid environment. Individual zeolite crystals are globular, euhedral, or anhedral, and they range between 0.005 to 0.1 mm in either length or diameter.

Phillipsite has formed in a basaltic rubble subsoil environment and desert pavement of the Cima volcanic field in southeastern California (McFadden et al. 1987). The zeolite formed under saline, alkaline conditions caused by eolian influx of highly alkaline sediments from playas, which interacted with water and the basaltic rubble to form euhedral, lath-shaped phillipsite crystals. The authors suggest that the source of Al and Si necessary for the formation of phillipsite was authigenic phyllosilicates, possibly a mixed-layer illite-smectite or illite-vermiculite that had formed in rubble samples.

Gibson et al. (1983) reported the occurrence of chabazite in a cold, sodic desert soil from Wright Valley in Antarctica. The area was known to have experienced past volcanic activity. These authors suggested that the chabazite must be authigenic because the 5 to 10 μm -sized crystals are euhedral, unabraded, and unfractured, which suggest *in situ* formation (Fig. 1). The zeolite occurs throughout the soil profile, including the permanently frozen zone. The presence of dissolution features and authigenic minerals throughout the profile suggests that chemical weathering may still be occurring, even in the permanently frozen zone.

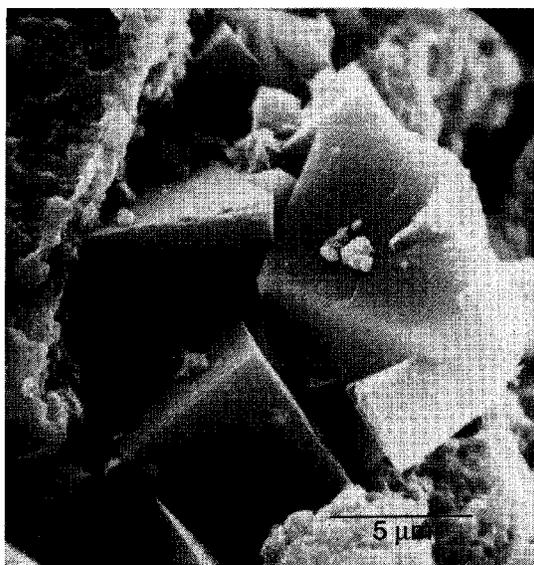


Figure 1. Scanning electron microscope image of chabazite from the permanently frozen zone of a cold desert soil from the Wright Valley in Antarctica (Gibson et al. 1983).

Lithogenic zeolites inherited *in situ* from volcanic parent materials

Large deposits of authigenic zeolites formed as alteration products of volcanic glass in open hydrologic systems are very common around the world (Sheppard and Hay, this volume). Ground water percolating through columns of volcanic ash or glass becomes increasingly enriched in dissolved Si and Al as well as in various alkali and alkaline earth cations. As the ion activity products of zeolites are exceeded, zeolites (e.g. clinoptilolite) will precipitate from solution in areas where volcanic glass has dissolved. When these zeolite-rich sedimentary deposits are later exposed at the land surface, weathering and soil formation occur. Hence, the zeolites are incorporated into the soil as residual mineral phases (i.e. lithogenic). Because these types of zeolite-bearing deposits are very common and extensive, the majority of the reported occurrences of zeolites in soils result from lithogenic zeolites inherited *in situ* during soil formation. Clinoptilolite is the most abundant sedimentary zeolite; therefore, it is expected that clinoptilolite is the most abundant zeolite reported in soils (Table 3). However, there have also been reports of soils containing analcime, chabazite, gismondine, heulandite, mordenite, and stilbite inherited *in situ* from zeolite-rich, volcanic parent materials.

Clinoptilolite is widespread in calcareous soils formed on tuffaceous sediments of the Catahoula Formation in South Texas (Ming 1985, Ming and Dixon 1986). About 2 to 5 wt % clinoptilolite was found in the A and B horizons of a calcareous Mollisol (soil with thick A horizon and high-base saturation). Clinoptilolite concentrations progressively increased with soil depth to ~20 wt % in the C horizons. The zeolite was concentrated in the silt fractions and occurred as clusters of closely spaced laths that were 1 to 2 μm in thickness and 5 to 10 μm in length (Fig. 2). The smooth, angular, euhedral shape of individual crystals indicated their relative stability in the arid soil environment. Slightly pitted and fractured crystals in the A and B horizons suggested minimal weathering of the zeolite (Fig. 2). Clinoptilolite separated from the soil was dominantly Ca exchanged, which can be attributed to the calcareous nature of these soils.

A similar occurrence of clinoptilolite inherited *in situ* from volcanic-rich parent materials was also reported in West Texas (Jacob and Allen 1990). The zeolite occurred in sand, silt, and clay fractions of several soils along a topographic sequence in an arid to

Table 3. Lithogenic zeolites inherited *in situ* from volcanic parent materials.

<i>Zeolite</i>	<i>Soil locality</i>	<i>References</i>
Analcime	Italy	Portegies Zwart et al. (1975); Baroccio (1962)
	Japan	Morita et al. (1985)
	Washington, U.S.A.	Bockheim & Ballard (1975)
Chabazite	Italy	Portegies Zwart et al. (1975)
Clinoptilolite	Alabama, U.S.A.	Karathanasis (1982)
	Alaska, U.S.A.	Ping et al. (1988)
	Bulgaria	Atanassov et al. (1982); Atanassov & Do Vang Bang (1984)
	Hungary	Nemecz & Janossy (1988)
	Japan	Morita et al. (1985); Kaneko et al. (1971)
	Lebanon	Darwish et al. (1988)
	Mississippi, U.S.A.	Raybon (1982)
	Oregon, U.S.A.	Paeth et al. (1971)
	Romania	Asvadurov et al. (1978)
	Former U.S.S.R.	Gorbunov & Bobrovitsky (1973); Travnikova et al. (1973)
	Texas (southern), U.S.A.	Ming & Dixon (1986); Ming (1985)
	Texas (western), U.S.A.	Jacob & Allen (1990)
Utah, U.S.A.	Southard & Kolesar (1978)	
Gismondine	Arkansas, U.S.A.	Reynolds & Bailey (1990)
	Italy	Portegies Zwart et al. (1975)
	Japan	Morita et al. (1985)
Heulandite	India	Bhattacharyya et al. (1993); Bhattacharyya et al. (1999)
Mordenite	Hungary	Nemecz & Janossy (1988)
	Japan	Kaneko et al. (1971)
	New Zealand	Kirkman (1976)
Stilbite	California, U.S.A.	Reid et al. (1988)

semi-arid environment. The abundance and crystallinity of clinoptilolite in the fine clay fraction (<0.2 μm) varied with soil depth and landscape position. In the well-drained Aridisols (arid soils with subsoil development) of summit and backslope positions, fine clay-sized clinoptilolite was less abundant and less crystalline (i.e. broader XRD peaks) in the A horizon than in deeper horizons. There was no clinoptilolite in the fine-clay fraction of the upper 90 cm of the soil in the Entisol (weakly developed soil) in the concave footslope position, which suggested a higher degree of weathering in this wetter site. It

