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MINERALOGY, CHEMISTRY, GAS ADSORPTION, AND NH_4^+-EXCHANGE CAPACITY

FOR SELECTED ZEOLITIC TUFFS FROM THE WESTERN UNITED STATES

By

Richard A. Sheppard and Arthur J. Gude, 3d

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INTRODUCTION

Zeolites belong to a group of naturally occurring minerals known as framework silicates, which also include feldspars and feldspathoids. Specifically, zeolites are crystalline hydrated aluminosilicates of the alkali and the alkaline-earth elements. They have an infinitely extended framework structure that encloses interconnected cavities occupied by the relatively large exchangeable cations and water molecules. The fundamental building block of the zeolites is a tetrahedron of four oxygen atoms surrounding a relatively small silicon or aluminum atom. The framework structure of zeolites consists of SiO_4 and AlO_4 tetrahedra such that each oxygen is shared between two tetrahedra. Thus, the atomic ratio, $O:(Al+Si)$, is equal to 2. Because aluminum has one less positive charge than silicon, the framework has a net negative charge and is balanced by the exchangeable cations. These cations are chiefly monovalent sodium and potassium and divalent calcium and magnesium.

Since zeolites were discovered more than two centuries ago, more than 40 distinct species have been recognized. Numerous zeolites have also been synthesized, but most of these have no natural counterparts. Zeolites occur in rocks that are diverse in lithology and age, and they have formed in many different geological environments. The common and perhaps best known occurrences are in the cavities and fractures of igneous rocks, particularly basaltic rocks. Most of the large, attractive zeolite specimens in museum collections have been obtained from igneous rocks. In recent years, zeolites have been recognized as important rock-forming constituents in low-grade metamorphic rocks and in various sedimentary rocks (Hay, 1966). The zeolites in sedimentary rocks are very finely crystalline and do not appeal to mineral collectors, but deposits of this type are voluminous and have economic potential for many industrial and agricultural processes.

Zeolites are among the common authigenic silicate minerals that occur in sedimentary rocks. Although about 20 different zeolites have been reported from sedimentary rocks throughout the world, only analcime, chabazite, clinoptilolite, erionite, heulandite, laumontite, mordenite, and phillipsite commonly make up the major part of zeolitic rocks. Clinoptilolite is by far the most commonly reported zeolite in sedimentary deposits.

Most zeolites in sedimentary deposits formed after burial of the enclosing sediments by the reaction of aluminosilicate materials with the interstitial water. Silicic volcanic glass is the aluminosilicate material that most commonly served as a precursor for the zeolites, although materials such as clay minerals, feldspars, feldspathoids, and gels have also reacted locally to form zeolites. Except for laumontite and possibly some heulandite, the common zeolites generally occur in tuffaceous sedimentary rocks that have not been deeply buried or exposed to hydrothermal solutions. Zeolitic tuffs generally are white, or pastel shades of green, yellow, orange, or brown, relatively hard, and dull or earthy. The zeolitic tuffs commonly break with a blocky or conchoidal fracture. Unlike fresh volcanic ash, the zeolitic tuffs

are resistant and ledge forming, particularly in arid areas. Most zeolitic tuffs consist of two or more zeolites as well as authigenic clay minerals, silica minerals, or feldspar, relict glass, and crystal and rock fragments. Extensive and relatively pure beds of zeolite, however, occur in Cenozoic deposits of the Western United States.

Most natural zeolites show considerable ranges in chemical composition, including ranges in the water content, the cation content, and the Si:Al ratio. Summaries of their composition are given by Deer, Howie, and Zussman (1963), Hay (1966), Sheppard (1971), and Utada (1970).

The wide diversity of applications and potential applications of natural zeolites is due to a unique set of properties, some of which were recognized more than a century ago. These properties include reversible dehydration, cation exchange, adsorption, and thermal and acid stability. The commercial utilization of natural zeolites in the United States is in its infancy, but the seemingly useful physical and chemical properties of zeolites, the high grade of many deposits, and the probable low cost of mining suggest greatly increased utilization in many industrial and agricultural processes in the near future (Mumpton, 1978).

This report presents new data on the mineralogy, chemistry, gas adsorption, and NH_4^+-exchange capacity for a suite of 40 samples of high-grade zeolitic tuffs from 23 deposits in nine western states. Some of the deposits are being mined or have been mined, and others have been prospected in anticipation of future mining. Tuffs rich in analcime, chabazite, clinoptilolite, erionite, mordenite, and phillipsite comprise the suite. Where possible, only those samples that were nearly monomineralic were chosen for further analysis. No attempt was made to beneficiate the zeolite phase prior to analysis. All samples were crushed, and the various analyses were performed on splits.

