CATION-EXCHANGE CAPACITY (CEC) OF ZEOLITIC VOLCANICLASTIC MATERIALS: APPLICABILITY OF THE AMMONIUM ACETATE SATURATION (AMAS) METHOD

KONSTANTINOS P. KITSOPOULOS

Geology Department, Leicester University, Leicester, LE1 7RH, UK

Abstract—The ammonium acetate saturation (AMAS) method was used to study the cation-exchange capacity (CEC) of zeolitic volcaniclastic materials from Santorini and Polyegos Islands, Greece. The AMAS method was tested with respect to the time required to saturate the samples of zeolites with ammonium (NH_4^+) ions, the efficient liberation of NH_4^+ ions, and the suitability of two widely used techniques to measure ammonia (NH_3) (Kjeldahl ammonia distillation technique and the ammonia electrode technique). By using the inductively coupled plasma-mass spectrometry (ICP-MS) technique and measuring the number of cations exchanged during ammonium acetate (NH_4OAc) saturation, it was found that the saturation period for zeolitic materials must be increased to 12-day cycles to ensure effective saturation. Following NH_4OAc saturation, the AMAS method produces NH_4^+ solutions, after the NH_4^+-saturated samples of zeolites are washed with 10% NaCl. The amount of the NH_4^+ ions in solution (*i.e.,* exchangeable cations) is a measure of the CEC. The NH_4^+ ions can not be directly measured and must be converted to NH_3. The Kjeldahl ammonia distillation technique and the ammonia electrode technique for measuring NH_3 give identical CEC results. However, the ammonia electrode technique, when used directly with the NH_4^+ samples of zeolite without 10% NaCl treatment, generally gives higher CEC values. The amount of NH_4^+ treated (converted to NH_3), when the NH_4^+-saturated zeolitized samples were used directly, was higher than the amount of the NH_4^+ treated when the NH_4^+ solutions were obtained after washing the NH_4^+-saturated zeolitized samples with 10% NaCl. Therefore, washing with 10% NaCl does not facilitate the release of all NH_4^+ initially within the zeolite structure. A modified AMAS technique is proposed for measuring the CEC of zeolitic material.

Key Words—Ammonium Acetate Saturation (AMAS) Method, Ammonia Electrode, Cation-Exchange Capacity (CEC), Clinoptilolite, Greece, Kjeldahl Ammonia Distillation, Mordenite, Polyegos, Santorini, Zeolites.

INTRODUCTION

The cation-exchange capacity (CEC) is an important property of zeolites. CEC results from the presence of loosely bound cations of alkali and alkaline earths elements, often called exchangeable cations, in the structure of the zeolites. These loosely bound cations are easily exchanged when zeolites are in contact with solutions of "saturating" or "indexing" ions. The exchange reaction between a zeolite and an ionic solution is described as $M_1(Z) + M_2(S) \leftrightarrow M_2(Z) + M_1(S)$ where M_1 is the exchangeable cation present in zeolite Z, and M_2 is the saturating ion in solution S.

The methods of ammonium acetate saturation (AMAS) (Chapman, 1965; Bain and Smith, 1987) and methylene blue absorption (MBA) (Nevins and Weintritt, 1967) are commonly used to measure the CEC of finely crystalline materials. The MBA method is based on the measurement of the maximum absorption of a sample for 0.01 N solution of methylene blue. Kitsopoulos (1997a) suggested, however, that the MBA method is not suitable for zeolites because the size and the projected plan area of the methylene-blue molecule are usually greater than the size of the zeolitic channels. The AMAS method involves the saturation of the zeolites with ammonium (NH_4^+) ions that replace exchangeable cations.

Theoretically, the number of NH_4^+ ions retained by the zeolite is a measure of the CEC.

The AMAS method was introduced by Schollenberger and Dreibelbis (1930), Schollenberger and Simon (1945), and Peech (1945) to measure the CEC of soils. Improvements were made by Chapman (1965). In the AMAS method, material is saturated using neutral 1 N solution of ammonium acetate (NH_4OAc). NH_4OAc is highly buffered and when neutral 1 N NH_4OAc solution is used to saturate a soil, the resultant solution leached through the soil has the same pH as the original solution (Chapman, 1965). Bain and Smith (1987) modified the method to be used with clays. In this study, we use the method of Bain and Smith (1987), which includes three steps: (1) NH_4OAc saturation, (2) release of the saturating NH_4^+ ions and generation of NH_4^+ solutions, and (3) measurement of the released NH_4^+ ions (*i.e.,* the CEC) by converting NH_4^+ ions to NH_3 and measuring the resultant NH_3.

The purpose of this study was to investigate the CEC of zeolitized volcaniclastic materials from Santorini and Polyegos Islands, Greece, using the AMAS method. However, the lack of a detailed description of the AMAS method for use with zeolites has led to the use of this method as if it is applied to clays. In this study, the suitability of the AMAS method was determined at each stage of analysis. Based on these results, modifications are suggested for the use of the AMAS method when applied to zeolites.

Present address: 16 Aiolou Str., Paleo Faliro, Athens, 175-61, Greece.
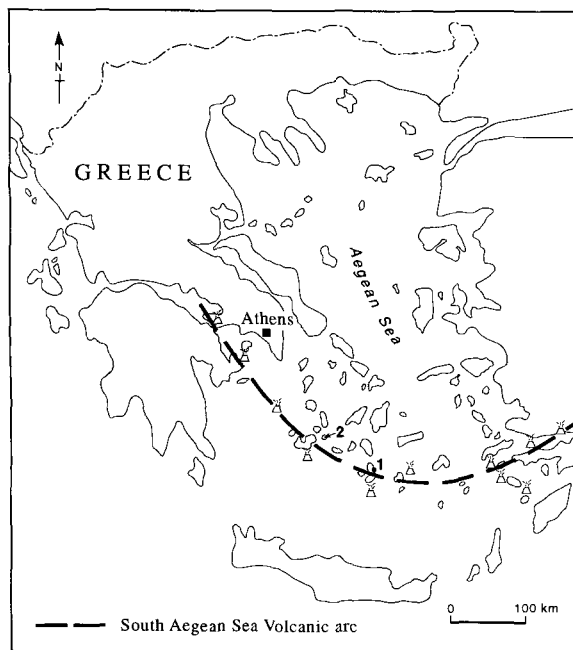
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Figure 1. South Aegean Sea Volcanic Arc (dashed line). 1: Santorini, 2: Polyegos.