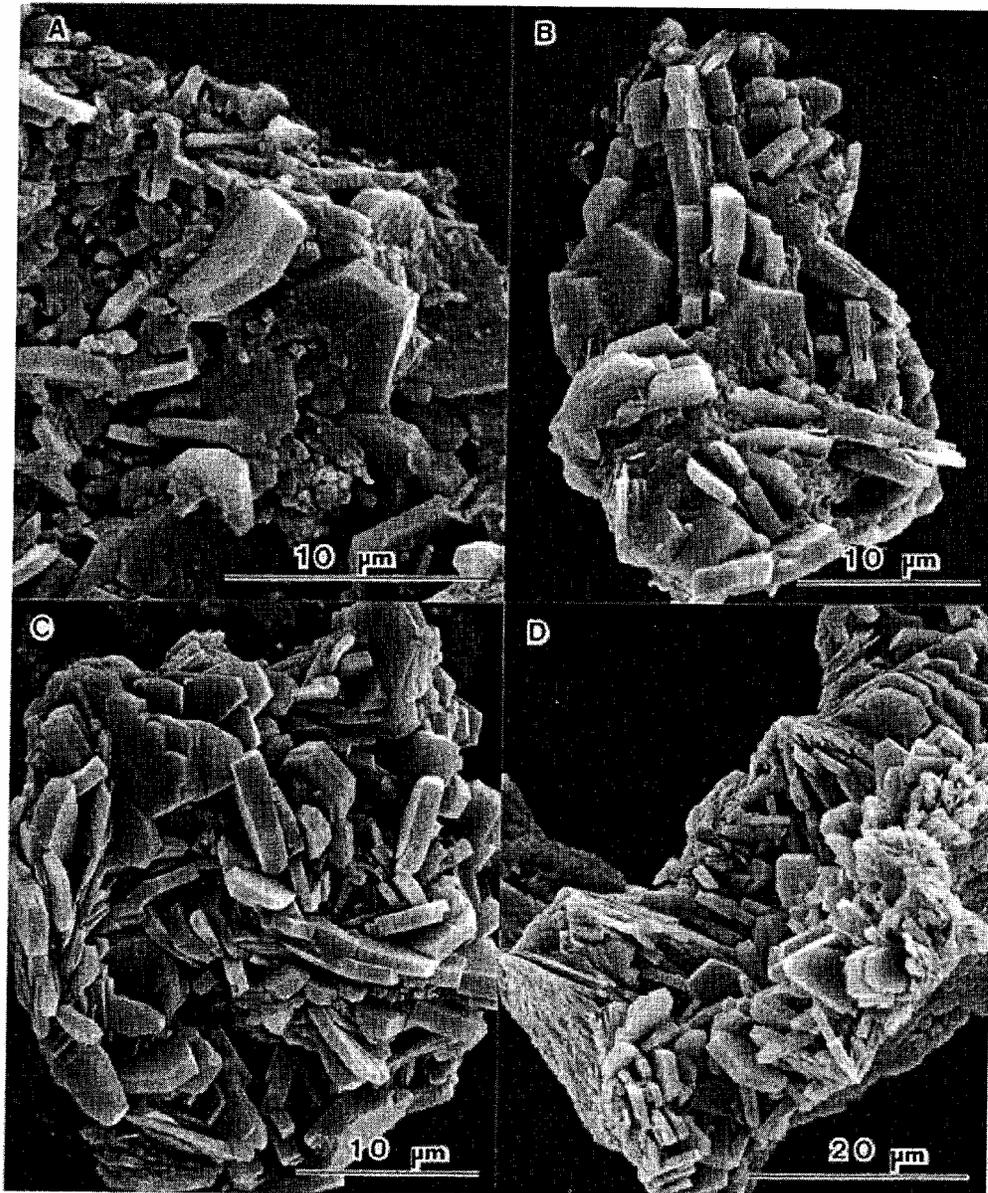


Figure 2. Scanning electron microscope images of clusters of clinoptilolite crystals from a Mollisol located in south Texas (Ming and Dixon 1986): (A) A horizon; (B) Bk1 horizon; (C) and (D) CBk1 horizons.

appears that the finer particle sizes of clinoptilolite are more susceptible to weathering in these upper soil horizons.

Other occurrences of soils containing lithogenic clinoptilolite inherited from volcanic parent materials, are listed in Table 3. The soils exhibit a wide range of weathering and pedogenesis, and they occur in a variety of climates. In general, lithogenic clinoptilolite in soils seems most persistent in larger particle sizes, in deeper horizons, in younger soils, on more recent geomorphic surfaces, in colder climates, and in drier environments.

In several occurrences of zeolites in soils, investigators did not distinguish between isostructural heulandite and clinoptilolite. In most of these cases, it is likely that clinoptilolite is the zeolite occurring in these soils, primarily because they are more likely to be inherited from common clinoptilolite-rich, sedimentary deposits (Ming and Dixon 1986). However, a very interesting occurrence of heulandite has been observed in Alfisols (soils with subsoil clay accumulation and high-base saturation), Vertisols (clay-rich soils capable of significant shrink-swell), and Inceptisols (in this case, intergrades to Vertisols) in India (Bhattacharyya et al. 1993 1999). These soils have developed upon the Deccan flood basalt of the Western Ghats in the state of Maharashtra. Heulandite is widespread in the vesicular or amygdular top of compound flows, although the zeolite is also common at the base of the highly amygdular part of compound flows (Phadke and Kshirsagar 1981, Sabale and Vishwakarma 1996). The zeolite has been inherited from the basalt during soil formation. Heulandite was found in almost all size fractions and composed up to 50 wt % of the weathered basalt C horizons of Vertisols and Inceptisols in the semi-arid zone (500-1000 mm annual rainfall) of the plateau (Bhattacharyya et al. 1993 1999). In high-altitude (~1100 meters) Alfisols of the humid region, partially-weathered heulandite grains were restricted to 5 to 10 wt % of the sand fraction (>50 μm). Bhattacharyya et al. (1999) attributed the persistence of the Alfisols in the tropical humid climate (>5000 mm annual rainfall) to the occurrence of the zeolite in these soils. The authors suggest that heulandite dissolution contributes base cations and Si into solution which facilitates the persistence of smectite in these acidic soils and prevents advanced weathering to kaolinitic or oxidic soils.

Two Ca-rich zeolites, chabazite and gismondine, appear to be stable in calcareous Mollisols weathered from alluvial materials interbedded with volcanic ash in South-Central Italy (Portegies Zwart et al. 1975). Analcime was also found to occur in these soils, however, the authors suggested that it was unstable in the soil environment because the soil solution was undersaturated with respect to analcime. Mordenite, which often occurs with clinoptilolite in sedimentary deposits, has been reported to occur in the clay fraction (<2 μm) of an acid (pH = 5.7) sandy loam soil in New Zealand (Kirkman 1976). Rarely are zeolites reported to persist in acid soils; however, an unusual occurrence of analcime has been observed in extremely acidic (pH around 2), "hydrothermal" soils on Mt. Baker in Washington (Bockheim and Ballard 1975). The zeolite was found to be concentrated in the silt and clay fractions (< 50 μm).

A rare occurrence of stilbite has been reported in the calcareous weathered rock C horizon of an arid Entisol near Red Rock Canyon in southern California (Reid et al. 1988). The occurrence of stilbite in the hydrothermally-altered basalt suggests that the zeolite was inherited *in situ* during soil formation.

Lithogenic zeolites inherited *in situ* from non-volcanic parent materials

Boettinger and Graham (1995) suggested the addition of this new category of zeolite occurrence in soils to the original classification system of Ming and Mumpton (1989). Previous reports of soils containing clinoptilolite/heulandite inherited from non-volcanic parent materials and recent reports of laumontite in California soils, also inherited from non-volcanic parent materials, warranted their separation into a distinct category of occurrence (Table 4).

As mentioned earlier, most reported occurrences of clinoptilolite in soils have been inherited from clinoptilolite-rich, volcanic parent materials. However it is often difficult to determine the origin of the zeolite, or there appears to be no volcanic influence on the soil parent material. For example, Brown et al. (1969) observed clinoptilolite and/or heulandite in soils derived from calcareous, fine-grained siliceous rock of the Upper Greensand Formation in England. There appeared to be no influence from volcanic materials. The

Table 4. Lithogenic zeolites inherited *in situ* from non-volcanic parent materials.

<i>Zeolite</i>	<i>Soil locality</i>	<i>References</i>
Clinoptilolite	England	Talibudeen & Weir (1972); Brown et al. (1969)
	Sicily	Bellanca et al. (1980)
Heulandite	Denmark	Nørnberg & Dalsgaard (1985); Nørnberg et al. (1985); Nørnberg (1990)
Laumontite	California, U.S.A.	Graham et al. (1988); Taylor et al. (1990); Boettinger (1988); Boettinger & Southard (1995); Liu (1988)*

*Not clear if parent material was volcanic or non-volcanic

authors suggested that the zeolite, which occurred mainly in the 1-20 μm size fraction, formed by diagenetic processes after biogenic opal formation and then was inherited by these soils. The high exchangeable K^+ in these soils has been attributed in part to the presence of clinoptilolite and/or heulandite (Talibudeen and Weir 1972). A similar occurrence of clinoptilolite has been observed in calcareous soils in Sicily (Bellanca et al. 1980).

Nørnberg et al. (1985) originally reported the occurrence of clinoptilolite in the A and C horizons of three Mollisols that had developed over Danian bryozoan chalk in northeastern Denmark. Later, Nørnberg (1990) concluded that the zeolite in these soils was heulandite and not clinoptilolite, based upon a Si/Al ratio of 2.88 for the soil zeolite. Heulandite in these soils was K-exchanged, which likely increased its thermal stability (to 600°C, similar to K-exchanged clinoptilolite). Nørnberg (1990) suggested that the heulandite formed under burial diagenetic conditions during chalk formation and was then inherited by the soil, where it became K-exchanged over time. The presence of heulandite in the A and C horizons of some soils, but not the B horizons, was not well understood. However, Nørnberg et al. (1985) suggested that the zeolite may have been added to the A horizon by sediments eroding from calcareous, chalk-derived soils at higher positions in the landscape. Heulandite occurred primarily in the silt (2 to 63 μm) and coarse clay (0.2 to 2 μm) fractions of these soils.

Laumontite has rarely been reported to occur in soils; however, the zeolite has been identified in several soils of southern California (Graham et al. 1988, Boettinger 1988, Taylor et al. 1990, Boettinger and Southard 1995). Taylor et al. (1990) identified laumontite throughout three Entisols in the San Gabriel Mountains of California. These three soils have formed on steep slopes in colluvium of anorthosite, granodiorite, and arkosic sandstone, respectively. Parent materials have been previously hydrothermally-altered by dilute, low-temperature solutions (McCulloh and Stewart 1982) and the laumontite that formed was inherited by the overlying soils. Soil pH ranged from 5.0 in the A horizon of the soil developed on arkosic sandstone to 7.2 in the Cr horizon of the anorthosite-derived soil. Laumontite was found in sand, silt, and clay fractions, however, the particle size of the zeolite depended on its grain size in the parent rock. Comparisons of laumontite grain morphology showed rounded, dissolution-pitted, and crusted weathering products on grains in the A horizons, whereas particles in the Cr horizons tended to be more angular, with fresher crystal faces (Fig. 3).

