QUANTITATIVE DETERMINATION OF CLINOPTILOLITE IN SOILS BY A CATION-EXCHANGE CAPACITY METHOD

Douglas W. Ming[1] and Joe B. Dixon

Department of Soil and Crop Sciences, Texas A&M University
College Station, Texas 77843

Abstract—A cation-exchange capacity (CEC) method based on ion-sieving properties was developed for the quantitative determination of clinoptilolite in soils. In this method, both zeolitic and non-zeolitic exchange sites in the soil sample are saturated with Na^+. The CEC of the non-zeolitic exchange sites is determined by replacing the Na^- in these sites with tert-butylammonium ions. The tert-butylammonium ion cannot be exchanged into the zeolitic exchange sites because it is too large to pass through the channels in the clinoptilolite structure. The sample is next washed with NH_4OAc to replace the Na^+ in the zeolitic exchange sites. The amount of soil zeolite is then estimated by comparing the CEC of zeolitic exchange sites to the total zeolite CEC (175 meq/100 g for pure clinoptilolite). Prior to the CEC analyses, carbonates and organic matter must be removed to minimize interference with the exchange process. A high correlation ($r^2 = .96$) was observed between the abundance of clinoptilolite estimated using the CEC method and the abundance estimated by semiquantitative X-ray powder diffraction analysis.

The CEC procedure was used to quantify clinoptilolite in an Aridic Calciustoll soil from south Texas. About 2–5% clinoptilolite occurs in the A and B horizons, and concentrations progressively increase with soil depth to as much as 20% in the CBk2 horizon.

Key Words—Cation-exchange capacity, Clinoptilolite, Quantitative mineralogy, Smectite, Soil, Tert-butylammonium, Zeolite.

INTRODUCTION

Few procedures deal with the direct quantitative determination of minerals in soils and sediments, primarily due to the heterogeneity of the system and the time required to conduct such analyses. Most quantitative mineralogy is accomplished by X-ray powder diffraction (XRD) methods. XRD procedures are protracted if the analysis of each soil separate (i.e., sand, silt, clay fractions) must be made to minimize the effects of particle size on crystal orientation. Also, it becomes difficult to establish an accurate estimate of the mineral in question in the whole soil sample. Thus, a procedure that quantifies a mineral directly on a whole-soil basis would vastly improve the accuracy of the estimate and probably save time.

The occurrence of natural zeolites in soils is not well known and has only recently gained the attention of soil scientists. Therefore, very little has been done to quantify these minerals in soils. Of the more than 40 natural zeolite species, clinoptilolite, $[(Na,K)_{6-2x}Ca_x] \cdot (Al_6Si_{30}O_{72}) \cdot 24H_2O$, seems to be the most abundant zeolite in soils and sediments (Ming and Mumpton, 1987). Clinoptilolite has been reported in slightly acid to strongly alkaline soils (Ming and Dixon, 1986; Speirs *et al.*, 1984; Jacob, 1984; Graham and Southard, 1983; Fanning *et al.*, 1983; Southard and Kolesar, 1978; Asvadurov *et al.*, 1978; Travnikova *et al.*, 1973; Gorbunov and Bobrovitskiy, 1973).

The zeolite of primary interest in this study is clinoptilolite, which is widespread in soils derived from the Oligocene Catahoula Formation of southern Texas (Ming and Dixon, 1986). Most of the clinoptilolite-bearing soils are Mollisols that contain calcite. To aid in determining the distribution and stability of the zeolite in soils, a rapid, quantitative method of determining the amount of clinoptilolite in unfractionated soils was developed.

THEORY

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that possess a three-dimensional structure (i.e., tektosilicates). The negative charge created where Al^{3+} replaces Si^{4+} in the structural tetrahedra is counterbalanced by cations (e.g., Na^+, K^+, and Ca^{2+}, Mg^{2+}). These charge sites are located in large structural channels and cavities throughout the structure and will be referred to as zeolitic exchange sites throughout this paper. Small ions and molecules can pass through these channels, but large ions and molecules are excluded. This ion selectivity, based on size, is known as ion sieving. Zeolites have high cation-exchange capacities (CEC) (100–300 meq/100 g), depending on the amount of Al^{3+} that replaces Si^{4+} in the structure. The procedure for quantifying clinoptilolite has been developed on the basis of the ion-sieving properties and high CEC of this zeolite.