LOCALITY INFORMATION

Information on the localities from which the analyzed zeolitic tuffs were collected is given in table 1. The locations of the 23 sampled deposits are shown on figure 1. For each of the 40 samples, table 1 gives the field number; the U.S. Geological Survey's laboratory number; the name, latitude, and longitude of the locality; the name and age of the stratigraphic unit from which the sample was collected; and one or more references that contain additional information on the zeolite occurrence.

All of the samples are from tuffs that originally consisted chiefly of silicic glass and only minor crystal and rock fragments. Most of the zeolitic tuffs are from alkaline, saline-lake deposits, but some clinoptilolite-rich tuffs are from fluviatile deposits. Three clinoptilolite-rich samples and one mordenite-rich sample are from ash-flow tuffs that were deposited on the land surface. Although the age of the host rocks containing the zeolite deposits is Eocene to Pleistocene, most of the analyzed zeolitic tuffs occur in Neogene rocks.

Table 1.--*Sample localities for the analyzed zeolitic tuffs*

[Localities are shown on figure 1. F. A. Mumpton provided those samples that have five-digit field numbers and begin with "27"]

Field No.	Laboratory No.	Locality Name	Latitude N.	Longitude W.	Stratigraphic unit and age	References
		Analcime-rich tuff				
M4-58A	D-228278	Barstow, San Bernardino County, Calif.	35°02'	117°02'	Miocene Barstow Formation	Sheppard and Gude (1969a)
SW-3-2	D-228279	Wikieup, Mohave County, Ariz.	34°42'	113°34'	Pliocene Big Sandy Formation	Sheppard and Gude (1973)
		Chabazite-rich tuff				
W7-19B	D-228280	Wikieup, Mohave County, Ariz.	34°45'	113°35'	Pliocene Big Sandy Formation	Sheppard and Gude (1973)
SD-4-2	D-228281	Durkee, Baker County, Oreg.	44°35'	117°24'	Pliocene lacustrine deposit	Gude and Sheppard (1978); Sheppard and Gude (1980a)
SD-4-16	D-228282	Durkee, Baker County, Oreg.	44°35'	117°24'	Pliocene lacustrine deposit	Gude and Sheppard (1978); Sheppard and Gude (1980a)
27113	D-228310	Bowie, Graham County, Ariz.	32°29'	109°27'	Late Cenozoic lacustrine deposit	Sheppard and others (1978); Eyde (1982)
27123	D-228311	Christmas, Gila County, Ariz.	33°07'	110°46'	Late Cenozoic lacustrine deposit	Eyde (1982)
		Clinoptilolite-rich tuff				
M4-22A	D-228283	Barstow, San Bernardino County, Calif.	35°01'	117°00'	Miocene Barstow Formation	Sheppard and Gude (1969a)
27023	D-228312	Hector, San Bernardino County, Calif.	34°49'	116°30'	Tertiary lacustrine deposit	Ames and others (1958)
AMN-1	D-228290	Death Valley Junction, Inyo County, Calif.	36°19'	116°20'	Tertiary ash-flow tuff	Santini and Knostman (1979)
27163	D-228319	Death Valley Junction, Inyo County, Calif.	36°19'	116°20'	Tertiary ash-flow tuff	Santini and Knostman (1979)
W7-36B	D-228284	Wikieup, Mohave County, Ariz.	34°37'	113°32'	Pliocene Big Sandy Formation	Sheppard and Gude (1973)
HD-2A	D-228289	Horseshoe Dam, Maricopa County, Ariz.	33°59'	111°43'	Late Cenozoic Verde Formation	Sheppard (1971)
DO-54H	D-228285	Durkee, Baker County, Oreg.	44°35'	117°26'	Pliocene lacustrine deposit	Sheppard and Gude (1980a)
27073	D-228317	Sheaville, Malheur County, Oreg.	43°09'	117°02'	Miocene Sucker Creek Formation	Kittleman and others (1965)