Boettinger and Southard (1995) identified laumontite in the silt and sand fractions of deep, calcareous B horizons in an Aridisol in the western Mojave Desert of California. The soil formed on weathered and coherent granitic saprolite, previously reported to have been subject to hydrothermal alteration (Dibblee 1963). Laumontite was absent from a soil

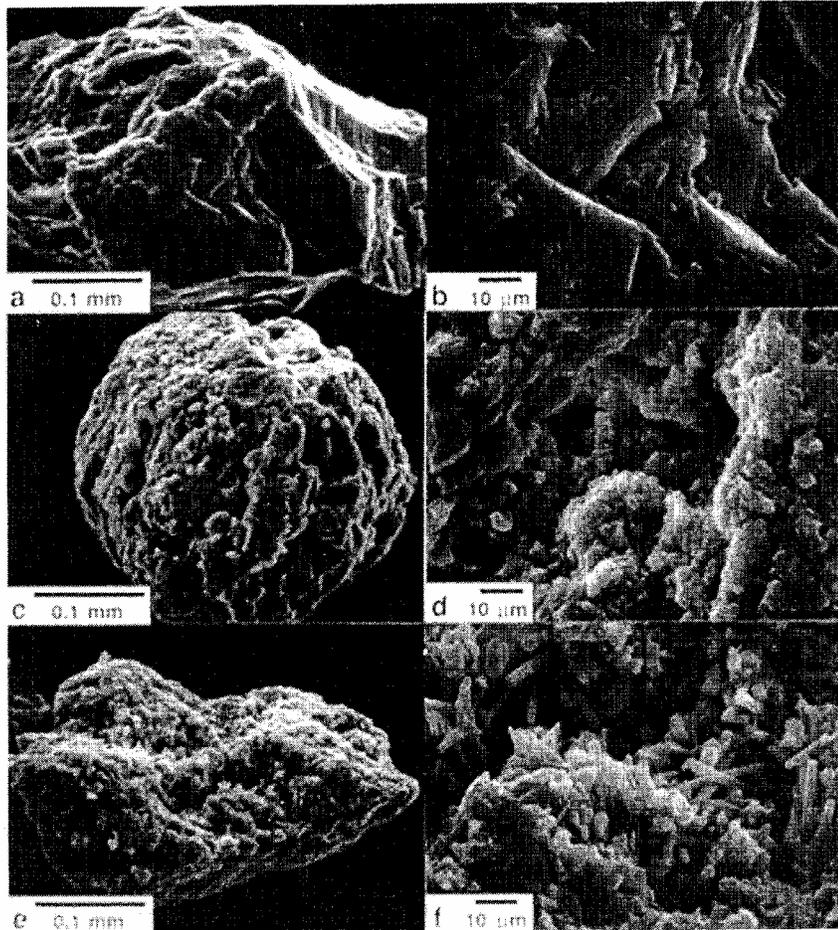


Figure 3. Scanning electron microscope images of sand-sized laumontite grains from an Entisol derived from anorthositic parent materials in the San Gabriel Mountains of southern California (Taylor et al. 1990). (a) angular grain from the Cr horizon; (b) up close surface image of grain in (a); (c) rounded grain from the A horizon, (d) up close surface image of grain in (c); (e) subangular grain from the A horizon; and (f) halloysite tubes on surface of grain in (e).

sampled 50 cm away (Boettinger 1988), suggesting that the zeolite was probably inherited from hydrothermally-altered plagioclase of the parent rock. Laumontite was also identified in two acidic soils (pH 4.8) derived from granitic rock that received additions of volcanic glass in Sequoia National Park in California's southern Sierra Nevada (Liu 1988). It is not clear whether laumontite was inherited as a hydrothermally altered phase in the granitic rock or as a diagenetic product of the volcanic ash.

Lithogenic zeolites from eolian or alluvial deposition

Zeolites have low specific gravities (1.9 to 2.2) and may therefore be removed from erosional surfaces rich in zeolites (e.g. sedimentary deposits) and carried considerable distances by wind or water before being deposited at a soil surface. In this type of soil occurrence, greater quantities of zeolites may be expected in the topsoil or A horizons and, in many cases, zeolites may be completely absent in the lower horizons (e.g. C horizons). Eolian and alluvial additions of chabazite, clinoptilolite, phillipsite, and stilbite have been

Table 5. Lithogenic zeolites from eolian or fluvial deposition.

<i>Zeolite</i>	<i>Soil locality</i>	<i>References</i>
Chabazite	Poland	Brogowski et al. (1980); Brogowski et al. (1983)
Clinoptilolite	Former U.S.S.R.	Gorbunov & Bobrovitsky (1973)
	Texas (southern), U.S.A.	Ming (1985)
	Utah, U.S.A.	Graham & Southard (1983)
Phillipsite	Poland	Brogowski et al. (1980); Brogowski et al. (1983)
Stilbite	Utah, U.S.A.	Jalalian & Southard (1986)

identified in soils (Table 5).

A Vertisol and a Mollisol derived from the Norwood Tuff Formation in northern Utah were reported to contain substantial quantities of heulandite or clinoptilolite (probably clinoptilolite) in the surface soil, progressively decreasing in quantity with increasing soil depth (Graham and Southard 1983). The zeolite was absent or nearly absent in the C horizons of these soils. Other unstable minerals, such as mica and amphiboles, were also found in higher quantities in the upper compared with the lower horizons. Because these unstable minerals were concentrated in the topsoil where weathering should be more intense, Graham and Southard (1983) suggested that the zeolite was introduced into these soils by eolian additions. Zeolites and the other weatherable minerals mostly occurred in the coarse clay and silt fractions. The authors suggest that the some of the eolian source materials may have originated from as far away as the basalt-rich Snake River Plain in Idaho (250 km to the northwest), or the source material for clinoptilolite may have been the nearby clinoptilolite-rich tuffs of the Salt Lake Formation.

In a similar occurrence, Jalalian and Southard (1986) identified stilbite in the medium-silt fraction (5-20 μm) A horizons of a Mollisol and an Alfisol in northern Utah. Stilbite, chlorite, amphiboles, and Ca-feldspar occurred together in the A horizon but were not found in the subsurface horizons. An abrupt change in mineralogy and texture suggested that the upper horizons resulted from recent additions of eolian material. The authors suggested that the zeolite-bearing eolian material had been transported from Lake Bonneville sediments and the Snake River Plain, mantling soils already developed in colluvium and residuum.

A recent study by Clausnitzer and Singer (1999) identified analcime, chabazite, offretite, and phillipsite, along with other mineral groups (e.g. feldspars, phyllosilicates, Fe and Ti oxides, pyroxenes, silica minerals, etc.), in respirable dust particles produced by farming activities from a soil located near Davis, California. The zeolites were identified in the dust using transmission electron microscopy (TEM) selected-area electron-diffraction (SAED) and energy dispersive X-ray spectroscopy (EDXS); however, no zeolites were detected in the source soil by XRD analysis. The original source of the zeolites in the soil is not known; however, it is likely that these particles may have been deposited at the soil surface as eolian additions from a distant source. This study suggests that zeolites may be widespread in soils, but in quantities below the detection limits of most standard soil mineralogical analytical procedures (e.g. XRD analysis).

Zeolites from zeolite-rich tuffs or soils may be eroded by water and transported hundreds of km before being deposited as alluvium. Clinoptilolite is commonly found in

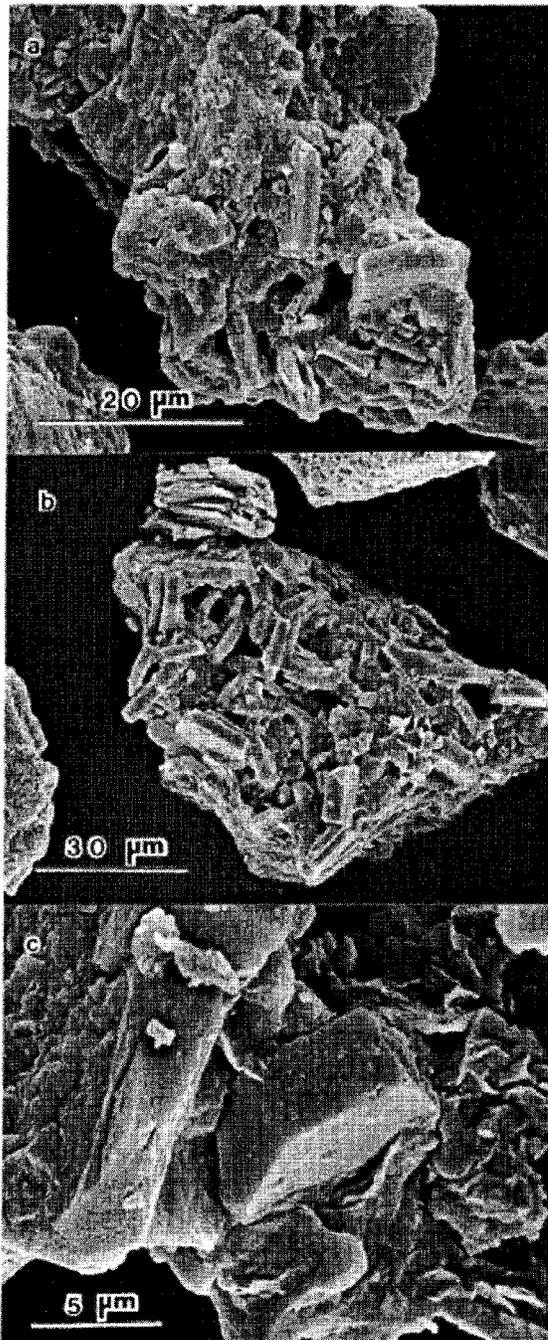


Figure 4. Scanning electron microscope image of a cluster of clinoptilolite crystals from the topsoil of an alluvial soil located along the Rio Grande River, south Texas (Ming 1985).