MATERIALS

Zeolitized pyroclastic materials from the Santorini and Polyegos Islands of the South Aegean Sea Volcanic Arc, Greece (Figure 1) were used in this study. At Santorini Island (Figure 2), clinoptilolite and smectite or illite-smectite have replaced the vitreous matrix of the Akrotiri pyroclastics. The clinoptilolite was characterized by X-ray diffraction (XRD), thermal tests, and electron microprobe analysis. Clinoptilolite ranges from 40 to 75%. Tsolis-Katagas and Katagas (1989) proposed that the formation of zeolites resulted from the activity of interstitial water in the volcaniclastic material. According to these authors, the alteration minerals are not related to vertical or lateral zonation, and the irregular distribution of the assemblages is attributed to variations in heat flow, ionic activity in interstitial waters, and permeability. Kitsopoulos (1997b) suggested that a typical zeolitization model, which involves successive stages of alteration of the outer parts of glass shards to clays, dissolution of glass, and finally precipitation of clinoptilolites in cavities of the previously dissolved glass shards, may not be applied as such. Instead, the clinoptilolites formed as a result of reactions between solid and fluid components within the glass shards, which acted as small semi-closed subdomains. The composition of the clinoptilolite ranges from $(Na_{2.12}K_{2.56}Ca_{0.40}Mg_{0.19})(Si_{29.97}Al_{6.08}O_{72})\cdot24H_2O$ and $(Na_{2.60}K_{2.28}Ca_{0.48}Mg_{0.27})(Si_{29.71}Al_{6.20}O_{72})\cdot24H_2O$ to $(Na_{1.56}K_{1.26}Ca_{1.19}Mg_{0.58})(Si_{29.35}Al_{6.71}O_{72})\cdot24H_2O$ (Kitsopoulos, 1995a, 1995b).

On Polyegos Island (Figure 3), the authigenic minerals are mainly mordenite and illite, and more rarely illite-smectite. Mordenite ranges from 50 to 80%. Clinoptilolite (heulandite type 3) was found within a few samples. Kitsopoulos (1997c) suggested that heulandite-type minerals were the primary precursors for mordenite. Mordenite formed as a result of elevated temperature and high Na^+ concentration. In addition to mordenite of composition $(Ca_{0.68}Mg_{0.49}Na_{4.05}K_{0.52})(Si_{41.06}Al_{6.94}O_{96})\cdot24H_2O$, a K-rich mordenite occurs of composition $(Ca_{1.20}Mg_{0.20}Na_{2.31}K_{2.39})(Si_{40.61}Al_{7.41}O_{96})\cdot24H_2O$ (Kitsopoulos, 1995a, Kitsopoulos and Dunham, 1998).

METHODS

The ammonium acetate saturation (AMAS) method

NH_4OAc saturation. Zeolite powders of the <125-μm size fraction were used instead of the <2-μm size fractions typically used for clays. Samples were washed with deionized water to remove soluble phases which may interfere with the measurement of the CEC. Samples were dried. About 50–150 mg of each sample were weighed accurately and transferred to a centrifuge tube where 10 mL of 1 N NH_4OAc of pH 7 were added. The suspension was well shaken by hand, left overnight, and then centrifuged. The clear liquid was discarded and the NH_4OAc-saturation procedure repeated four times, adding fresh 10 mL of NH_4OAc solution each time (Bain and Smith, 1987). Because time may be an important variable for NH_4OAc saturation, we used ten-day cycles, although Mackenzie (1951) used overnight saturation and Bain and Smith (1987) used five-day cycles for clays. Also, the saturating NH_4OAc solutions were not discarded after saturation; Na^+, K^+, Ca^{2+}, and Mg^{2+} were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). For this purpose, saturating NH_4OAc solutions of 1 mL were diluted in 10% HCl and compared to standard solutions of Na^+, K^+, and Ca^{2+}. Solutions of 1 mL of fresh NH_4OAc diluted in 10% HCl, were also used to correct for interference effects. After the completion of the ten-day cycles of NH_4OAc saturation, the excess NH_4OAc was washed with 99% isopropyl alcohol. An amount of 10 mL of alcohol was added to the sample, well shaken by hand, and centrifuged. The clear supernatent liquid was discarded and the procedure repeated five times. Afterwards, the samples were dried thoroughly, but without heating. Following the NH_4OAc saturation, the NH_4^+ ions are retained by the zeolites, having replaced all the exchangeable cations.