27053	D-228315	Fish Creek Mountains, Lander County, Nev.	40°13'	117°22'	Tertiary ash-flow tuff	Deffeyes (1959)
27033	D-228313	Castle Creek, Owyhee County, Idaho	42°58'	116°23'	Pliocene Chalk Hills Formation	Malde and Powers (1962)
V-1B	D-228288	Sand Wash, Moffat County, Colo.	40°48'	108°27'	Eocene Bridger Formation	Sheppard (1971)
27043	D-228314	Creede, Mineral County, Colo.	37°50'	106°55'	Oligocene Creede Formation	Steven and Van Loenen (1971)
27063	D-228316	Mountain Green, Morgan County, Utah	41°09'	111°47'	Tertiary Salt Lake Formation	Sheppard (1971)
27083	D-228318	Buckhorn, Grant County, N. Mex.	33°01'	108°42'	Pliocene and Pleistocene Gila Conglomerate	Olander (1979); Eyde (1982)
TX-2	D-228286	Tilden, McMullen County, Tex.	28°28'	98°38'	Eocene Manning Formation	Dickinson (1975, 1978)
TP-10	D-228287	Alamito Creek, Presidio County, Tex.	29°47'	104°00'	Oligocene Tascotal Formation(?)	C. G. Groat (written commun., 1973)
		Erionite-rich tuff				
27103	D-228307	Tecopa, Inyo County, Calif.	35°56'	116°17'	Pleistocene lacustrine deposit	Sheppard and Gude (1968)
SW-26-4B	D-228291	Wikieup, Mohave County, Ariz.	34°39'	113°33'	Pliocene Big Sandy Formation	Sheppard and Gude (1973)
DO-288	D-228292	Durkee, Baker County, Oreg.	44°33'	117°23'	Pliocene lacustrine deposit	Sheppard and Gude (1980a)
D1-81	D-228293	Durkee, Baker County, Oreg.	44°34'	117°23'	Pliocene lacustrine deposit	Sheppard and Gude (1980a)
R-13B	D-228294	Rome, Malheur County, Oreg.	42°47'	117°43'	Miocene Rome beds	Sheppard and Gude (1969b); Wolf and Ellison (1971); Campion (1979)
E4-1B	D-228295	Eastgate, Churchill County, Nev.	39°18'	117°56'	Pliocene Monarch Mill Formation	Papke (1972); Sheppard and Gude (1980b)
27093	D-228306	Pine Valley, Eureka County, Nev.	40°18'	116°08'	Pliocene and Pleistocene Hay Ranch Formation	Regnier (1960); Papke (1972)
		Mordenite-rich tuff				
M4-54B	D-228297	Barstow, San Bernardino County, Calif.	35°03'	117°05'	Miocene Barstow Formation	Sheppard and Gude (1969a)
27133	D-228308	Union Pass, Mohave County, Ariz.	35°13'	114°24'	Tertiary Golden Door Volcanics	T. H. Eyde (written commun., 1975)
R-5C	D-228298	Rome, Malheur County, Oreg.	42°51'	117°41'	Miocene Rome beds	Sheppard and Gude (1969b); Wolf and Ellison (1971); Campion (1979)
E5-11A	D-228299	Eastgate, Churchill County, Nev.	39°17'	117°56'	Pliocene Monarch Mill Formation	Papke (1972); Sheppard and Gude (1980b)
27143	D-228309	Lovelock, Pershing County, Nev.	40°17'	118°38'	Tertiary lacustrine deposit	Regis (1970)
		Phillipsite-rich tuff				
T4-76A	D-228301	Tecopa, Inyo County, Calif.	35°57'	116°13'	Pleistocene lacustrine deposit	Sheppard and Gude (1968)
T4-85A	D-228302	Tecopa, Inyo County, Calif.	35°54'	116°12'	Pleistocene lacustrine deposit	Sheppard and Gude (1968)
W8-63A	D-228303	Wikieup, Mohave County, Ariz.	34°38'	113°32'	Pliocene Big Sandy Formation	Sheppard and Gude (1973)
R-4B	D-228304	Rome, Malheur County, Oreg.	42°51'	117°41'	Miocene Rome beds	Sheppard and Gude (1969b); Wolf and Ellison (1971); Campion (1979)
27153	D-228305	Pine Valley, Eureka County, Nev.	40°15'	116°07'	Pliocene and Pleistocene Hay Ranch Formation	Regnier (1960); Papke (1972)