alluvial soils along the lower 200 to 300 km of the Rio Grande River that separates the United States and Mexico (Ming 1985). Ming (1985) identified clinoptilolite in an Entisol near Brownsville, Texas. The zeolite was found primarily as silt-sized particles and composed less than 5 wt % of the top soil. Morphological characteristics of clinoptilolite were similar to those found in the A and B horizons of soils that had formed on the clinoptilolite-rich Catahoula Formation in South Texas (Fig. 4). It is likely that the source of clinoptilolite in the alluvial soils along the Rio Grande River is the Catahoula and Jackson Formations, which intersect the river about 150 to 200 km upstream from Brownsville. It is also possible that the clinoptilolite may have been transported down the Rio Grande River from the clinoptilolite-rich tuffs in the Trans-Pecos Mountains in western Texas, nearly 1200 km from Brownsville. Interestingly, clinoptilolite was also identified in the muds on the bottom of the river, further indicating that the zeolite had been removed from an erosional surface and transported down river (Ming 1985).

Similar occurrences of clinoptilolite and heulandite are common in alluvial soils along the lower regions of the Rioni River in Russia (Gorbunov and Bobrovitsky 1973). Zeolites in these soils decreased with increasing soil depth and coexisted with kaolinite, "hydromica," chlorite, vermiculite, smectite, and randomly interstratified mica/smectite. The sources of

these alluvial materials is thought to be a siliceous zeolitic tuff cut upstream by a tributary of the Rioni River. Brogowski et al. (1980, 1983) suggested the possibility of zeolites

occurring in alluvial soils in Poland. Chabazite and phillipsite were tentatively identified on the basis of morphology by scanning electron microscopy (SEM); however, definitive XRD analyses were not reported. Brogowski et al. (1983) suggested that the zeolites were transported by the Vistula River from areas where these minerals are known to occur (e.g. Podkarpace).

Zeolites in other soil environments

As with nearly any classification system, there are unusual cases or cases in which not enough information has been provided so that the occurrence can be placed into a specific category; hence, an "other" category was created in the classification system (Table 6). However, nearly all of the zeolite occurrences that we have examined fit into the previous five categories. An exception to this is an occurrence of clinoptilolite in a post-active acid sulfate Ultisol (soil with subsurface accumulation of clay and low-base saturation) in Maryland located on a bluff along the Potomac River (Fanning et al. 1983). Clinoptilolite was identified in both the oxidized and reduced zones. No volcanic ash is known to occur in the parent materials at this site and the origin of clinoptilolite in this soil is a mystery. The other exceptions are occurrences of laumontite in soils considered to be weathering products of plagioclase (Capdecombe 1952, Furbish 1965), where hydrothermal alteration of the parent materials was not mentioned.

Table 6. Zeolite occurrences in other soil environments.

<i>Zeolite</i>	<i>Soil locality</i>	<i>References</i>
Clinoptilolite	Maryland, U.S.A.	Fanning et al. (1983)
Laumontite	France	Capdecombe (1952)
	North Carolina, U.S.A.	Furbish (1965)

IDENTIFICATION OF ZEOLITES IN SOILS

Soils are very complicated mineralogical and chemical systems. A soil is defined as the unconsolidated mineral or organic matter on the surface of the earth that has been subject to and influenced by genetic and environmental factors of parent material, climate (including water and temperature effects), macro- and microorganisms, and topography, all acting over a period of time. A soil can be quite different from the material from which it was derived. Because of this complex system, it is sometimes difficult to detect and identify small quantities of minerals in soils, particularly zeolites. In the A and B horizons of most soils, the quantity of zeolites rarely exceeds 5 to 10 wt %, and special precautions and procedures may be required to concentrate or separate zeolites in soils for proper identification and characterization.

Separation and quantification techniques

Special precautions should be exercised when preparing a soil sample containing zeolites for subsequent mineralogical analyses. It is not uncommon for soil scientists to use chemical pretreatments (e.g. 1 M NaOAc buffered to pH = 5, 30% H₂O₂, and dithionite-citrate-bicarbonate) to remove cementing agents (e.g. carbonates, organic matter, and iron oxides, respectively) and to enhance dispersion of a sample before particle-size fractionation and subsequent mineralogical analyses. Zeolites react differently when subjected to various pH solutions. For example, zeolites with high Si/Al atomic ratios (e.g. clinoptilolite) can withstand acid treatments to a pH below 2 before structural degradation is

detectable; however, zeolites with low Si/Al atomic ratios (e.g. analcime) tend to dissolve during acidic treatments around and below a pH of 5. Ming and Dixon (1987b) found that the above-mentioned chemical pretreatments caused no readily discernible modification to the structure of clinoptilolite found in soils of south Texas. In fact, pretreatments aided in the XRD identification of the zeolite as indicated by increases in peak intensities, probably due to concentrating clinoptilolite by removing calcite and allowing fractionation and separation of the zeolite from other minerals such as smectite. On the other hand, Baldar and Whittig (1968) found that analcime from soils of the San Joaquin Valley of California was destroyed by acid treatments and, hence, they avoided chemical pretreatments designed to enhance disaggregation and dispersion of the soil to eliminate any possible alteration of the analcime. Because pretreatments may have adverse effects on some zeolite minerals, it is possible that some zeolite occurrences in soils may have been missed if they were removed from the sample during chemical pretreatments.

Table 7. Exchangeable cations on zeolitic exchange sites and Si/Al atomic ratios of clinoptilolite separated from a calcareous Mollisol in South Texas (Ming and Dixon 1986).

<i>Horizon</i>	<i>Soil</i>	<i>Exchangeable cations</i>				<i>Si/Al</i>
	<i>depth</i>	<i>Na</i>	<i>K</i>	<i>Mg</i>	<i>Ca</i>	<i>atomic ratio</i>
	cm	-----cmol _c kg ⁻¹ -----				
A	0-25	2	7	5	127	5.1
Bk1	25-38	6	3	7	127	4.7
Bk2	38-66	13	2	7	124	4.7
BCK	66-89	29	3	7	123	4.8
CBk1	89-104	39	5	5	120	4.9
CBk2	104-137	40	5	5	121	5.1

In order to detect chemical and mineralogical differences of a zeolite that occurs throughout a soil profile, the separation of the mineral from the soil becomes an important aspect of the study. By separating the zeolite from the soil, important physical and chemical properties of the mineral can be studied without the interference of other minerals. Ming and Dixon (1987b) used the low specific gravity (≈ 2.16) and fine particle-size (2 to 50 μm) of clinoptilolite to separate the zeolite from soils of South Texas using gravity separation. Initially, representative soil samples were pretreated to remove carbonates, Fe-oxides, and organic matter to enhance particle separation of the clinoptilolite. Clinoptilolite was then separated from other silt-sized particles in the <2.28 sp. gr. heavy-liquid separate. Once clinoptilolite is separated from the soil, a variety of properties can be determined, including exchangeable cations and Si/Al atomic ratios (Table 7). In this example, clinoptilolite in a calcareous Mollisol in South Texas was predominantly Ca-exchanged, which can be attributed to the calcareous nature of the soil (Ming and Dixon 1986). The Si/Al atomic ratio of clinoptilolite did not vary significantly throughout the profile including the parent materials, suggesting that the zeolite was inherited in the soil from clinoptilolite-rich, volcanic parent materials.

A variety of methods may be used to quantify zeolites in soils. Quantification of a mineral in the soil aids in determining the distribution and stability of the mineral

throughout a pedon. Most zeolites in soils are sufficiently crystalline to enable semi-quantitative estimations by XRD powder techniques. El-Nahal and Whittig (1973) compared the XRD peak heights of soil analcime from the San Joaquin Valley of California with those of a reference analcime, and they found the top 15 cm of the soil to contain approximately 22 wt % analcime. Pretreatments were avoided to prevent damage to the analcime crystals. Ming (1985) developed standard XRD curves for clinoptilolite in soils derived from the Catahoula Formation in southern Texas. Standard mixtures were prepared using a high-grade clinoptilolite from Castle Creek, Idaho, a Na-montmorillonite, and varying amounts of quartz, feldspar, and calcite to simulate the matrices of the sand, silt, and clay fractions of the soils. A regression equation ($r^2 = 0.99$) was established that estimated the percentage of clinoptilolite present from the XRD intensity ratios of the zeolite and an internal Al_2O_3 standard.