Release of the saturating NH_4^+ ions and generation of NH_4^+ solutions. The air-dried, NH_4^+-saturated zeolite samples were weighed and transferred to a 15-mL centrifuge tube. An amount of 10 mL of 10% NaCl solution, acidified to 0.005 M in HCl, was added to the tube, shaken well by hand, and centrifuged. The clear
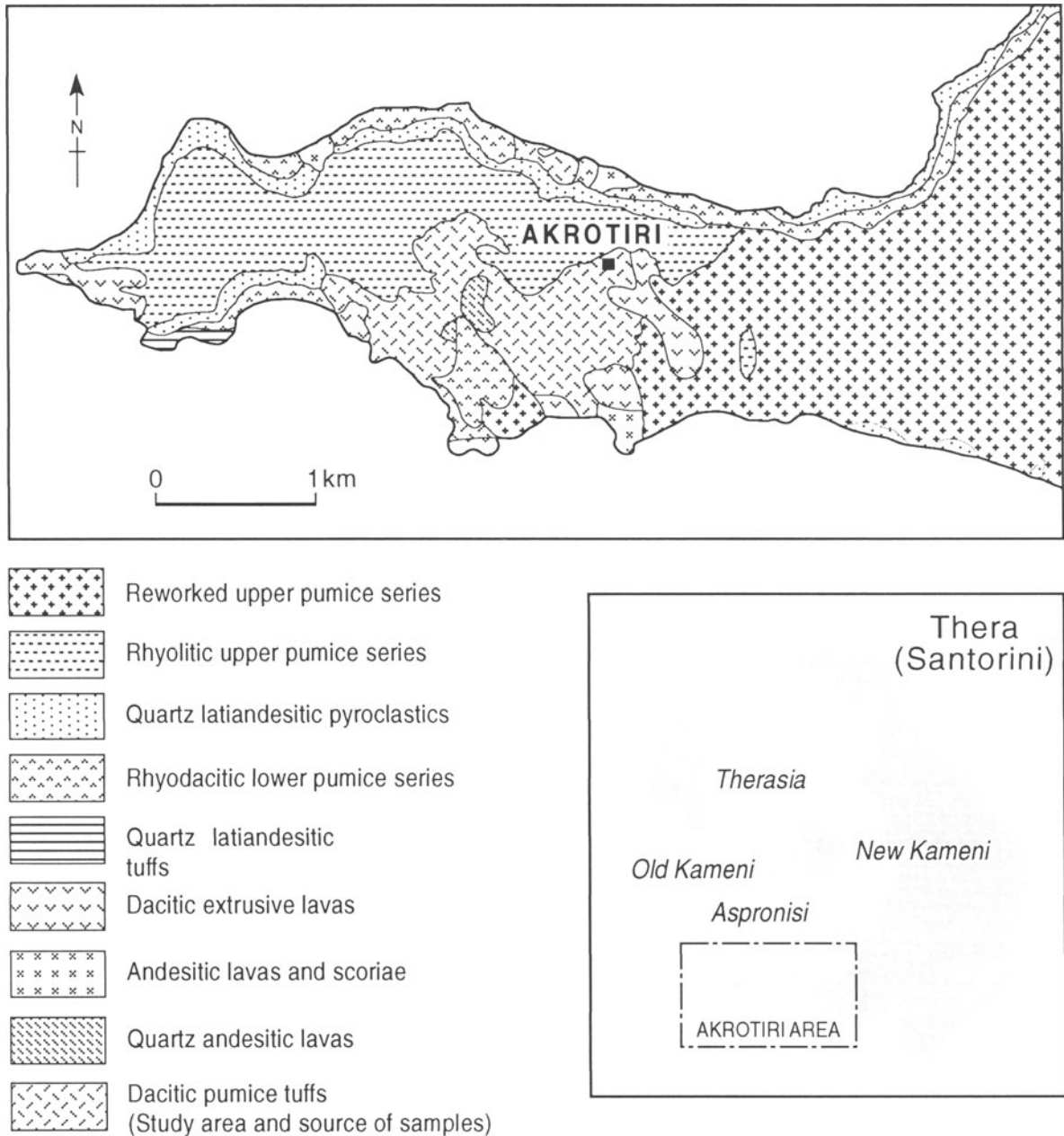
Figure 2.   Geological map of the Akrotiri area of Santorini island (IGME, 1980).

supernatant liquid was transferred to a Teflon bottle and the procedure repeated six times. Then, the bottle was filled to 100 mL with deionized water. After washing the NH_4^+-saturated zeolite samples with NaCl, the NH_4^+ ions, which were retained by the zeolites after NH_4OAc saturation, were replaced by Na^+ ions, and NH_4^+ solutions were obtained. The released NH_4^+ ions is a measure of the CEC of the samples.

Conversion of NH_4^+ to NH_3 and the determination of the CEC. Because NH_4^+ ions can not be directly mea-

sured, they are converted using a strong base to NH_3, which may be analyzed by Kjeldahl ammonia distillation, by using an ammonia electrode (Busenberg and Clemency, 1973), or by spectrophotometry (Fraser and Russel, 1969). In this study, the Kjeldahl ammonia distillation and the ammonia electrode techniques were used.

Kjeldahl ammonia distillation technique

To convert NH_4^+ to NH_3, 50 mL of the NH_4^+-containing solutions were transferred to a distillation flask
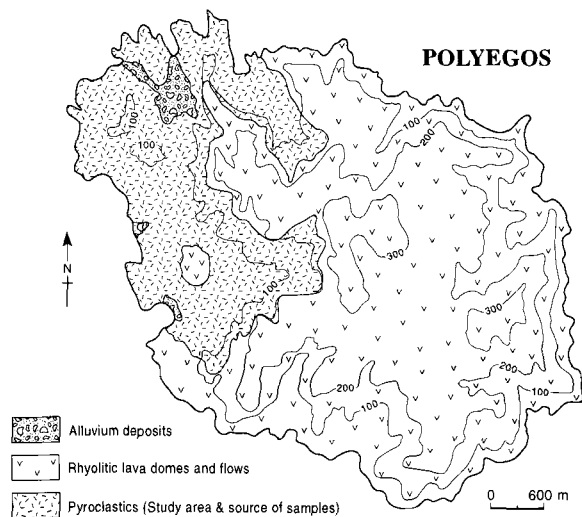
Figure 3. Geological map of Polyegos island (Kanaris, 1989).

and diluted with 200 mL of NH_3-free deionized water. One gram of granulated zinc (a few fragments of porous porcelain are suitable also) was added to the flask to promote regular ebullition in the subsequent distillation. An amount of 100 mL of 0.1 N HCl was placed in the receiver. The flask was adjusted so the end of the condenser just dips into the acid. An amount of 100 mL of 10% NaOH was placed in the funnel above the distillation flask. The 10% NaOH was quickly introduced to the distillation flask; when all the alkali passed, the tap was securely closed. The addition of the 10% NaOH produced the complete conversion of the NH_4^+ ions to NH_3 by: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$. The contents of the flask were boiled gently for ~1 h and all the NH_3 passed through to the HCl of the receiver. The tap was opened before switching off the heating unit, the top of the condenser disconnected, and the receiver lowered and rinsed with deionized water. A few drops of methyl red or a mixture of methyl red-bromocresol green was added in the receiver flask. The excess of HCl in the receiver was measured by titration using 0.1 N NaOH. The accuracy of the distillation experiments was determined by comparing to standard 1 M NH_4Cl solutions.