Figure 1.--Map showing the sampled zeolite deposits (dots). Locality data are given in table 1. Symbols for the deposits are as follows: AC, Alamito Creek, Presidio County, Tex.; BE, Bowie, Graham County, Ariz.; BH, Buckhorn, Grant County, N. Mex.; BW, Barstow, San Bernardino County, Calif.; CC, Castle Creek, Owyhee County, Idaho; CE, Creede, Mineral County, Colo.; CS, Christmas, Gila County, Ariz.; DE, Durkee, Baker County, Oreg.; DV, Death Valley Junction, Inyo County, Calif.; EG, Eastgate, Churchill County, Nev.; FC, Fish Creek Mountains, Lander County, Nev.; HD, Horseshoe Dam, Maricopa County, Ariz.; HR, Hector, San Bernardino County, Calif.; LK, Lovelock, Pershing County, Nev.; MG, Mountain Green, Morgan County, Utah; PV, Pine Valley, Eureka County, Nev.; RE, Rome, Malheur County, Oreg.; SV, Sheaville, Malheur County, Oreg.; SW, Sand Wash, Moffat County, Colo.; TA, Tecopa, Inyo County, Calif.; TN, Tilden, McMullen County, Tex.; UP, Union Pass, Mohave County, Ariz.; WP, Wikieup, Mohave County, Ariz.

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MINERALOGY OF THE ZEOLITIC TUFFS

The mineralogy of the zeolitic tuffs was determined by study of X-ray diffractometer patterns of powdered samples. The samples were first ground to a powder, packed in aluminum sample holders, and then exposed to copper radiation. Relative abundances of the zeolites and other constituents were estimated from the diffractometer patterns by using peak intensities and the procedure described by Sheppard and Gude (1973). These results are given in table 2 where the abundance is expressed as "parts of ten." Inasmuch as no numerical value was assigned to trace amounts of constituents, most samples total 10 plus traces. Estimates are probably less reliable for samples containing authigenic opal C-T because this material yields a rather poor X-ray record.

Most of the analyzed zeolitic tuffs contain at least 90 percent of the stated zeolite, and only several of the tuffs contain less than 60 percent of the stated zeolite. The most common impurities in the tuffs are clay minerals, other zeolites, opal C-T, plagioclase, and quartz. Several of the zeolitic tuffs from lacustrine deposits also contain impurities of authigenic potassium feldspar.

MAJOR-ELEMENT CHEMISTRY

The major-element chemistry of the zeolitic tuffs was determined by X-ray spectographic analysis in the laboratories of the U.S. Geological Survey in Denver. Results of the analyses are given in table 3 in weight percent of the oxides. Loss on ignition (LOI) was determined at 900°C. The LOI is chiefly H_2O, but it does include CO_2 in those samples that contain calcite impurities. We do not know the cause of the relatively low total for sample No. T4-85A, a phillipsite-rich tuff.

Because most of the analyzed tuffs consist of a single zeolite and because this zeolite is the predominant phase, the analyses in table 3 resemble analyses of the constituent zeolites. All of the samples contain at least minor impurities; however, and some samples contain substantial impurities, such as opal C-T, clay minerals, quartz, and feldspars. Thus, these analyses must be treated as what they actually are--analyses of rocks and not analyses of zeolites.

Nevertheless, some generalizations are possible. As expected, the analcime-rich tuffs show a relatively low $SiO_2:Al_2O_3$ ratio, the chabazite-rich, erionite-rich, and phillipsite-rich tuffs show an intermediate $SiO_2:Al_2O_3$ ratio, and the clinoptilolite-rich and mordenite-rich tuffs show a high $SiO_2:Al_2O_3$ ratio. Of the chabazite-rich tuffs, only sample No. SD-4-16 shows a predominance of alkaline-earth elements; all others show a predominance of alkalis. Of the clinoptilolite-rich tuffs, only sample Nos. HD-2A and 27083 show a predominance of alkaline-earth elements; all others show a predominance of alkalis. Most of the alkalic, clinoptilolite-rich tuffs are sodic, but sample Nos. 27053, 27063, and 27073 are potassic. Sample No. 27043 is also a potassic, clinoptilolite-rich tuff, but this sample contains a significant amount of authigenic potassium feldspar. The erionite-rich and phillipsite-rich tuffs have a consistently high K_2O content which is characteristic of the constituent zeolites. Of the erionite-rich tuffs, only sample No. DO-28B shows a predominance of calcium. The phillipsite-rich tuffs

Table 2.—*Mineralogic composition of zeolitic tuffs, as estimated from X-ray diffractometer patterns of bulk samples*

[--, looked for but not found; Tr., trace. Clay, 10A: illite, biotite, and muscovite. Other: calcite in sample Nos. SW-3-2, R-13B, and R-5C; gypsum in sample No. 27033]