A cation exchange capacity (CEC) method based on the ion-sieving properties of clinoptilolite was developed for quantitative determination in soils of southern Texas (Ming and Dixon 1987a). Initially, both zeolitic and non-zeolitic exchange sites were exchanged with Na^+ . The CEC of non-zeolitic exchange sites was determined by replacing Na^+ on these sites with tert-butylammonium ions, which are too large to fit into the channels of clinoptilolite (i.e. ion-sieving). Next, the CEC of clinoptilolite was determined by exchanging Na^+ off of the zeolitic exchange sites with NH_4^+ . The amount of soil clinoptilolite was estimated by comparing the measured CEC of zeolitic exchange sites with the total estimated CEC for clinoptilolite ($175 \text{ cmol}_c \text{ kg}^{-1}$). Ming and Dixon (1987a) found a high correlation ($r^2 = 0.96$) between the abundance of clinoptilolite estimated using the CEC method and the abundance estimated by semi-quantitative XRD analysis (Table 8). The CEC procedure described by Ming and Dixon (1987a) was developed strictly to quantify clinoptilolite, and the procedure would have to be modified in order to quantify zeolites other than clinoptilolite. It should be noted that there are more than 60 zeolites that occur in nature and each has unique crystal structures, ion-sieving properties, cation selectivities, and cation-exchange capacities.

Table 8. Comparison of XRD and cation-exchange capacity (CEC) methods for determining clinoptilolite content in various soil separates for a calcareous Mollisol in South Texas (Ming and Dixon 1987a).

Horizon	Clinoptilolite content (%)							
	Sand (2.0-0.05 mm)		Coarse silt (0.05-0.02 mm)		Fine & medium silt (0.02-0.002 mm)		Clay (<0.002 mm)	
	CEC	XRD	CEC	XRD	CEC	XRD	CEC	XRD
A	1	0	2	3 (1)	20	29 (8)	1	2 (1)
Bk1	1	0	2	4 (2)	9	17 (6)	1	1 (1)
Bk2	2	3 (1)	4	7 (4)	6	12 (6)	1	2 (1)
Bck	6	10 (4)	8	14 (3)	21	38 (4)	1	2 (1)
CBk1	12	14 (6)	24	33 (8)	28	33 (5)	2	4 (1)
CBk2	12	16 (5)	24	30 (9)	45	47 (8)	2	3 (1)

Numbers in parenthesis represent a 95% confidence interval ($n=4$) for semi-quantitative XRD data only. CEC quantitative numbers are average of 2 determinations.

Identification and characterization methods

X-ray diffraction analysis. The most definitive method for identifying zeolites in soils is XRD analysis. For most reported occurrences of zeolites in soils, XRD patterns of zeolites consist of sharp, narrow diffraction peaks, suggesting highly ordered materials. Most of the primary XRD reflections for zeolites and those of other soil minerals do not coincide, making the identification of the zeolite relatively easy. However, several zeolites may be confused with other isostructural zeolites because their XRD patterns are nearly identical, e.g. isostructural phillipsite and merlinoite or isostructural clinoptilolite and heulandite.

To prevent a mistake in identifying the zeolite type in a soil, it may be necessary to use means other than XRD analysis to distinguish the two mineral phases. For example, it may be necessary to determine the Si/Al ratio and exchangeable-cation composition to distinguish isostructural zeolites, such as heulandite and clinoptilolite (see Bish and Boak, this volume). Jacob and Allen (1990) used Si/Al atomic ratios to identify clinoptilolite in Aridisols of the Texas Tans-Pecos volcanic field. Because the zeolite occurred in a calcareous soil, zeolitic exchange sites in the upper horizons had become Ca^{2+} exchanged, which greatly reduces the thermal stability of clinoptilolite and it behaves thermally like heulandite (e.g. Shepard and Starkey 1964). However, clinoptilolite in the lower horizons had both Na and Ca on zeolitic exchange sites and it was thermally stable after heating to 500°C. Jacob and Allen (1990) used a combination of thermal analysis and measurements of the Si/Al atomic ratio (between 5 and 6) and exchangeable cations to identify clinoptilolite. As mentioned earlier, Nørnberg (1990) showed by XRD analysis, Si/Al atomic ratios, exchangeable cations, and heat treatments that the zeolite occurring in Mollisols in Denmark was heulandite, and not clinoptilolite as previously reported based on XRD and heat treatments only (Nørnberg et al. 1985).

Cation-exchange characterization. Because of their unique cation-exchange properties, zeolites can cause abnormal cation-exchange behavior in a soil. These abnormal and unusually high cation-exchange capacities in soils have led to several discoveries of zeolites in soils. As mentioned above, the abnormally high ESPs found in soils of the San Joaquin Valley in California were caused by the presence of analcime (Schultz et al. 1964, El-Nahal and Whittig 1973). Southard and Kolesar (1978) attributed an unusually high extractable K^+ and CEC in Utah soils to clinoptilolite. The clay (<2 μm) content of the A horizon was below 20%, however, the CEC was around 50 $\text{cmol}_c \text{ kg}^{-1}$ (Table 9). An inverse trend was observed for the clay content and the CEC as soil depth increased, unlike the expected trend in most soils where the CEC increases with increasing clay content. Although the authors did not quantify the amount of clinoptilolite in the soil profile, the high cation-exchange capacities in the topsoil combined with the low clay content (15%) suggested that most of the CEC originates with the zeolite. A similar occurrence of clinoptilolite in a soil near Oxford, England, is responsible for the high K-supplying power of the soil (Brown et al. 1969, Talibudeen and Weir 1972).

Although important cation exchange information can be obtained from CEC measurements, standard methods to measure the CEC of a soil may not be appropriate for determining the CEC contribution from a zeolite. Each zeolite species has unique cation selectivity and ion sieving properties. Therefore, special methods may be necessary to characterize the cation-exchange properties of a zeolite in a soil. Ming et al. (1993) developed a method to determine the CEC and native cation composition for sedimentary and soil clinoptilolite. A K^+/Cs^+ exchange method (i.e. K-saturation/Cs-replacement) was used to determine CEC because clinoptilolite is more selective for K^+ than for Na^+ , Ca^{2+} , or Mg^{2+} ; Cs^+ was used as the replacement cation because it is selected over K^+ .

Table 9. Selected chemical and physical properties of a Mollisol that contains clinoptilolite in northern Utah (Southard and Kolesar 1978).

Note the inverse trend between clay content and CEC with depth.

(cm)	%	-----cmol _c kg ⁻¹ -----	
0-30	15	52	42
30-65	19	47	32
65-90	21	44	24
90-115	20	40	23
115-145	30	35	8

For determination of native exchangeable cations, Cs⁺ was used as the replacement cation because of clinoptilolite's high selectivity for Cs⁺. The sum of exchangeable cations removed by this step nearly equaled the total CEC measured for various sedimentary and soil clinoptilolites. The high selectivity of clinoptilolite for Cs facilitated complete exchange of the cation-exchange sites in clinoptilolite.

Taylor et al. (1990) determined the CEC over different time frames for laumontite from a vein outcrop at the site of the anorthosite-derived Entisol in the San Gabriel Mountains in California. Only 17.3 cmol_c kg⁻¹ of native cations were extracted using Na⁺ as the replacement cation (Table 10). Fewer native cations were replaced by other cations (i.e. Ba²⁺, Sr²⁺, Cs⁺, NH₄⁺). The theoretical or calculated CEC for laumontite based upon the mineral's Al/Si ratio is around 420 cmol_c kg⁻¹ (Ming and Mumpton 1989). The unexpectedly low measured CEC was attributed to apparently slow diffusion of cations from the one-dimensional channels of laumontite. Hence, laumontite did not contribute significantly to the CEC of these soils.

Table 10. Cumulative sums of native cations displaced by various replacement cations over time for a laumontite sample from the San Gabriel Mountains in California (Taylor et al. 1990).

Extracting solution	Time of extraction		
	3 days	10 days	17 days
	-----cmol _c kg ⁻¹ -----		
NaCl*	7.3	11.5	17.3
BaCl ₂	3.8	4.0	4.2
NH ₄ Cl	5.4	6.7	7.5
SrCl ₂	2.1	2.4	2.6
CsCl	1.8	1.9	2.1

*Displaced cation values do not include native Na.