Ammonia electrode technique

In aqueous solutions, the potential recorded by an ammonia electrode is related to the activity of the dissolved NH_3. Thus, NH_4^+ may be analyzed as follows. The solutions of NH_4^+ are treated with strong NaOH and converted to NH_3, which then may be analyzed by the ammonia electrode. This technique is much less tedious than distillation. The ammonia electrode is connected either to a pH meter or to an ion meter/analyzer, and a small magnetic stirrer (air-driven stirrers are not recommended). For the use of a pH meter, a calibration

curve of known NH_3 concentrations *vs.* mV (potential) is first determined. The concentration of NH_3 is then estimated using the calibration curve. An ion meter/analyzer measures directly the concentration of NH_3. In this study, an Orion 95-12 ammonia electrode, and a Jenway 3045 pH/mV/°C/ion analyzer were used. To convert NH_4^+ to NH_3, 50 mL of solution of NH_4^+ were added to a 100-mL Pyrex beaker containing a Teflon covered stirring bar. The ammonia electrode was immersed into the solution and no entrapment of air under the concave tip was allowed. Stirring was commenced and 0.5 mL of 10 M NaOH was added by syringe. Recordings of the NH_3 content were obtained at 0.5-min intervals until a constant level was achieved. The electrode was calibrated every 2 h using standard NH_4Cl solutions of 1, 0.1, 0.01, 0.001, and 0.0001 M. The accuracy of the measurements was determined by comparing to standard 1 M NH_4Cl solutions.

An advantage of the ammonia electrode technique is that NH_4^+-saturated samples may be used without prior washing with 10% NaCl. The measurement of CEC is both simple and rapid. In this study, NH_4^+ ions of the zeolites were analyzed also, but without washing the samples of the NH_4^+-saturated zeolites with 10% NaCl. An amount of 50–150 mg of the samples of NH_4^+ saturated zeolites was placed in a 100-mL Pyrex beaker containing a Teflon covered stirring bar. Deionized water (50 mL) was added and the solution stirred to suspend the sample. The electrode was immersed into the suspension taking care to prevent entrapment of air under the concave tip. An amount of 0.5 mL of 10 M NaOH was added by syringe and analyses of NH_3 were taken at 0.5-min intervals until a constant level was achieved. The electrode was calibrated every 2 h using NH_4Cl solutions of 1, 0.1, 0.01, 0.001, and 0.0001 M. The accuracy of the measurements was determined by comparing to standard 1 M NH_4Cl solutions.

RESULTS AND DISCUSSION

Exchangeable cations measured by ICP-MS after each saturation cycle are given in Table 1. The 8-d saturation period was sufficient to exchange Ca and Mg from the zeolites; the analyses for Ca and Mg after 9 d were extremely low. The results from the Santorini samples are consistent with the mineralogy where the tuffs are dominated by Na, K-rich clinoptilolites and Ca and Mg are lower in amount. The results show that Na and K account for 70–95% of the total exchangeable cations in the Santorini samples.

For the Polyegos samples, Na and K also dominate. They account for 84 to 91% of the total exchangeable cations, whereas Ca and Mg account for only 9–16% of the exchangeable cations in samples P5, P8, P10, P13, and P21. The release of low amounts of Ca and Mg suggests that most of Ca and Mg may be fixed in mordenite or fixed relative to NH_4^+. The high amount

Table 1. Na, K, Ca, and Mg analyses (ppm) by ICP-MS for different periods of ammonium acetate saturation of zeolitized volcaniclastics from Santorini (S) and Polyegos (P) Islands, Greece.

Sample	Cations	Days									
		1	2	3	4	5	6	7	8	9	10
Santorini Island											
S108	Na	876	78	20	10	1	20	7	4	18	8
	K	652	140	40	18	6	18	23	20	25	13
	Ca	88	22	9	9	6	5	7	4	5	4
	Mg	41	9	4	3	3	4	4	2	2	3
S117	Na	643	110	31	6	28	26	12	30	31	8
	K	84	47	29	3	19	19	7	18	12	15
	Ca	83	29	10	11	7	5	4	3	1	3
	Mg	8	4	3	0	1	1	0	1	1	1
S126	Na	1092	90	13	5	16	6	6	4	18	13
	K	555	128	37	11	16	1	18	24	23	9
	Ca	148	32	12	9	6	5	6	4	4	4
	Mg	27	8	5	4	4	3	3	2	4	2
S130	Na	1288	144	26	21	6	23	23	28	29	7
	K	385	124	40	21	5	17	18	21	18	12
	Ca	194	28	12	9	4	3	3	2	3	2
	Mg	16	7	7	4	1	2	2	2	1	2
S140	Na	709	57	8	10	6	19	21	7	16	9
	K	251	54	13	16	6	20	18	22	16	5
	Ca	293	48	14	13	9	8	10	7	4	5
	Mg	55	10	4	3	2	3	2	2	3	3
Polyegos Island											
P5	Na	614	45	9	15	26	25	3	2	24	18
	K	337	72	20	14	25	25	19	19	21	19
	Ca	165	21	5	8	3	3	3	2	3	3
	Mg	20	3	2	2	2	2	0	0	2	1
P8	Na	993	77	27	21	17	21	31	45	36	21
	K	234	60	32	24	11	15	23	31	19	22
	Ca	184	34	14	14	10	12	12	7	5	7
	Mg	16	3	1	1	0	1	1	1	0	1
P10	Na	864	80	34	21	28	37	5	4	23	11
	K	360	93	42	21	31	38	24	22	32	28
	Ca	62	11	4	3	3	4	5	4	4	3
	Mg	46	9	5	3	4	2	3	2	2	2
P13	Na	937	115	31	29	32	30	7	11	19	17
	K	516	132	43	26	23	23	3	7	13	12
	Ca	145	53	16	14	14	13	14	10	9	7
	Mg	27	9	3	2	3	3	2	2	1	2
P21	Na	307	38	7	−3	12	38	1	1	8	3
	K	94	30	4	−7	10	35	25	23	21	8
	Ca	15	3	0	0	1	1	1	1	0	1
	Mg	24	6	3	2	2	3	2	1	2	2

of K is related to exceptionally K-rich mordenite (Kitsopoulos and Dunham, 1998) and also to clinoptilolite (heulandite type 3) (Kitsopoulos, 1997c).