In clinoptilolite, 10- and 8-ring channels parallel the *c*-axis of the structure and have free dimensions of 4.4×7.2 Å and 4.1×4.7 Å, respectively. A third 8-

[1] Present address: Mail Code SN12, NASA Johnson Space Center, Houston, Texas 77058.

Table 1. Selected chemical and physical characteristics of the Aridic Calciustoll soil locality.

Horizon	Depth (cm)	CaCO₃ eq. (%)	Sand (2.0–0.05 mm) (%)	Coarse silt (0.05–0.02 mm) (%)	Fine and medium silt (0.02–0.002 mm) (%)	Clay (<0.002 mm) (%)
A	0–25	9	47	16	7	30
Bk1	25–38	17	34	14	16	36
Bk2	38–66	24	40	26	23	11
BCk	66–89	24	31	21	18	30
CBk1	89–104	24	46	18	20	16
CBk2	104–137	19	49	14	18	19

Soil constituents expressed as weight percentage of soil.

ring-channel system parallels the a-axis and has free dimensions of 4.0 × 5.5 Å. Small hydrated cations (e.g., Na^+, Ca^{2+}, K^+) can easily enter the channels of clinoptilolite and compete for exchange sites; however, large organic cations (e.g., tetramethylammonium and tert-butylammonium ions) are excluded from the channel system by ion sieving (Barrer *et al.*, 1967).

Thus, all of the exchange sites of both the zeolite and non-zeolite minerals may be saturated with Na^+, the Na^+ in non-zeolitic exchange sites may then be replaced by tert-butylammonium ions, and the zeolite CEC may be determined by replacing the Na^- in the zeolitic exchange sites with NH_4^+. These three steps and the reactions involved are explained below.

Step 1. Initially, all exchange sites in the soil are saturated with Na^+, which readily enters the zeolitic channels. Clinoptilolite shows a selectivity for certain cations (Ames, 1960), but this problem can be corrected by determining the Na-CEC of the clinoptilolite. Smectite-clinoptilolite-feldspar-quartz-calcite mineral assemblages dominate the soils derived from the Catahoula Formation in southern Texas, so most of the non-zeolitic exchange capacity will be contributed by smectite. The smectite exchange sites should readily saturate with Na^+. The overall reaction for step 1 is therefore:
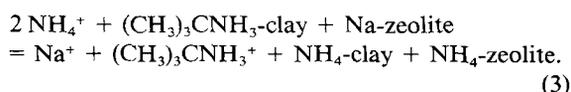
$$2\,Na^+ + X_{1/2}\text{-clay} + X_{1/2}\text{-zeolite}$$
$$= Na\text{-clay} + Na\text{-zeolite} + X^{2+}, \qquad (1)$$
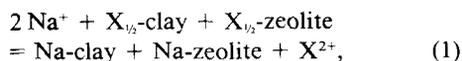
where $X = Ca^{2+}$, Mg^{2+}, etc.

Step 2. Na^+ is replaced from non-zeolitic exchange sites (i.e., smectitic exchange sites) by tert-butylammonium ions; the Na^+, however, will remain at the zeolitic exchange sites. Exchange of Na^+ by the large organic molecule on non-zeolitic sites is facilitated by heating the sample at 60°C during the exchange reaction. The Na^+ replacement by tert-butylammonium ions can be expressed as follows:

$$(CH_3)_3CNH_3^+ + Na\text{-clay} + Na\text{-zeolite}$$
$$= Na^+ + (CH_3)_3CNH_3\text{-clay} + Na\text{-zeolite}. \qquad (2)$$
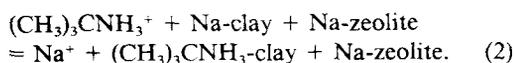
Step 3. The final step involves the replacement of the Na^+ from the zeolitic exchange sites by NH_4^+. The NH_4^+ ion is small enough to gain access to the zeolite

exchange sites and is preferred over Na^+ by the zeolite so it readily replaces Na^+ (Ames, 1960). The Na^+-NH_4^+ exchange reaction in the system is expressed as follows:

$$2\,NH_4^+ + (CH_3)_3CNH_3\text{-clay} + Na\text{-zeolite}$$
$$= Na^+ + (CH_3)_3CNH_3^+ + NH_4\text{-clay} + NH_4\text{-zeolite}. \qquad (3)$$