Other analytical techniques. Several techniques can complement XRD analysis in identifying zeolites in soils, including SEM, transmission electron microscopy (TEM), infrared analysis (IR), thermal analysis (TA), elemental analyses, nuclear magnetic resonance (NMR), and CEC measurements. Zeolites are very photogenic in sedimentary rocks (e.g. see Mumpton and Ormsby 1978, Ming and Mumpton 1989), however, little is

known about the morphology of zeolites in soil environments. Because most of the zeolites occurring in soils have been inherited from the parent rock, which is usually zeolite-rich sedimentary material, the morphology of zeolites in soils would be expected to be similar to those found in sedimentary deposits. The morphologies of clinoptilolite occurring in the soils from south Texas are very similar to the usual lath-shaped morphology found in sedimentary deposits (see Fig. 2). As might be expected, the clusters of clinoptilolite inherited in the upper horizons appear to be "weathered" (e.g. etched crystals) and cemented with other soil materials. However, if the zeolite is forming in the soil environment, the morphology would likely be euhedral, with little evidence of dissolution pitting and etching, similar to the occurrence of chabazite in the soils of the Antarctica Dry Valleys (Gibson et al. 1983) (Fig. 1).

A variety of analyses can be performed on a transmission electron microscope, including morphological studies, electron diffraction, and high-resolution lattice imaging. Kirkman (1976) identified mordenite as long laths in a sandy loam soil on North Island, New Zealand, using electron diffraction. Clinoptilolite crystals separated from the A horizon of a calcareous Mollisol from southern Texas had a well-defined platy morphology, however, they were intimately associated with irregularly shaped particles with diffuse boundaries (Ming 1985). These irregular shaped particles were identified by electron diffraction to be smectite, suggesting a weathering transformation from clinoptilolite to smectite in the upper horizons of this soil (Fig. 5). No smectite was found associated with clinoptilolite crystals in the lower horizons (i.e. CB horizons).

Infrared spectroscopy is rarely used in the identification of zeolites, but IR can be used to study structural features of zeolites (Flanigen et al. 1971, Ward 1971). Infrared analysis is sensitive to the framework Si/Al compositions in which the asymmetric modes ($900\text{-}1300\text{ cm}^{-1}$ for most zeolites) shift to lower frequencies with increasing Al contents (Flanigen et al. 1971). Ming (1985) examined the IR spectra of clinoptilolite separated from various soil horizons in southern Texas soils. Mid-infrared spectroscopy indicated slight or no variation in bond strengths for the (Si,Al)-O asymmetric and symmetric stretching modes of clinoptilolite separated from the various horizons, suggesting similar Si/Al atomic ratios for the zeolite throughout the soil profile. Ward and McKague (1994) developed non-destructive methods to differentiate between clinoptilolite and heulandite using static proton NMR, ^{27}Al magic angle spinning (MAS) NMR, and ^{29}Si MAS NMR techniques.

Thermal analysis (e.g. differential thermal analysis or DTA, differential scanning calorimetry or DSC, thermal gravimetric analysis or TGA) has been used occasionally to distinguish between zeolites with similar XRD properties (e.g. isostructural clinoptilolite and heulandite). However, variations in exchangeable cations will greatly influence the thermal behavior of zeolites. For example, Ca-exchanged clinoptilolite becomes thermally unstable around $250\text{-}350^\circ\text{C}$ and behaves similarly to heulandite, which has Ca as its predominant exchange cation in nature. Conversely, K-exchanged clinoptilolite is thermally stable to near 700°C (Shepard and Starkey 1964). In order to insure proper identification of isostructural zeolites (i.e. in addition to XRD analysis), it is best to combine information on the Si/Al atomic ratio and exchangeable cation content with thermal analysis characterization.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDY

Reported occurrences of zeolites in soils are rare, but it is probable that many occurrences of zeolites in soils are overlooked because they are present in minor or trace amounts. We anticipate that zeolites are widespread in soils, particularly in areas near zeolite-rich tuffs. For example, Ming (1985) conducted a reconnaissance study through south Texas and found clinoptilolite in numerous soils derived from the Catahoula

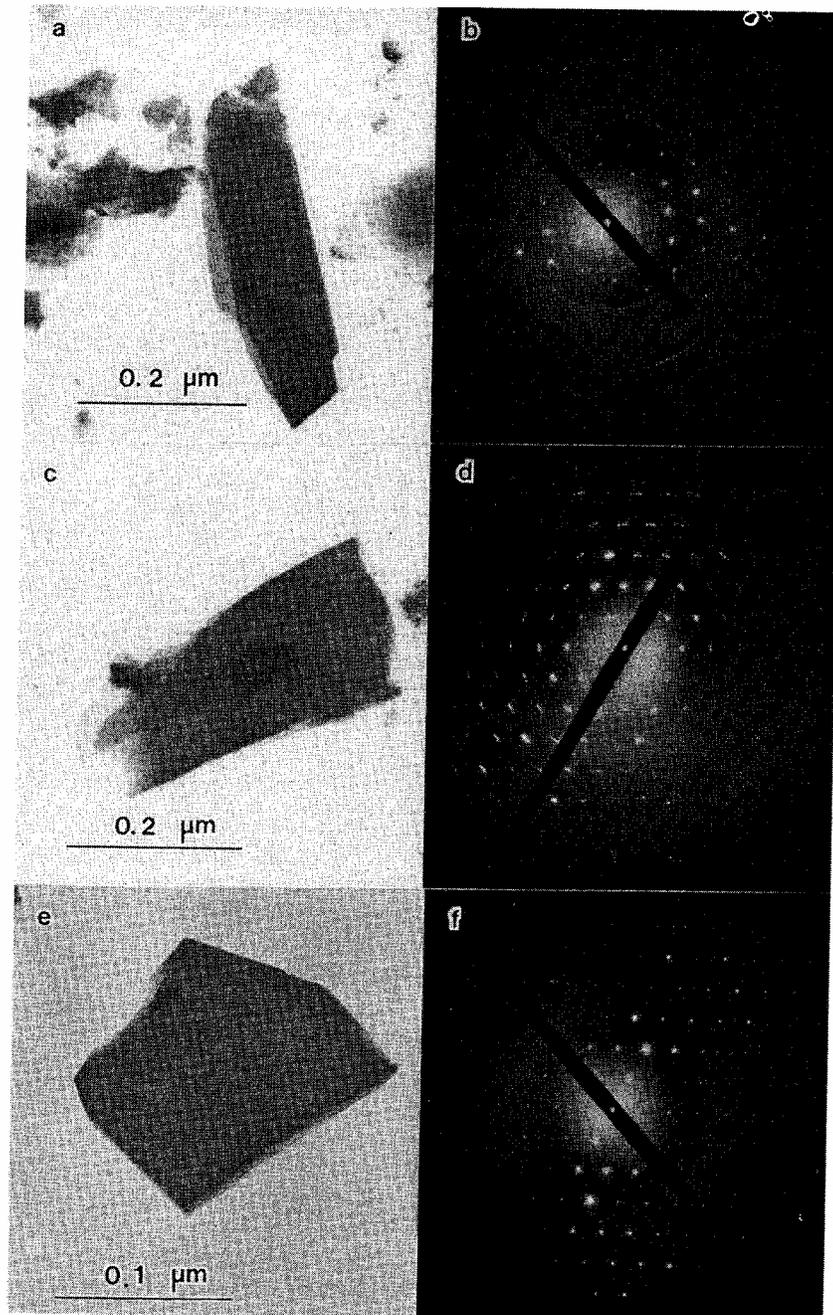


Figure 5. Transmission electron micrographs and electron diffraction patterns for clinoptilolite from a Mollisol located in south Texas (Ming 1985): (a) and (b) A horizon; (c) and (d) Bk2 horizon; and (e) and (f) CBk2 horizons.

Formation. These soils covered an area nearly 200 km long and 10 to 20 km wide. The zeolite content never exceeded 5 to 10% in the upper horizons (i.e. A and B horizons) and might have been missed if the objective of the reconnaissance study had not been to search for zeolites in these soils. Outcrops of zeolite-rich tuffs are common throughout the world,

hence, it is quite likely that zeolites have been inherited into soils that have developed on these tuffaceous materials. Additionally, soils that have not developed on zeolite-rich parent materials might contain zeolites that have been added to the soil surface by eolian and fluvial deposition from nearby sources, e.g. outcrops of zeolite-rich tuffs or zeolite-containing soils. The study by Clausnitzer and Singer (1999) suggests that zeolites may be very common in soils as eolian additions; however, they might not be detected in soils by conventional identification methods such as XRD analysis.

Although we expect fewer occurrences in which zeolites have actually formed in the soil, it is likely that many occurrences of zeolite formation in soils are unreported. As described by Hay (1963 1964 1970 1978), zeolites form from volcanic and non-volcanic sediments at the land surface under saline, alkaline conditions. Several other reports have described the formation of zeolites in soils at the margins of saline, alkaline lakes. Saline, alkaline lakes and deposits occur in many arid regions in the world, therefore, there exists the potential for the discovery of additional occurrences of zeolites forming in soils.

We recommend that soil scientists look closely for zeolites in areas where zeolites might be expected to exist in soils, e.g. soils developed on volcanic sediments, soils near a zeolite-rich outcrop, or soils developing in volcanic materials at the margin of a saline, alkaline lake. Chemical and mineralogical characterization of the zeolite and soil, climatic conditions of soil formation, parent material, etc., will provide valuable information on the stability and persistence of zeolites in soils. Not only is this interesting from a pedological standpoint, but this information will also aid researchers as they evaluate the possibilities of adding zeolites to soils for agricultural and environmental applications. In addition, standard mineralogical analyses of soils often exclude analysis of the silt and sand fractions, in which most zeolites in soil occur. We also recommend expanding mineralogical investigations to larger size fractions, especially in areas where lithogenic or pedogenic zeolites may be expected to occur.