Field No. (See table 1)	X-ray analysis (parts of ten)												
	Analcime	Chabazite	Clinoptilolite	Erionite	Mordenite	Phillipsite	Potassium feldspar	Plagioclase	Quartz	Opal C-T	Clay, 10A	Clay, 14A	Other
Analcime-rich tuff													
M4-5BA	8	--	--	--	--	--	--	Tr.	2	--	Tr.	Tr.	--
SW-3-2	10	--	--	--	--	--	--	Tr.	--	--	Tr.	--	Tr.
Chabazite-rich tuff													
W7-19B	--	10	--	--	--	--	--	Tr.	--	--	Tr.	--	--
SD-4-2	--	10	Tr.	Tr.	--	--	--	Tr.	--	--	--	--	--
SD-4-16	--	10	--	Tr.	--	--	--	--	--	--	--	--	--
27113	--	8	--	2	--	--	--	--	--	--	--	--	--
27123	--	8	--	--	2	--	--	--	Tr.	--	Tr.	Tr.	--
Clinoptilolite-rich tuff													
M4-22A	--	--	10	--	--	--	--	--	--	--	Tr.	Tr.	--
27023	--	--	9	--	--	--	--	Tr.	1	--	Tr.	Tr.	--
AMN-1	--	--	10	--	--	--	--	--	--	Tr.	--	--	--
27163	--	--	10	--	--	--	--	--	--	--	--	Tr.	--
W7-36B	--	--	8	Tr.	--	--	--	Tr.	--	--	Tr.	2	--
HD-2A	--	--	9	--	--	--	--	--	1	--	Tr.	Tr.	--
DO-54H	Tr.	--	10	--	--	--	--	--	--	--	Tr.	Tr.	--
27073	--	--	10	--	--	--	--	--	--	--	--	Tr.	--
27053	--	--	8	--	--	--	--	2	--	--	--	--	--
27033	--	--	10	--	--	--	--	--	--	--	Tr.	Tr.	Tr.
V-1B	--	--	6	--	--	--	--	1	2	--	1	Tr.	--
27043	--	--	5	--	--	--	2	--	--	3	Tr.	Tr.	--
27063	--	--	9	--	--	--	--	--	--	1	Tr.	Tr.	--
27083	--	--	10	--	--	--	--	--	--	--	--	Tr.	--
TX-2	--	--	3	--	--	--	--	--	--	4	1	2	--
TP-10	--	--	4	--	--	--	--	2	--	3	Tr.	1	--
Erionite-rich tuff													
27103	--	--	--	9	--	1	--	--	--	--	--	--	--
SW-26-4B	--	--	--	9	--	--	1	--	--	--	--	--	--
DO-28B	--	--	--	9	--	--	--	--	1	--	Tr.	Tr.	--
D1-81	--	--	--	10	--	--	--	--	--	--	--	--	--
R-13B	--	--	2	8	--	--	--	--	--	--	--	--	Tr.
E4-1B	--	--	--	10	--	--	--	--	--	--	--	--	--
27093	--	--	Tr.	9	--	1	--	--	--	--	--	Tr.	--
Mordenite-rich tuff													
M4-54B	--	--	3	1	6	--	--	--	--	--	--	Tr.	--
27133	--	--	--	--	10	--	--	--	--	--	--	--	--
R-5C	--	--	--	--	7	--	3	--	--	--	--	--	Tr.
E5-11A	--	--	--	--	9	--	--	--	--	--	--	1	--
27143	--	--	--	--	8	--	2	--	--	--	--	--	--
Phillipsite-rich tuff													
T4-76A	--	--	--	--	--	10	--	--	Tr.	--	Tr.	--	--
T4-85A	--	--	--	--	--	10	--	--	--	--	--	Tr.	--
W8-63A	2	--	--	--	--	7	--	--	--	--	1	Tr.	--
R-4B	--	--	--	--	--	9	--	1	--	--	Tr.	Tr.	--
27153	--	--	--	Tr.	--	10	--	--	--	--	--	--	--

Table 3.--Chemical analyses of zeolitic tuffs

[Analysts: J. S. Wahlberg, J. E. Taggart, and J. W. Baker]