MATERIALS AND METHODS

A soil pedon known to contain as much as 20% clinoptilolite was selected for this study. This Aridic Calciustoll (Houla series) was derived from the zeolitic tuffaceous sediments of the Catahoula Formation in eastern Webb County, Texas. Morphological descriptions for the Houla soil were reported by Ming (1985). Particle-size data and calcium carbonate equivalent values of a typical Houla soil are presented in Table 1. Air-died samples from each horizon were passed through a 2-mm mesh sieve and treated with 1 N NaOAc buffered to pH 5, 30% H_2O_2, and dithionite-citrate-bicarbonate to remove free carbonates, organic matter, and free iron oxides, respectively (Jackson, 1974). Samples of the soil horizons were size fractionated by conventional sieving and sedimentation methods (Jackson, 1974). All soil samples (i.e., soil separates and unfractionated, chemically dispersed soil) were freeze-dried and placed in a desiccator containing Drierite for storage free from atmospheric H_2O.

Zeolite estimation by X-ray powder diffraction

Mixtures containing known amounts of sand (2.0–0.05 mm) and silt (0.05–0.002 mm), approximating the soil matrices, were prepared using a highly crystalline clinoptilolite purified from the CBk2 horizon of the soil described above (Ming and Dixon, 1987a) and varying amounts of quartz and feldspar. A uniform weight percentage of crystalline Al_2O_3 was added to each of the standard mixtures and unknowns as an internal standard. Standards and unknowns were thoroughly mixed by wet grinding in acetone. Powdered samples were then pressed into a depression on a glass slide for X-ray powder diffraction (XRD) analysis. A scan rate of $\frac{1}{2}°2\theta$/min was utilized to record the 9.01-Å peak (020) of clinoptilolite and the 2.55-Å peak (104) of Al_2O_3. Regression equations were calculated ($r^2 =$

Table 2. Cation-exchange capacities (CEC) determined for mixtures of a purified clinoptilolite and a standard smectite.

Mixtures[1]	CEC (meq/100 g)[2]		
	Na^+-TBA	Na^+-NH_4^+	Total
100% Cp	10	165	175
75% Cp + 25% S	23	124	147
50% Cp + 50% S	38	79	117
25% Cp + 75% S	53	40	93
100% S	67	0	67

[1] Cp = clinoptilolite; S = smectite. Clinoptilolite purified from soil pedon developed on Catahoula Formation. Smectite = montmorillonite, Texas.

[2] Na^+-TBA = Na^+ replaced by tert-butylammonium (TBA); Na^+-NH_4^+ = Na^+ replaced by NH_4^-; Total = sum of Na^+-TBA and Na^+-NH_4^+.

.99 for both fractions) and used to estimate the percentages of zeolite from the XRD peak-height ratios of the zeolite to the Al_2O_3 internal standard for unknown samples.

Clay standards were prepared from <2-μm clinoptilolite (purified from the soil and ground to size) and Mg-montmorillonite (SMt5, Source Clays Repository of The Clay Minerals Society). Clay samples (Mg-saturated) from the soil and the standard mixtures were mixed with acetone and smeared on glass slides. A scan speed of ½°2θ/min was used to record the 14–15-Å peak of smectite and the 9.01-Å peak of clinoptilolite. A regression equation (r^2 = .99) was then derived by comparing the peak area of the zeolite to that of the smectite. Peak areas were estimated with a Lasico model 40 planimeter. A Philips X-ray diffractometer with monochromatic CuKα radiation was used for XRD analysis.