The bulk of cation exchange occurred within 2 d. Na and K exchanged slightly faster from clinoptilolite than from mordenite. The Santorini samples released 85–95% of the exchangeable cations in the first three days, whereas the Polyegos sample released 75–90% in the same time. Na and K in the Santorini samples decreased between 4–6 d. However, after this decrease, 20–30 ppm Na, K were released between 6–9 d. For the Polyegos samples, K was released again following the initial release, between 6–8 d, and some samples showed additional release of Na between 8–10 d. In conclusion, there is an active release of cat-

ions in zeolites even after 5 d, the maximum saturation period for clays.

Although clays can be adequately saturated in short periods (Mackenzie, 1951; Bain and Smith, 1987), zeolites require longer periods for saturation. Noda (1980), for example, used a saturation period of ~4 wk for clinoptilolite, although such periods are inconvenient. Cations will probably be continuously released even after an extensive saturation period. The main objective, however, is to provide near complete NH_4OAc saturation within a reasonable period. Therefore, the results presented here suggest a NH_4OAc saturation period for zeolites of 12 days.

The CEC values in Table 2 were obtained by Kjeldahl ammonia distillation of NH_4^+ solutions obtained

Table 2. CEC values (meq/100 g) of zeolitized volcaniclastics from Santorini (S) and Polyegos (P) Islands, Greece. The CEC values were obtained using the Kjeldahl ammonia distillation technique with the NH_4^+ solutions obtained by washing the NH_4^+-saturated samples of zeolites with 10% NaCl.

Sample	X	Y	Mean	[(Y − X)/2]
		Santorini Island		
S103	184.44	184.83	184.63	0.20
S104	117.11	117.11	117.11	0.00
S105	109.57	109.86	109.71	0.15
S106	161.57	162.17	161.87	0.30
S108	130.54	130.91	130.72	0.19
S110	183.42	184.43	183.92	0.51
S113	119.47	119.47	119.47	0.00
S115	120.39	120.87	120.63	0.24
S116	170.92	171.15	171.03	0.12
S117	111.46	111.66	111.56	0.10
S119	145.25	145.39	145.32	0.07
S120	151.45	152.08	151.76	0.32
S121	175.18	175.60	175.39	0.21
S124	199.98	200.77	200.37	0.40
S126	168.65	169.79	169.22	0.57
S130	188.92	189.29	189.10	0.19
S132	126.20	126.45	126.19	0.13
S137	182.14	182.42	182.28	0.14
S139	142.77	143.48	143.12	0.35
S140	142.34	142.58	142.46	0.12
S141	187.55	187.55	187.55	0.00
S142	163.00	163.19	163.09	0.09
S145	146.97	148.06	147.51	0.55
S146	117.63	118.15	117.89	0.26
[1]Mean				0.22
		Polyegos Island		
P2	109.22	110.13	109.67	0.45
P4	142.10	142.74	142.42	0.32
P5	132.43	133.63	133.03	0.60
P6	86.85	87.84	87.34	0.50
P8	128.33	128.52	128.43	0.09
P10	102.71	103.29	103.00	0.29
P11	132.32	133.22	132.77	0.45
P13	157.21	157.30	157.25	0.05
P14	118.00	118.34	118.17	0.17
P17	154.61	155.78	155.19	0.58
P19	109.70	109.91	109.80	0.10
P21	18.04	18.15	18.09	0.05
P23	1.67	1.76	1.71	0.05
P27	2.31	2.47	2.39	0.08
P30	2.27	2.37	2.33	0.06
P34	146.43	147.23	146.83	0.40
[2]Mean				0.27

[1] Standard deviation: 0.16.
[2] Standard deviation: 0.21.

Table 3. CEC values (meq/100 g) of zeolitized volcaniclastics from Santorini (S) and Polyegos (P) Islands, Greece. The CEC values were obtained using the ammonia electrode technique with the NH_4^+ solutions obtained by washing the NH_4^+-saturated samples of zeolites with 10% NaCl.

Sample	X	Y	Mean	[(Y − X)/2]
		Santorini Island		
S103	185.04	185.04	185.04	0.00
S104	117.21	117.28	117.24	0.04
S105	111.24	111.44	111.35	0.10
S106	164.01	164.24	164.13	0.12
S108	133.75	133.89	133.82	0.07
S110	184.99	185.18	185.09	0.09
S113	120.06	120.10	120.08	0.02
S115	122.22	122.22	122.22	0.00
S116	171.14	171.14	171.14	0.00
S117	112.52	112.81	112.67	0.15
S119	147.67	147.89	147.78	0.11
S120	154.06	154.11	154.08	0.03
S121	176.82	176.83	176.82	0.01
S124	201.90	202.10	202.01	0.10
S126	169.19	169.57	169.38	0.19
S130	189.92	190.01	189.97	0.05
S132	129.68	130.00	129.84	0.16
S137	182.46	182.56	182.51	0.05
S139	145.83	145.97	145.90	0.07
S140	144.79	145.12	144.98	0.16
S141	188.55	188.61	188.58	0.03
S142	163.42	163.43	163.42	0.01
S145	150.33	150.35	150.33	0.01
S146	118.18	118.51	118.33	0.16
[1]Mean				0.07
		Polyegos Island		
P2	113.01	113.36	113.18	0.17
P4	143.62	143.71	143.66	0.05
P5	134.27	134.62	134.44	0.17
P6	89.34	89.45	89.44	0.05
P8	128.02	128.39	128.20	0.18
P10	103.38	103.39	103.38	0.01
P11	133.88	133.88	133.88	0.00
P13	159.61	159.75	159.68	0.07
P14	119.72	120.01	119.86	0.15
P17	157.12	157.17	157.14	0.02
P19	112.08	112.08	112.08	0.00
P21	18.76	18.89	18.82	0.06
P23	1.67	1.74	1.70	0.04
P27	2.38	2.46	2.42	0.04
P30	2.36	2.37	2.36	0.01
P34	148.33	148.75	148.54	0.21
[2]Mean				0.08