As suggested by Boettinger and Graham (1995), studies should be considered that examine zeolite distribution and weathering in soil sequences over chronological and climatic gradients. Studies should be conducted on the weathering of zeolites in a variety of environments, e.g. acid vs. neutral vs. alkaline soils. Additional studies of the chemical changes and stabilities of zeolites throughout a soil profile are warranted, i.e. comparison of zeolites in the parent material with those that have been inherited into the topsoil.

At present, we can only speculate on the stability of zeolites when added to a soil for an agricultural or environmental application. We expect that the mode of formation will shed some light on the expected stabilities of zeolites. Zeolites that readily form in saline, alkaline environments at the land surface, such as the more aluminous zeolites (e.g. analcime and phillipsite), will likely not persist very long if added to acidic soils. In fact, in very acidic environments (e.g. $\text{pH} < 5$), these zeolites may survive only a few days or weeks. On the other hand, more siliceous zeolites (e.g. clinoptilolite, mordenite) that formed under diagenesis and hydrothermal alterations at temperatures and pressures higher than in soil environments will likely be much more stable when introduced into soils. Lithogenic zeolites appear to weather more rapidly when in finer particle sizes and in near-surface horizons where weathering intensity is greatest in most soil environments. These zeolites may persist for years or up to, perhaps, millions of years, depending on the soil environment. No doubt, numerous factors such as zeolite type and particle size, soil pH, climatic conditions, etc., will have a major impact on the how long these zeolites may persist in soils. Because of the scant knowledge available on the occurrences of zeolites in soil environments, we are a long way from being able to adequately predict the behavior of zeolite additions into soils.

ACKNOWLEDGMENTS

We thank John Gruener for his helpful comments on the manuscript. We also thank Dr. Takashi Mikouchi for translation of articles from Japanese to English. This work was supported in part by NASA's Advanced Life Support program. We are very grateful to the guidance, wisdom, and encouragement provided by our colleague, Fred Mumpton.

REFERENCES

- Asvadurov H, Popescu F, Constantinescu M (1978) Soluri si roci cu continut ridicat de potasiu schimbabil. *An Inst Cerc Pedol Agrochim* 43:115-123
- Atanassov I, Dimitrov DN, Etropolis H (1982) General characteristics of soils developed upon zeolite rocks in the East Rodopa Mountain. *Soil Sci Agrochem* 17:64-70
- Atanassov I, Do Vang Bang (1984) Minerals of fine dispersion and the evolution of the mineral portion of soils overlying zeolites. *Pochvoznanie i Agrokhimiia*, 19:47-57
- Baldar NA (1968) Occurrence and formation of soil zeolites. PhD dissertation, University of California, Davis, California, 150 p
- Baldar NA, Whittig LD (1968) Occurrence and synthesis of soil zeolites. *Soil Sci Soc Am Proc* 32:235-238
- Baroccio A (1962) Prove di concimazione su terreni vulcanici ad analcite. *L'Agricoltura Italiana* 7:207-217
- Bellanca A, Di Caccamo A, Neri, R (1980) Mineralogia e geochimica di alcuni suoli della Sicilia Centro-Occidentale: Studio delle variazioni composizionali lungo profili pedologici in relazione ai litotipi d'origine. *Mineral Petrogr Acta* 24:1-15
- Bhattacharyya T, Pal DK, Deshpande SB (1993) Genesis and transformation of minerals in the formation of red (Alfisol) and black (Inceptisol and Vertisol) soils on Deccan basalt in the western Ghats, India. *J Soil Sci* 44:159-171
- Bhattacharyya T, Pal DK, Srivastava P (1999) Role of zeolites in persistence of high altitude ferruginous Alfisols of the humid tropical Western Ghats, India. *Geoderm* 90:263-276
- Bockheim JG, Ballard TM (1975) Hydrothermal soils of the crater of Mt. Baker, Washington. *Soil Sci Soc Am Proc* 39:997-1001
- Boettinger JL (1988) Duripan genesis on granitic pediments of the Mojave Desert. MS thesis, Univ California, Davis, California, 195 p
- Boettinger JL, Graham RC (1995) Zeolite occurrence in soil environments: An updated review. In Ming DW, Mumpton FA (eds) *Natural zeolites '93: Occurrence, Properties, Use*. Int'l Committee on Natural Zeolites, Brockport, New York, p 23-27
- Boettinger JL, Southard RJ (1995) Phyllosilicate distribution and origin in Aridisols on the granitic pediment, Western Mojave Desert. *Soil Sci Soc Am J* 59:1189-1198
- Breazeale JF (1928) Soil zeolites and plant growth. *Agricultural Experiment Station Tech Bull No. 21:499-520*, Univ Arizona, Tucson, Arizona
- Brogowski Z, Dobrzanski B, Kocon JE (1980) Morphology of natural zeolites occurring in soil as determined by electron microscopy. *Bull Acad Polonaise Sci, Ser Sci Terre* 27:115-117
- Brogowski Z, Dobrzanski B, Kocon JE, Zaniowska-Chlipalska (1983) The possibility of zeolites occurrence in the soils of Poland. *Zeszyty Problemowe Postepow Nauk Rolniczych* 220:489-494
- Brown G, Catt JA, Weir AH (1969) Zeolites of the clinoptilolite-heulandite type in sediments of south-east England. *Mineral Mag* 37:480-488
- Burgess PS, McGeorge WT (1926) Zeolite formation in soils. *Science* 64:652-653
- Capdecombe L (1952) Laumontite du Pla des Aveillans (Pyrénées-Orientales). *Bull Soc Hist Nat Toulouse* 27:299-304
- Clausnitzer H, Singer MJ (1999) Mineralogy of agricultural source soil and respirable dust in California. *J Environ Qual* 28:1619-1629
- Darwish TM, Gradusov BP, Sfeyr S, Abdelnur L (1988) Mineralogy and chemical composition of finely dispersed fraction and properties of mountain soils of Lebanon. *Pochvovedeniye* 4:85-95
- Dibblee TW Jr (1963) Geology of the Willowsprings and Rosamond quadrangles, California. *U S Geol Surv Bull* 1089-C, 255 p
- El-Nahal MA, Whittig LD (1973) Cation exchange behavior of a zeolitic sodic soil. *Soil Sci Soc Am Proc* 37:956-958
- Fanning DS, Rabenhorst MC, Wagner DP, Snow PA (1983) Soils-geomorphology field trip in Maryland (Guidebook). August, 1983, in conjunction with American Society of Agronomy Annual Meetings. Washington, DC, 119 p
- Flanigen EM, Khatami H, Szymanski HA (1971) Infrared structural studies of zeolite frameworks. In Gould RF (ed) *Molecular sieve zeolites-I*. *Adv Chem Ser* 101:201-229