Preparation of tert-butylammonium chloride

Tert-butylammonium chloride for this study was synthesized by a procedure analogous to that employed by Ruehlicke and Kohler (1981) for preparing n-alkylammonium chlorides. Starting materials for the synthesis of the tert-butylammonium chloride were equal volumes of tert-butylamine (98%) and ethanol (95%). The only variation from Ruehlicke and Kohler's procedure was to freeze dry the crystalline powder after synthesis, thereby removing any excess acetone, ethanol, or water.

Clinoptilolite estimation by CEC procedures

For this study, 2.5, 1.0, 1.0, 0.5, and 0.1 g of freeze-dried, chemically treated whole soil and sand-, coarse silt-, fine and medium silt-, and clay-size fractions of the soil, respectively, were added to 40-ml centrifuge tubes. Samples were then washed four times with 1 N NaOAc buffered to pH 5 to ensure complete Na-saturation of exchange sites. Excess Na^+ (interstitial) was removed by one washing with distilled deionized H_2O and three washings with ethanol (95%). Non-zeolitic

exchangeable Na^+ was removed by adding 30 ml of 0.5 N tert-butylammonium chloride, $(CH_3)_3CNH_3Cl$, and heating the suspension at 60°C for 24 hr to enhance the exchange of Na^+ by $(CH_3)_3CNH_3^+$. Following the heating process, samples were washed two more times with 0.5 N $(CH_3)_3CNH_3Cl$. Tert-butylammonium chloride washings were decanted into 100-ml volumetric flasks and saved for analysis of the Na^+ contributed by the non-zeolitic CEC. Excess $(CH_3)_3CNH_3Cl$ was removed by washing the sample once with ethanol (95%). Na^+ on zeolitic exchange sites was removed by washing the sample three times with 1.0 N NH_4OAc. The NH_4OAc washings were decanted into 100-ml volumetric flasks and saved for analysis of the Na^+ from the zeolitic CEC. Samples were analyzed in duplicate and dispersed by ultrasonification during each washing step. Na^- was determined with a Perkin-Elmer 603 atomic adsorption spectrophotometer. The Na-CECs for the zeolitic and non-zeolitic phases are expressed as meq/100 g based on the freeze-dried weight of the samples.

Standards were prepared to test the CEC procedure by preparing mixtures composed of 100, 75, 50, 25, and 0 wt. % clinoptilolite that had been purified previously from the CBk2 horizon (Ming and Dixon, 1987a) and corresponding smectite (montmorillonite from Gonzales, Texas) quantities of 0, 25, 50, 75, and 100%, respectively. The CEC procedure described above was duplicated for 0.25 g of each standard mixture. Based on the CEC values obtained from the standard mixtures (see Table 2), the following equation was developed to quantify the zeolite as a weight percentage:

$$\% \text{ clinoptilolite} = [CEC (Na^+ - NH_4^+)/165] \times 100$$

RESULTS AND DISCUSSION

Quantification of standards

It is important initially to establish the Na-exchange capacity of the clinoptilolite indigenous to the soil before obtaining quantitative CEC values that accurately reflect the amount of that zeolite in samples of that soil. Clinoptilolite in natural environments may have several cations on the exchange sites, however, the dominant cations are Na^+, K^+, and Ca^{2+}. Clinoptilolite exhibits cation selectivity; e.g., Ca^{2+} is easily replaced by Na^+, but K^- in the zeolite is replaced with difficulty by either Ca^{2+} or Na^+ (Ames, 1960). The degree of Na-saturation on the zeolitic exchange sites in step 1 of the procedure described above (see Eq. (1)) depends on the original amount of K^+ on the zeolitic exchange sites. Therefore, to avoid problems caused by cation selectivity, the CEC ($Na^+ - NH_4^+$) was determined for the clinoptilolite that had been separated from the soil. NH_4^+, like K^+, is highly selective on the zeolitic exchange sites and readily replaces Na^+.