[1] Standard deviation: 0.06.
[2] Standard deviation: 0.07.

by treatment with 10% NaCl. Two values were determined for each sample, with the lower value given as X and the higher value as Y. The mean values of CEC range from 109.71 to 200.37 meq/100 g for the Santorini samples, and from 1.71 to 157.25 meq/100 g for Polyegos. These values are larger than the variation (0.22 ± 0.16 and 0.27 ± 0.21) between the pair of measurements. The three Polyegos samples (P23, P27, and P30), which showed very low CEC values (1.7–2.5 meq/100 g), contain kaolinite, halloysite, alunite,

and amorphous silica in variable amounts, but no zeolite minerals. Sample P21 from Polyegos, with a CEC of ~18 meq/100 g, is a kaolinite sample, but some mordenite was present also. Therefore, the low CEC values for these four samples, relative to the other samples, are consistent with mineralogy. The results obtained using the standard 1 M NH_4Cl solutions were very satisfactory (mean value 0.997, s.d. 0.028).

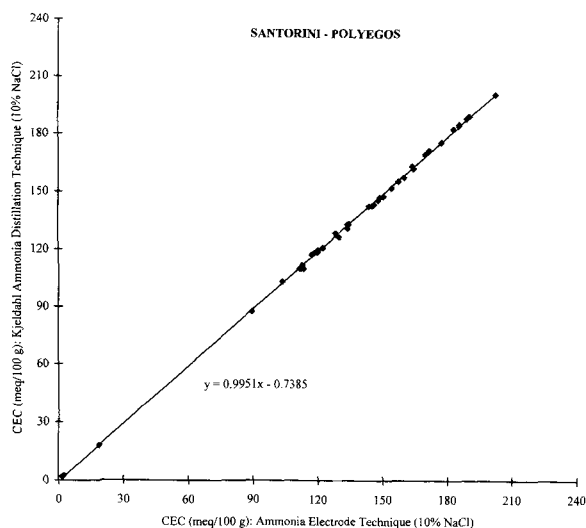The CEC values in Table 3 were obtained with an ammonia electrode and the NH_4^+ solutions obtained

SANTORINI - POLYEGOS

$y = 0.9951x - 0.7385$

Figure 4. CEC values (meq/100 g) obtained using the ammonia electrode technique with the NH_4^+ solutions obtained by washing the NH_4^+-saturated samples of zeolites with 10% NaCl *vs.* CEC values (meq/100 g) obtained using the Kjeldahl ammonia distillation technique with the same NH_4^+ solutions. The correlation coefficient is 0.999 for the regression analysis.

by treatment with 10% NaCl. The results are presented in the same way as for Table 2. The mean values of CEC range from 111.35 to 202.01 meq/100 g for the Santorini samples, and from 1.70 to 159.68 meq/100 g for Polyegos; values all much larger than the variation (0.07 ± 0.06 and 0.08 ± 0.07) between the pair of measurements. The results obtained using the standard 1 M NH_4Cl solutions were very satisfactory (mean value 0.999, s.d. 0.019). Figure 4 shows the data of Tables 2 and 3 and indicates that the two techniques give similar results. However, the ammonia electrode technique can dramatically reduce the time of performing a CEC measurement.

The CEC values in Table 4 were obtained with an ammonia electrode directly with the NH_4^+-saturated samples, but the samples were not treated with 10% NaCl. The results are presented following the format of Table 2. The mean values of CEC range from 126.58 to 221.60 meq/100 g for the Santorini samples, and from 1.71 to 188.00 meq/100 g for the Polyegos samples; values all much larger than the variation (0.06 ± 0.05 and 0.05 ± 0.05) between the pair of measurements. The results obtained using the standard 1 M NH_4Cl solutions were very satisfactory (mean value 1.000, s.d. 0.017).

The results shown in Tables 3 and 4 indicate that the CEC values obtained from the NH_4^+-saturated samples were generally higher than those obtained from the NH_4^+ solutions obtained after washing with 10% NaCl. Differences to 72.36 meq/100 g were recorded for the Santorini samples and to 59.27 meq/

Table 4. CEC values (meq/100 g) of zeolitized volcaniclastics from Santorini (S) and Polyegos (P) Islands, Greece. The CEC values were obtained using the ammonia electrode technique directly with the NH_4^+-saturated samples of zeolites (no prior washing with 10% NaCl).

Sample	X	Y	Mean	[(Y − X)/2]
Santorini Island				
S103	186.05	186.14	186.09	0.04
S104	131.62	131.86	131.74	0.12
S105	126.52	126.65	126.58	0.07
S106	192.92	193.12	193.02	0.10
S108	132.27	132.27	132.27	0.00
S110	165.64	165.79	185.71	0.08
S113	131.11	131.11	131.11	0.00
S115	137.87	138.14	138.00	0.13
S116	197.71	197.73	197.72	0.01
S117	151.60	151.92	151.76	0.16
S119	217.57	217.80	217.68	0.12
S120	189.81	189.95	189.88	0.07
S121	178.81	179.07	178.94	0.13
S124	214.59	214.78	214.68	0.09
S126	197.56	197.56	197.56	0.00
S130	221.60	221.60	221.60	0.00
S132	130.34	130.50	130.42	0.08
S137	180.48	180.49	180.48	0.01
S139	182.40	182.52	182.46	0.06
S140	153.21	153.24	153.22	0.02
S141	186.82	186.82	186.82	0.00
S142	183.02	183.22	183.12	0.10
S145	161.44	161.49	161.44	0.03
S146	134.41	134.42	134.41	0.00
[1]Mean				0.06
Polyegos Island				
P2	113.01	113.16	113.08	0.07
P4	170.03	170.33	170.18	0.15
P5	139.58	139.70	139.64	0.06
P6	114.89	114.90	114.89	0.01
P8	148.63	148.70	148.66	0.03
P10	116.07	116.11	116.09	0.02
P11	187.90	188.11	188.00	0.11
P13	161.73	161.75	161.74	0.01
P14	150.92	151.15	151.04	0.12
P17	179.59	179.59	179.59	0.00
P19	169.01	169.14	169.07	0.06
P21	33.29	33.39	33.34	0.05
P23	1.66	1.76	1.71	0.05
P27	2.46	2.46	2.46	0.00
P30	2.38	2.39	2.38	0.01
P34	160.02	160.02	160.02	0.00
[2]Mean				0.05

[1] Standard deviation: 0.05.
[2] Standard deviation: 0.05.