Field No. (See table 1)	Chemical analysis, in weight percent											
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI	Total
Analcime-rich tuff												
M4-58A	62.1	16.8	1.35	0.65	0.93	8.8	0.70	0.1	0.1	0.04	7.91	99.48
SW-3-2	58.2	17.6	2.09	0.80	1.0	9.9	0.77	0.1	<0.1	0.02	8.95	99.43
Chabazite-rich tuff												
W7-19B	55.7	15.4	2.39	2.1	3.37	2.2	3.06	0.38	0.1	0.05	14.7	99.45
SD-4-2	58.4	14.2	0.41	0.5	3.80	2.6	1.36	0.19	<0.1	<0.02	18.5	99.96
SD-4-16	58.3	13.6	1.48	1.4	3.62	1.0	1.71	0.16	<0.1	<0.02	18.5	99.77
27113	54.8	13.1	3.49	1.2	3.54	3.0	0.98	0.28	<0.1	0.08	19.6	100.07
27123	53.1	14.7	1.88	2.7	3.40	3.5	1.50	0.32	<0.1	<0.02	18.4	99.50
Clinoptilolite-rich tuff												
M4-22A	63.1	12.7	0.47	0.5	0.23	5.9	1.76	0.12	<0.1	<0.02	13.5	98.28
27023	68.2	11.9	0.82	0.5	1.28	4.7	1.30	0.1	<0.1	<0.02	12.8	101.60
AMN-1	66.5	11.1	0.76	0.4	0.93	3.0	4.34	0.08	<0.1	0.02	12.2	99.33
27163	67.7	11.3	0.79	0.4	0.81	3.4	3.78	0.09	<0.1	<0.02	12.0	100.27
W7-36B	60.7	12.9	3.11	1.6	2.71	3.0	2.49	0.45	<0.1	0.03	12.5	99.49
HO-2A	66.7	10.2	1.63	2.3	2.05	0.5	2.29	0.19	<0.1	<0.02	12.8	98.66
DO-54H	62.3	11.6	4.51	0.96	1.67	3.0	2.42	0.16	<0.1	<0.02	13.2	99.82
27073	65.9	11.3	2.15	0.3	1.30	1.5	4.55	0.28	<0.1	<0.02	11.68	98.96
27053	65.4	12.5	1.33	0.90	3.07	1.0	3.32	0.11	<0.1	<0.02	12.70	100.33
27033	61.9	11.9	2.11	1.6	0.91	4.0	1.53	0.23	<0.1	0.11	14.8	98.79
V-1B	64.2	13.3	2.10	1.3	1.54	4.3	2.33	0.31	0.3	<0.02	10.0	99.68
27043	68.2	12.8	1.53	0.83	2.56	1.3	3.87	0.23	<0.1	0.02	7.92	99.26
27063	68.4	10.8	1.74	0.4	2.00	1.0	4.47	0.19	<0.1	<0.02	11.00	100.00
27083	63.4	12.2	1.33	1.7	3.37	1.4	1.12	0.13	<0.1	<0.02	15.06	99.71
TX-2	73.9	11.5	0.92	0.84	1.52	1.3	0.59	0.22	<0.1	<0.02	8.84	99.63
TP-10	67.7	13.1	1.63	0.60	1.69	3.7	2.04	0.26	0.1	<0.02	8.89	99.71
Erionite-rich tuff												
27103	57.2	13.7	2.07	0.4	0.52	5.5	3.87	0.05	<0.1	<0.02	15.5	98.81
SW-26-4B	58.9	13.5	1.46	1.3	2.81	2.1	5.20	0.16	<0.1	<0.02	13.8	99.23
DO-28B	57.4	12.8	3.42	2.2	5.40	0.8	2.78	0.36	0.1	0.06	14.8	100.12
D1-81	59.7	13.7	0.39	1.4	0.74	4.5	3.52	0.02	<0.1	<0.02	16.3	100.27
R-13B	58.1	13.4	1.53	0.82	5.46	1.1	4.10	0.25	<0.1	<0.02	14.9	99.66
E4-1B	58.3	13.0	1.68	1.0	1.24	4.1	4.04	0.14	<0.1	<0.02	16.1	99.60
27093	61.6	13.2	1.63	0.84	2.60	3.0	4.58	0.16	<0.1	0.03	11.5	99.14
Mordenite-rich tuff												
M4-54B	63.9	12.6	1.84	1.2	1.97	3.6	1.92	0.29	<0.1	<0.02	12.6	99.92
27133	69.2	11.3	0.70	0.3	2.67	1.3	3.07	0.08	<0.1	0.03	11.0	99.65
R-5C	58.6	11.6	4.36	2.1	3.55	2.6	5.32	0.61	<0.1	0.08	10.0	98.82
E5-11A	61.2	8.93	2.67	6.07	2.81	2.7	2.45	0.32	0.1	0.02	11.8	99.07
27143	70.3	11.1	1.29	0.4	2.00	2.4	4.39	0.09	<0.1	<0.02	7.92	99.89
Phillipsite-rich tuff												
T4-76A	59.5	14.4	1.04	0.79	0.26	3.0	7.77	0.07	<0.1	<0.02	13.6	100.43
T4-85A	52.7	13.2	1.58	1.3	0.03	7.0	4.64	0.11	<0.1	<0.02	15.2	95.76
W8-63A	58.6	14.1	2.96	1.3	1.29	3.9	4.42	0.43	<0.1	0.1	11.0	98.10
R-4B	55.9	13.6	4.94	1.8	1.56	3.6	5.29	0.99	0.1	0.05	11.2	99.03
27153	54.8	15.6	1.83	0.4	0.64	7.9	2.75	0.16	<0.1	<0.02	16.0	100.08