For this study, the measured CEC ($Na^+ - NH_4^+$) of

Table 3. Comparison of clinoptilolite content determined by X-ray powder diffraction (XRD) and cation-exchange capacity (CEC) methods in soil separates.

	Clinoptilolite content (%)							
	Sand (2.0–0.05 mm)		Coarse silt (0.05–0.02 mm)		Fine and medium silt (0.02–0.002 mm)		Clay (<0.002 mm)	
Horizon	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 semiquantitative XRD data only. CEC quantitative numbers are average of 2 determinations (n = 2).

the soil clinoptilolite was about 175 meq/100 g, slightly lower than the theoretical CEC of clinoptilolite of 200–220 meq/100 g (Ming and Mumpton, 1987). Ca^{2+} and Na^+ account for more than 95% of the cations on the zeolitic exchange sites in the soil (Ming and Dixon, 1986). Ca^{2+} is the dominant cation on the exchange sites, reflecting high concentrations of Ca^{2+} in the soil solution due to the calcareous nature of these soils. It is unlikely that the lower CEC measured for clinoptilolite isolated from the soil is due to cation selectivity.

The ion-sieving properties of clinoptilolite are illustrated by its exchange of Na^+ by NH_4^+ but not by $(CH_3)_3CNH_3^+$ (Table 2). The amount of Na^+ replaced by $(CH_3)_3CNH_3^+$ for the monomineralic clinoptilolite standard was 10 meq/100 g, indicating that a few of the charged sites of clinoptilolite are accessible to the large organic ion or that a small amount of undetected smectite was present in the purified standard. Most of this charge probably arises from external surface sites (i.e., non-channel sites) and half-cage sites, which are zeolitic exchange sites near the aperture of a channel where the $(CH_3)_3CNH_3^+$ has partial access to remove the Na^+ from that site. The particle size of the zeolite may have an effect on the amount of charge contributed by half-cage and external surface sites, but this effect was not detected for the clinoptilolite used in the present study. Although the charge apparently contributed by external surface and half-cage sites was low, a correction factor was used to determine the amount of zeolite (see Eq. (4)). The zeolite CEC corrected for external surface and half-cage sites was 165 meq/100 g (i.e., (175 meq/100 g) − (10 meq/100 g)). The correction permitted a more accurate calculation of the amount of clinoptilolite in the standards (r^2 = .99). Actual zeolite percentages of 0, 25, 50, 75, and 100 were calculated to be 0, 24, 48, 75, and 100, respectively, by inserting the CEC measured in step 3 of the procedure into Eq. (4).

In a soil system containing as much as 20% of clinoptilolite in the clay fraction, smectite cannot be quantified using the conventional CEC procedure of Alexiades and Jackson (1965) because the CEC of the zeolite is extremely large. In developing this zeolite quantification procedure, the only mineral other than clinoptilolite contributing to the CEC of the soil is assumed to be smectite. Vermiculite was excluded because it rarely occurs with clinoptilolite and was not found with the zeolite in the present study.

Quantification of soil clinoptilolite

Initial attempts at determining the amount of clinoptilolite in whole soils by the CEC procedure failed. Apparently, calcite in the soil (see Table 1) dissolved in the $(CH_3)_3CNH_3Cl$ solution, and released Ca^{2+} replaced Na^+ at the zeolitic exchange sites. Calcite, therefore, was dissolved prior to the CEC procedure by 1 N NaOAc buffered to pH 5.

Organic matter and free iron oxides were also removed from the soil to enhance particle-size fractionation. Destroying the organic matter also eliminated any cation-exchange capacity that it might have contributed; however, the CEC procedure will probably quantify the amount of zeolite even in the presence of organic matter because most of the Na^+ on charged sites of the organic matter will be replaced by $(CH_3)_3CNH_3^+$. Chemical treatments caused no structural change or damage to clinoptilolite (Ming and Dixon, 1987a) and, in fact, aided its identification in soils and sediments by XRD analysis. The only major effect of the chemical treatments was a change in the type of cation on zeolitic exchange sites.