100 g for the Polyegos samples. Figure 5 is the plot of Table 4 *vs.* Table 3.

It is unlikely that these differences in the CEC are related to laboratory or experimental conditions or interference problems from the electrode. Care was taken that a) the starting samples were well homogenized, b) duplicate measurements were randomly taken for all samples, c) NH_4^+ was treated by a strong alkali to ensure complete conversion to NH_3, and d) the accuracy of the experiments was determined by using stan-
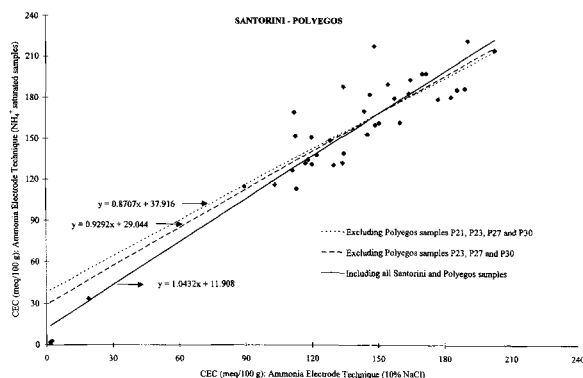
Figure 5. CEC values (meq/100 g) obtained using the ammonia electrode technique with the NH_4^+ solutions obtained by washing the NH_4^+-saturated samples of zeolites with 10% NaCl vs. CEC values (meq/100 g) obtained using the ammonia electrode technique directly with the NH_4^+-saturated samples of zeolites (no prior washing with 10% NaCl). The correlation coefficient is 0.948 (including all samples from Santorini and Polyegos) for the regression analysis. If the three kaolinite samples P23, P27, and P30 from Polyegos, which exhibit minimal differences in their CEC values, are omitted, then, the correlation coefficient value is 0.884. If P21 is omitted also the correlation coefficient value is 0.823.

dard 1 M NH_4Cl solutions. Although ion selective electrodes may suffer in accuracy when ions of similar valency are present (Busenberg and Clemency, 1973), the ammonia electrode is not an ion selective electrode. The ammonia electrode is a gas-detecting electrode sensitive to dissolved ammonia (not ammonium). The electrode has a hydrophobic membrane permeable to ammonia, but not to any ionic species. Busenberg and Clemency (1973) used the electrode successfully with NH_4^+-saturated clays, and they found that the ammonia electrode has virtually no interferences, in contrast to most other electrodes.

Thus, the differences in CEC are not related to experimental or laboratory conditions, or ion interference. Apparently, the NH_3 obtained from the NH_4^+-saturated samples was higher than the NH_3 produced by the NH_4^+ solutions obtained by washing the NH_4^+-saturated samples with 10% NaCl. Presumably, the release of the saturating NH_4^+ ions, after the NH_4^+-saturated samples were washed with 10% NaCl, was not complete for the majority of samples used here and some NH_4^+ ions remain trapped in the zeolite minerals.

The CEC of zeolites should reflect the amount of a saturating ion (principally NH_4^+) adsorbed at a specific pH when the zeolite samples come in contact with a relevant solution. Problems may occur in the measurement of the CEC of zeolites using methods that may be applicable to other minerals. For example, the insufficient exchange of NH_4^+ ions as described above is a serious drawback in applying AMAS to zeolites if the procedures of Bain and Smith (1987) for clays are followed. Other factors influencing the CEC may

include improper grinding procedures (i.e., reducing size), the application of heat, the change of composition of the zeolite to a single cationic form (e.g., Na exchange), or the change in nature and concentration of the saturating ion. The simultaneous application of more than one of these treatments in all their possible combinations may further change the apparent CEC. By applying the various physical and chemical treatments we may obtain the highest possible CEC value for a zeolite sample. However, comparable CEC values for zeolites may be difficult to obtain. Instead, a technique that provides a common approach and comparable CEC values for zeolites is most valuable.

SUGGESTED TECHNIQUE FOR MEASURING THE CEC OF ZEOLITES

The technique proposed here consists of three major parts: (1) sample preparation, (2) saturation of the sample with NH_4OAc and exchange, and (3) conversion of NH_4^+ ions to NH_3 and measurement of the NH_3 produced.

Sample preparation

Fine powders (<125 μm) are required for the proposed technique. To produce the <125-μm powders, representative large blocks of a zeolite sample are crushed to 2–3 mm by use of a "fly-press" or similar grinding technique. Select a few of the 2–3-mm size samples representative of the zeolite, and grind very gently by hand in a mortar and pestle. Generally, grinding mills should be avoided because of contamination. Also, when mills are used, excessive grinding (by hand as well) should be avoided to prevent structural deterioration of the mineral. After grinding, the material is passed through a 125-μm aperture sieve. Nylon mesh sieves are recommended. The use of dry and wet grinding or ultrasonic bath techniques are not recommended because they may produce material that is too fine. Note, during grinding and sieving, no fraction of the sample is discarded; any pieces that remain in the sieve are ground and sieved again.

The <125-μm powders are then washed with NH_3-free deionized water to remove any soluble phases present, which could interfere with the measurement of CEC. Note that NH_3-free deionized water should be used at all stages. NH_3-free deionized water can be prepared easily by passing deionized water through a column of an ordinary commercial ion-exchange resin. This will reduce the concentration of NH_3 below the detection limit of the electrode. The washed powders are then left to dry thoroughly without heating.