are characterized by a relatively low CaO content. The mordenite-rich tuffs show a variety of cation types.

MINOR- AND TRACE-ELEMENT CHEMISTRY

The minor- and trace-element chemistry of the zeolitic tuffs was determined by visual, 6-step, semiquantitative, emission spectroscopy in the laboratories of the U.S. Geological Survey in Denver. Results of the analyses are given in table 4 in parts per million (ppm). Of the minor and trace elements, only Ba, Cu, Ga, Nb, Pb, Sr, V, Y, Yb, and Zr were detected in most samples. Ba, Sr, and Zr are generally the most abundant elements detected. The Zr is probably in zircon impurities, but the Ba and Sr are probably in the zeolites. Phillipsite-rich tuffs seem to have a consistently high content of Ba. Except for sample No. 27153 which contains only 150 ppm Ba, the phillipsite-rich tuffs have at least 1,500 ppm Ba. One phillipsite-rich tuff, sample No. W8-63A, contains as much as 10,000 ppm Ba. Sample No. D1-81, an erionite-rich tuff, is remarkably low in minor and trace elements, including Ba and Sr. This sample contains only 30 ppm Ba and 30 ppm Sr.

ADSORPTION CAPACITY FOR CARBON DIOXIDE AND OXYGEN

The unique adsorption properties of the zeolites are a consequence of their crystal structure and chemistry. Once water is removed from the large central cavities and entry channels of the zeolite, molecules of gases having effective cross-sectional diameters small enough to pass through the entry channels are readily adsorbed in the central cavities and channels. The adsorbate gas is dispersed through the internal voids of the zeolite without displacing any of the atoms that comprise the permanent crystal structure. The adsorption is affected by temperature, pressure, nature of the adsorbate gas, conditions of dehydration and desorption, and particle size and chemistry of the zeolite.

The adsorption-capacity data for CO_2 and O_2 for the zeolitic tuffs were supplied by Minerals Research, Clarkson, N.Y.[1]. Prior to measuring the adsorption capacity, the zeolitic tuffs were activated to remove the water from the intracrystalline voids and channels of the zeolites. All samples were activated by heating at 450°C and 1 millitorr for 16 hours. The CO_2-adsorption capacity was then measured at 25°C and 250 torr, and the O_2-adsorption capacity was measured at -183°C and 100 torr. These data are reported in table 5.

The adsorption capacities of the zeolitic tuffs that contain at least 80 percent of the stated zeolite have the following approximate ranges for CO_2 in weight percent: analcime, <1-1; chabazite, 11-17; clinoptilolite, 7-11; erionite, 7-16; mordenite, 6-8; and phillipsite, 6-13. Adsorption capacities of the zeolitic tuffs have the following approximate ranges for O_2 in weight percent: analcime <1; chabazite, 15-22; clinoptilolite, <1-7; erionite, 8-18; mordenite, 7-10; and phillipsite, <1-2. Those factors responsible for values

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[1] Trade names in this report are for descriptive purposes only and do not constitute endorsement by the U.S. Geological Survey.
Table 4