A comparison of clinoptilolite determinations in soil separates by XRD and the CEC procedure is presented in Table 3. The results show similar trends in zeolite concentrations with depth for both methods. A high correlation exists between the two procedures (r^2 = .96).

The amount of clinoptilolite in whole soils can be estimated from XRD analysis by summing the zeolite fraction for each soil separate; however, particle-size distribution (PSD) data are required. A primary objective for developing this CEC procedure is to elim-

Table 4. Clinoptilolite content determined by X-ray powder diffraction (XRD) and cation-exchange capacity (CEC) methods in carbonate-free and carbonate-containing soils.

Horizon	Clinoptilolite by XRD[1]	Clinoptilolite by CEC[2]	Clinoptilolite in carbonate-containing soils[3]
A	3 (1)[4]	3	3
Bk1	4 (1)	2	2
Bk2	6 (3)	3	2
BCk	13 (3)	9	7
CBk1	19 (5)	15	11
CBk2	21 (5)	20	16

[1] Zeolite contents calculated from carbonate-free fractions (Table 1) and zeolite contents for soil separates (Table 3).

[2] Zeolite contents on carbonate-free soil determined by CEC procedure.

[3] Zeolite percentages have been rounded to the nearest whole number.

[4] Numbers in parenthesis represent a 95% confidence interval (n = 4) for semiquantitative XRD data only. CEC quantitative values are average of 2 determinations (n = 2).

inate the time-consuming particle-size fractionation procedure and XRD analysis of each soil separate. Good agreement between the clinoptilolite content estimated by the CEC procedure and by XRD of the size fractions suggests that the particle size of clinoptilolite had little effect on the results of the CEC quantification procedures (see Table 4). The size of the individual crystals of clinoptilolite in these soils is 2 to 20 μm (Ming and Dixon, 1986). Sand- and coarse silt-size zeolite particles consist of aggregates of individual crystals, whereas, only fragments of crystals are in the clay fractions. The clay-size fragments probably resulted from mechanical breaking. Therefore, zeolite crystals in the soils examined are relatively uniform in size regardless of the fraction in which they occur; therefore, particle-size per se has little effect on the CEC quantification procedure.

About 2–5% clinoptilolite was found in the A and B horizons of the soil used in the present study, and concentrations progressively increased with depth to as much as 20% in the CBk2 horizon (Table 4). The underlying sediments or parent materials also contained substantial amounts of clinoptilolite (i.e., 20–25%). An increasing concentration of clinoptilolite with an increasing soil depth suggests a weathering trend of the zeolite. Apparently, the zeolite has persisted as a residual mineral during the formation of the soil by the weathering of clinoptilolite-rich, volcanic parent materials (see Ming and Dixon, 1986).

Precautions and limitations of the CEC procedure

Knowledge of the mineralogy of the soil or sediment is necessary before trying to quantify the abundance of clinoptilolite. Generally, soils and sediments that contain clinoptilolite have smectite-quartz-feldspar-calcite mineral assemblages, but the only minerals likely to contribute to the total CEC are smectite and cli-

noptilolite. Therefore, in developing this CEC quantification procedure, only smectite and clinoptilolite were assumed to have charged sites. The presence of other charged materials (e.g., volcanic glass, opal-CT, vermiculite) may, however, introduce error into the procedure. Possibly, the large tert-butylammonium ion may not completely penetrate all of these non-zeolitic phases, thereby producing an overestimation of zeolite abundance.

Each of the >40 zeolites that occur in nature has a unique crystal structure, ion-sieving properties, cation selectivities, and cation-exchange capacity. The CEC procedure reported here is strictly intended for quantifying clinoptilolite; the presence of another zeolite will complicate the exchange reactions; however, clinoptilolite generally does not coexist with another zeolite in soils (Ming and Mumpton, 1986; Ming and Dixon, 1986c).

CONCLUSIONS

In the last decade, zeolites have been found with increasing regularity in soils. Clinoptilolite, the most abundant zeolite in soils and sediments, is one of the highest charged minerals occurring in soils and where it is present complicates the interpretation of soil CECs. The CEC quantification procedure developed in this study differentiates between the charge contributed by clinoptilolite and that contributed by other charged materials, chiefly smectite. Because of clinoptilolite's agronomic importance (see Pond and Mumpton, 1984), the abundance of this zeolite in soils should be determined. The CEC procedure reported here will aid in that determination.