- Frankart RP, Herbillon AJ (1970) Présence et genèse d'analclime dans les sols sodiques de la Basse Rusizi (Burundi). *Bull Groupe Franc Argiles* 22:79-89
- Furbish WJ (1965) Laumontite-loenhardite from Durham County, North Carolina. *Southeastern Geol* 6:189-200
- Gibson EK, Wentworth SJ, McKay DS (1983) Chemical weathering and diagenesis of a cold desert soil from Wright Valley, Antarctica: An analog of martian weathering processes. *Proc XIII Lunar Planet Sci Conf, Part 2, J Geophys Res* 88:A912-A928
- Goh TB, Pawluk S, Dudas MJ (1986) Adsorption and release of phosphate in chernozemic and solodized solonchak soils. *Can J Soil Sci* 66:521-529
- Gorbunov NI, Bobrovitsky AV (1973) Distribution, genesis, structure, and properties of zeolite. *Pochvovedeniye* 5:93-101
- Graham RC, Herbert BE, Ervin JO (1988) Mineralogy and incipient pedogenesis of Entisols in anorthosite terrane of the San Gabriel Mountains, California. *Soil Sci Soc Am J* 52:738-746
- Graham RC, Southard AR (1983) Genesis of a Vertisol and an associated Mollisol in Northern Utah. *Soil Sci Soc Am J* 47:552-559
- Hay RL (1963) Zeolitic weathering in Olduvai Gorge, Tanganyika. *Geol Soc Am Bull* 74:1281-1286
- Hay RL (1964) Phillipsite of saline lakes and soils. *Am Mineral* 49:1366-1387
- Hay RL (1970) Silicate reactions in three lithofacies of a semiarid basin, Olduvai Gorge, Tanzania. *Mineral Soc Am Spec Paper* 3:237-255
- Hay RL (1976) *Geology of the Olduvai Gorge*. Univ California Press, Berkeley, California, 203 p
- Hay RL (1978) Geologic occurrence of zeolites. In Sand LB, Mumpton FA (eds) *Natural zeolites: Occurrence, Properties, Use*. Pergamon Press, New York, New York, p 135-143
- Jacob JS, Allen BL (1990) Persistence of a zeolite in tuffaceous soils of the Texas Trans-Pecos. *Soil Sci Soc Am J* 54:549-554
- Jalalian A, Southard AR (1986) Genesis and classification of some Paleoborolls and Cryoborolls in Northern Utah. *Soil Sci Soc Am J* 50:668-672
- Kaneko S, Shoji S, Masui J (1971) Zeolite in paddy soils. I. Occurrence. *Nihon Dôjôgaku Hiryôgaku Zasshi* 42:177-182
- Kapoor BS, Singh HB, Goswami, SC (1980) Analclime in a sodic profile. *J Indian Soil Sci* 28, 513-515
- Karathanasis AD (1982) Characteristics of naturally acid soil smectites. PhD dissertation, Auburn University, Auburn, Alabama, 215 p
- Kirkman JH (1976) Clay mineralogy of Rotomahana sandy loam soils, North Island, New Zealand. *N Z J Geol Geophys* 19:35-41
- Liu WC (1988) The sensitivity of selected soils from the Sierra Nevada to acidic deposition. PhD dissertation, Univ California, Riverside, 105 p
- Maglione G, Tardy Y (1971) Néof ormation pédogénétique d'une zéolite, la mordénite, associée aux carbonates de sodium dans une dépression interdunaire des bords du lac Tchad. *CR Acad Sci Paris, Sér D* 272:772-774
- McCulloh TH, Stewart RJ (1982) Laumontite in the western Transverse Ranges, California: Mark of Neogene hydrothermal alteration coincident with transcurrent faults. *Geol Soc Am Abstr with Programs*, p 213-214
- McFadden LD, Wells SG, Jercinovich MJ (1987) Influences of eolian and pedogenic processes on the origin and evolution of desert pavements. *Geol* 15:504-508
- Ming DW (1985) Chemical and crystalline properties of clinoptilolite in South Texas soils. PhD dissertation, Texas A&M University, College Station, Texas, 257 p
- Ming DW, Allen ER, Galindo C Jr, Henninger DL (1993) Methods for determining cation exchange capacities and compositions of native exchangeable cations for clinoptilolite. In Rodríguez Fuentes G, González JA (eds) *Zeolites '91: Memoirs of the 3rd Int'l Conf Occurrence, Properties and Utilization of Natural Zeolites*, April 9-12, 1991, p 31-35. Int'l Conf Center, Havana, Cuba
- Ming DW, Dixon JB (1986) Clinoptilolite in South Texas soils. *Soil Sci Soc Am J* 50:1618-1622
- Ming DW (1987a) Quantitative determination of clinoptilolite in soils by a cation-exchange capacity method. *Clays & Clay Minerals* 35:463-468
- Ming DW (1987b) Technique for the separation of clinoptilolite from soils. *Clays & Clay Minerals* 35:469-472
- Ming DW (1987c) Zeolites: Recent developments in soil mineralogy. *Transactions, XIII Congress Int'l Society Soil Science, Vol V, Hamburg, Germany*, p 371-382
- Ming DW (1988) Occurrence and weathering of zeolites in soil environments. In Kalló D, Sherry HS (eds) *Occurrence, properties, and utilization of natural zeolites*. Akadémiai Kiadó, Budapest, Hungary, 699-715
- Ming DW, Mumpton FA (1989) Zeolites in Soils. In Dixon JB, Weed SB (eds) *Minerals in Soil Environments*. Soil Science Society of America, Madison, Wisconsin, p 873-911

- Morita Y, Ohsumi Y, Tanaka N (1985) On the nature, genesis and classification of eutrophic soils on the Coastal Hill (Mt. Komayama) in the Shonan District of Kanagawa Prefecture: (II) Distribution, clay mineral composition and properties of parent material of the eutrophic Brown Forest soil, and the assumption of its forming process. *Bull For & For Prod Res Inst* 333:67-91
- Mumpton FA, Ormsby WC (1978) Morphology of zeolites in sedimentary rocks by scanning electron microscopy. *In* Sand LB, Mumpton FA (eds) *Natural Zeolites: Occurrence, Properties, Use*. Pergamon Press, New York, p 113-132
- Nemecz E, Janossy AGS, Olaszi VJ (1988) Behavior of zeolitic minerals during soil formation. *In* Kalló D, Sherry HS (eds) *Occurrence, properties, and utilization of natural zeolites*. Akadémiai Kiadó, Budapest, Hungary, p 675-697
- Nørnberg P (1990) A potassium-rich zeolite in soil development on Danian chalk. *Mineral Mag* 54:91-94
- Nørnberg P, Dalsgaard K (1985) The origin of clay minerals in soils on Danian chalk. 5th Meeting European Clay Groups, Prague, p 553-561
- Nørnberg P, Dalsgaard K, Skammelsen E (1985) Morphology and composition of three Mollisol profiles over chalk, Denmark. *Geoderma* 36:317-342
- Paeth RC, Harward ME, Knox EG, Dyrness CT (1971) Factors affecting mass movement of four soils in the western Cascades of Oregon. *Soil Sci Soc Am J* 35:943-947
- Phadke AV, Kshirsagar LK (1981) Zeolites and other cavity minerals in Deccan Trap Volcanics of Western Maharashtra. *Proc Symp Decades of Development in Petrology, Mineralogy, and Petrochemistry in India*. Geological Survey of India, p 129-134
- Ping CL, Shoji S, Ito T (1988) Properties and classification of three volcanic ash-derived pedons for Aleutian Islands and Alaska Peninsula, Alaska. *Soil Sci Soc Am J* 52:455-462
- Pond WG (1995) Zeolites in animal nutrition and health: A review. *In* Ming DW, Mumpton FA (eds) *Natural zeolites '93: Occurrence, Properties, Use*. Int'l Committee on Natural Zeolites, Brockport, New York, p 449-457
- Portegies Zwart R, Vink APA, Van Schuylenborgh J (1975) The weathering of zeolitic and non-zeolitic calcareous materials in a lacustrine plain in south-central Italy. *Geoderma* 14:277-295
- Raybon SO (1982) Lithology and clay mineral variations in the middle phase of Paleocene Porters Creek Formation of Mississippi. MS thesis, Univ Mississippi, University, Mississippi, 101 p
- Reid DA, Graham RC, Edinger SB, Bowen LH, Ervin JO (1988) Celadonite and its transformation to smectite in an Entisol at Red Rock Canyon, Kern County, California. *Clays & Clay Minerals* 36:425-431
- Renaut RW (1993) Zeolitic diagenesis of late Quaternary fluviolacustrine sediments and associated calcrete formation in the Lake Bogoria Basin, Kenya Rift Valley. *Sedimentology* 40:271-301
- Reynolds WR, Bailey MA (1990) Gismondine in a lamproite intrusive and soil system. Program and Abstracts, Clay Minerals Society, 27th Ann Mtg, Columbia, Missouri, Oct. 6-11, 1990, p 106
- Sabale AB, Vishwakarma LL (1996) Zeolites and associated secondary minerals in Deccan volcanics: Study of their distribution, genesis and economic importance. National Symposium on Deccan Flood Basalts, India. *Gondwana. Geol Mag* 2:511-518
- Schultz RK, Overstreet R, Barshad I (1964) Some unusual ionic exchange properties of sodium in certain salt-affected soils. *Soil Sci* 99:161-165
- Shepard AO, Starkey HC (1964) Effect of cation exchange on the thermal behavior of heulandite and clinoptilolite. *U S Geol Surv Prof Paper* 475-D:89-92
- Southard AR, Kolesar PT (1978) An exotic source of extractable potassium in some soils of Northern Utah. *Soil Sci Soc Am J* 42:528-530
- Spiers GA, Pawluk S, Dudas MJ (1984) Authigenic mineral formation by solodization. *Can J Soil Sci* 64:515-532
- Surdam RC, Sheppard RA (1978) Zeolites in saline, alkaline-lake deposits. *In* Sand LB, Mumpton FA (eds) *Natural Zeolites: Occurrence, Properties, Use*. 145-174. Pergamon Press, New York, p 145-174
- Talibudeen O, Weir AH (1972) Potassium reserves in a 'Harwell' series soil. *J Soil Sci* 23:456-474
- Taylor K, Graham RC, Ervin JO (1990) Laumontite in soils of the San Gabriel Mountains, California. *Soil Sci Soc Am J* 54:1483-1489
- Travnikova LS, Gradusov BP, Chizhikova NP (1973) Zeolites in some soils. *Pochvovedeniye* 3:106-114
- Ward JW (1971) Infrared spectroscopic studies of zeolites. *In* Gould RF (ed) *Molecular Sieve Zeolites-I*. *Adv Chem Ser* 101:380-404
- Ward RL, McKague HL (1994) Clinoptilolite and heulandite structural differences as revealed by multinuclear magnetic resonance spectroscopy. *J Phys Chem* 98:1232-1237
- Zelazny LW, Calhoun FG (1977) Palygorskite, (attapulgitite), sepiolite, talc, pyrophyllite, and zeolites. *In* Dixon JB, Weed SB (eds) *Minerals in Soil Environments*. Soil Science Society of America, Madison, Wisconsin, p 435-470