NH_4OAc saturation

The NH_4OAc saturation follows the guidelines described above in Methods: "The ammonium acetate saturation (AMAS) method—NH_4OAc saturation." The major difference is that the NH_4OAc saturation should occur during a period of 12-day cycles. Over-

night saturation should occur in a tightly sealed centrifuge tube placed sideways on a stirring plate to ensure a well-mixed saturating NH_4OAc solution and sample. The samples of NH_4^+-saturated zeolites are then left to dry thoroughly without heating. If the NH_4^+-saturated samples are dried in an oven, the temperature should not exceed 40–50°C. Do not store or open ammonia reagent bottles in the same lab where the CEC experiments are processed.

Conversion of the NH_4^+ ions to NH_3 and measurement of the NH_3 produced

The samples of NH_4^+-saturated zeolites are not washed with any salt solution, but these samples are used directly. Kjeldahl ammonia distillation or the ammonia electrode are two satisfactory techniques recommended for measuring NH_3.

The Kjeldahl ammonia distillation procedure is applied as described above (see Methods: *Kjeldahl ammonia distillation technique*). Instead of NH_4^+ solutions, 50–150 mg of the dried, NH_4^+-saturated samples of zeolites are weighed and transferred to a distillation flask and the Kjeldahl ammonia distillation procedure is followed. The CEC can be calculated as CEC $= \{[(V_{HCl})(N_{HCl}) - (V_{NaOH})(N_{NaOH})]/(w)\}100$, where CEC is expressed in meq/100 g, (V_{HCl}) is the volume (in mL) of the HCl, (N_{HCl}) is the normality of the HCl, (V_{NaOH}) is the volume (in mL) of the NaOH used in the titration, (N_{NaOH}) is the normality of the NaOH, and (w) is the weight of the sample in g. Note that NH_3 may normally be distilled within a period of 1 h. However, care must be taken by routinely determining the pH.

The ammonia electrode is used directly with the NH_4^+-saturated samples of zeolites as described above (see Methods: *Ammonia electrode technique*). The CEC is obtained from CEC $= [(C)(V)/(w)]100$, where CEC is expressed in meq/100 g, (C) is the concentration of ammonia in moles/L, (V) is the volume (in L) of water added, and (w) is the weight of the sample in g.

REFERENCES

Bain, D.C. and Smith, B.F.L. (1987) Chemical analysis. In *A Handbook of Determinative Methods in Clay Mineralogy*, M.J. Wilson, ed., Blackie, Glasgow, 248–274.

Busenberg, E. and Clemency, C.V. (1973) Determination of the cation exchange capacity of clays and soils using an ammonia electrode. *Clays and Clay Minerals,* **21,** 213–217.

Chapman, H.D. (1965) Cation exchange capacity. In *Methods of Soil Analysis (Number 9 in the Series Agronomy), Part 2,* A. Black, ed., American Institute of Agronomy, Madison, Wisconsin, 891–901.

Fraser, A.R. and Russel, J.D. (1969) A spectrophotometric method for determination of cation exchange capacity of clay minerals. *Clay Minerals,* **8,** 229–230.

IGME (1980) Geological map "Thera". 1: 50,000. Institute of Geological and Mineralogical Research of Greece (IGME), Athens.

Kanaris, I.T. (1989) *Zeolites of the Island of Polyegos.* Report by IGME (Institute of Geological and Mineralogical Research of Greece), Athens, 21 pp. (in Greek).

Kitsopoulos, K.P. (1995a) The mineralogy, geochemistry, physical properties and possible industrial applications of volcanic zeolitic tuffs from Santorini and Polyegos islands, Greece. Ph.D. thesis, Leicester University, Leicester, UK, 442 pp.

Kitsopoulos, K.P. (1995b) The relation of the reduction of the 020 diffraction peak of heulandite with its mineral chemistry. *Geological Society of America 1995 Annual Meeting, New Orleans (Louisiana, USA), November 1995, Abstract with Programs,* **27,** A-362.

Kitsopoulos, K.P. (1997a) The comparison of the methylene blue absorption and ammonium acetate saturation methods for determine CEC values of volcanic zeolitic tuffs from Greece. *Clay Minerals,* **32,** 319–322.

Kitsopoulos, K.P. (1997b) Genesis of heulandite group of minerals in pyroclastics (Santorini, Greece). Implications for models of zeolitization of volcaniclastic materials. *Zeolite '97, 5th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, Ischia (Naples, Italy), September 1997, Program and Abstracts,* 195–197.

Kitsopoulos, K.P. (1997c) The genesis of a mordenite deposit by hydrothermal alteration of pyroclastics on Polyegos island, Greece. *Clays and Clay Minerals,* **45,** 632–648.

Kitsopoulos, K.P. and Dunham A.C. (1998) Compositional variations of mordenite from Polyegos island, Greece: Na-Ca and K-rich mordenite. *European Journal of Mineralogy,* **10,** 569–577.

Mackenzie, R.C. (1951) A micromethod for determination of cation-exchange capacity of clays. *Journal of Colloid Science,* **6,** 219–222.

Nevins, M.J. and Weintritt, D.J. (1967) Determination of CEC by methylene blue adsorption. *American Ceramic Society Bulletin,* **46,** 587–592.

Noda, S. (1980) A simple method for determining the cation exchange capacity of natural zeolites. *Nendo Kagaku,* **20,** 78–82.

Peech, M. (1945) Determination of exchangeable cations and exchange capacity of soils—Rapid micromethods utilizing centrifuge and spectrophotometer. *Soil Science,* **59,** 25–38.

Schollenberger, C.J. and Dreibelbis, F.R. (1930) Analytical methods in base-exchange investigations on soils. *Soil Science,* **30,** 161–173.

Schollenberger, C.J. and Simon, R.H. (1945) Determination of exchange capacity and exchangeable bases in soil. Ammonium acetate method. *Soil Science,* **59,** 13–24.

Tsolis-Katagas, P. and Katagas, C. (1989) Zeolites in Pre-Caldera pyroclastic rocks of the Santorini Volcano, Aegean Sea, Greece. *Clays and Clay Minerals,* **37,** 497–510.