REFERENCES

Alexiades, C. A. and Jackson, M. L. (1965) Quantitative determination of vermiculite in soils: *Soil Sci. Soc. Amer. Proc.* **29**, 522–527.

Ames, L. L., Jr. (1960) Cation sieve properties of clinoptilolite: *Amer. Miner.* **45**, 689–700.

Asvadurov, H., Popescu, F., and Constantinescu, M. (1978) Soluri si roci cu continut ridicat de potasiu schimbabil: *An. Inst. Cerc. Pedol. Agrochim.* **43**, 115–123.

Barrer, R. M., Papadopoulos, R., and Rees, L. V. C. (1967) Exchange of sodium in clinoptilolite by organic cations: *J. Inorg. Nucl. Chem.* **29**, 2047–2063.

Fanning, D. S., Rabenhorst, M. C., Wagner, D. P., and Snow, P. A. (1983) Soils-geomorphology field trip in Maryland, August 12 and 13, 1983: *Guidebook prepared in conjunction with American Society of Agronomy meeting, Washington, D.C., August 14–18, 1983,* 118 pp.

Gorbunov, N. I. and Bobrovitskiy, I. (1973) Distribution,

genesis, structure, and properties of zeolite: *Soviet Soil Sci.* **5**, 93–101.

Graham, R. C. and Southard, A. R. (1983) Genesis of a Vertisol and an associated Mollisol in northern Utah: *Soil Sci. Soc. Amer. J.* **47**, 552–559.

Jackson, M. L. (1974) *Soil Chemical Analysis—Advanced Course:* 2nd ed., published by the author, Madison, Wisconsin, 895 pp.

Jacob, J. S. (1984) Persistence of a zeolite tuffaceous soil of the Texas Trans-Pecos: M.Sc. thesis, Texas Tech University, Lubbock, Texas, 98 pp.

Ming, D. W. (1985) Chemical and crystalline properties of clinoptilolite in south Texas soils: Ph.D. dissertation, Texas A&M University, College Station, Texas, 257 pp.

Ming, D. W. and Dixon, J. B. (1986) Clinoptilolite in south Texas soils: *Soil Sci. Soc. Amer. J.* **50**, 1618–1622.

Ming, D. W. and Dixon, J. B. (1987a) Technique for the separation of clinoptilolite from soils: *Clays & Clay Minerals* **35**, 469–472.

Ming, D. W. and Dixon, J. B. (1987b) Occurrence and weathering of zeolites in soil environments: in *Zeolite '85,* D. Kalló, ed., Akadémiai Kiado, Budapest and D. Reidel, Dordrecht, Netherlands (in press).

Ming, D. W. and Mumpton, F. A. (1987) Zeolites in soils: in *Minerals in Soil Environments,* 2nd ed., J. B. Dixon and S. B. Weed, eds., Soil Science Society of America, Madison, Wisconsin (in press).

Pond, W. G. and Mumpton, F. A., eds. (1984) *Zeo-agriculture: Use of Natural Zeolites in Agriculture and Aquaculture:* Westview Press, Boulder, Colorado, 296 pp.

Ruehlicke, G. and Kohler, E. E. (1981) A simplified procedure for determining layer charge by the n-alkylammonium method: *Clay Miner.* **16**, 305–307.

Southard, A. R. and Kolesar, P. T. (1978) An exotic source of extractable potassium in some soils of northern Utah: *Soil Sci. Soc. Amer. J.* **42**, 528–530.

Speirs, G. A., Pawluk, S., and Dudas, M. J. (1984) Authigenic mineral formation by solodization: *Can. J. Soil Sci.* **64**, 515–532.

Travnikova, L. S., Gradusov, B. P., and Chizhikova, N. P. (1973) Zeolites in some soils: *Soviet Soil Sci.* **5**, p. 251.