Table 4.—*Semiquantitative spectrographic analyses of zeolitic tuffs*

Field No. (See table 1)	Parts per million															
	B	Ba	Be	Cr	Cu	Ga	La	Li	Nb	Nd	Pb	Sr	V	Y	Yb	Zr
Analcime-rich tuff																
M4-58A	300	300	1.5	L	1.5	30	70	L	15	L	30	300	15	15	1	100
SW-3-2	150	300	1.5	3	15	30	150	150	20	150	L	1,000	300	20	2	200
Chabazite-rich tuff																
W7-19B	L	500	1.5	15	15	15	50	L	15	N	15	700	50	15	1.5	150
SD-4-2	N	150	N	L	1.5	15	100	N	15	70	N	20	7	30	5	300
SD-4-16	L	150	N	1	3	15	L	N	L	N	10	50	30	30	2	200
27113	L	300	L	1.5	30	15	L	N	L	N	15	200	10	L	L	150
27123	L	200	N	7	30	15	N	200	15	N	30	700	30	10	1.5	100
Clinoptilolite-rich tuff																
M4-22A	30	7,000	1.5	L	3	15	L	N	15	N	30	3,000	30	30	N	70
27023	20	300	L	1.5	20	15	L	N	15	N	15	500	15	15	L	150
AMN-1	L	200	1.5	L	1.5	15	L	L	L	N	30	500	7	10	1.5	70
27163	L	300	L	L	3	15	L	N	10	N	20	150	7	15	1.5	70
W7-36B	20	700	L	7	15	15	L	300	10	70	15	500	300	20	3	200
HD-2A	50	500	1.5	1	3	15	100	N	20	70	30	5,000	30	30	3	200
DO-54H	L	700	L	L	20	15	L	N	15	N	15	700	150	10	1	300
27073	N	2,000	1.5	1.5	15	15	150	N	30	100	30	300	15	70	5	500
27053	L	150	7	3	7	20	L	N	30	N	30	200	15	30	2	70
27033	N	300	1.5	L	15	15	150	L	30	150	30	150	L	50	5	300
V-1B	L	1,000	L	30	5	15	70	N	15	L	20	500	30	20	3	300
27043	L	500	L	3	30	15	L	N	L	N	20	300	20	15	2	150
27063	L	500	3	2	7	15	150	N	30	150	30	200	10	70	5	300
27083	L	1,500	L	5	15	15	L	N	L	N	20	300	20	15	1.5	150
TX-2	100	100	L	L	1	15	50	N	10	L	N	300	15	30	2	70
TP-10	L	500	L	L	3	15	L	N	L	N	15	300	20	10	1	70
Erionite-rich tuff																
27103	50	150	L	1.5	15	30	150	N	20	100	30	150	15	15	L	150
SW-26-4B	70	2,000	1.5	1.5	3	15	70	150	15	L	30	3,000	30	30	3	150
DO-288	L	200	1.5	15	20	20	L	N	15	L	15	100	70	15	1.5	200
D1-81	L	30	N	L	5	20	N	N	N	N	15	30	15	L	N	70
R-13B	L	700	N	7	15	15	N	N	N	N	10	300	70	L	L	100
E4-1B	70	50	L	L	7	20	150	N	15	70	30	150	70	20	1	200
27093	200	300	2	3	7	20	150	N	30	100	30	300	10	30	3	150
Mordenite-rich tuff																
M4-54B	30	500	1.5	3	5	20	L	L	10	N	15	1,000	50	15	1.5	100
27133	L	5	3	L	7	20	L	N	30	70	10	30	7	15	1.5	70
R-5C	300	200	L	15	30	15	L	L	L	N	10	300	150	15	1.5	100
E5-11A	70	300	L	15	50	15	L	300	L	N	15	500	150	15	1.5	100
27143	L	70	1.5	1.5	10	15	50	N	15	70	30	150	7	30	3	150
Phillipsite-rich tuff																
T4-76A	70	2,000	1.5	1	7	15	N	N	15	N	10	150	10	N	N	70
T4-85A	70	1,500	1.5	1	7	20	150	N	30	150	30	150	7	30	1.5	150
W8-63A	30	10,000	1.5	30	15	15	L	200	L	N	15	1,000	70	15	2	300
R-4B	50	3,000	L	3	15	15	L	N	L	N	N	300	300	L	1.5	150
27153	20	150	L	2	30	15	N	N	L	N	30	50	50	N	N	100

Table 5.--*Adsorption and* NH_4^+-*exchange data*

[Adsorption data provided by Minerals Research, Clarkson, N.Y. and the
NH_4^+-exchange data provided by Manchester Laboratories, Inc.,
Manchester, Iowa]

Field No. (See table 1)	Adsorption capacity (In weight percent)		NH_4^+-exchange capacity (In milliequivalents NH_4^+ per gram)
	CO_2	O_2	
Analcime-rich tuff			
M4-58A	<1.0	<1.0	0.33
SW-3-2	1.1	<1.0	0.25
Chabazite-rich tuff			
W7-19B	12.9	14.8	1.38
SD-4-2	16.6	21.5	2.07
SD-4-16	17.3	22.4	1.57
27113	15.6	21.2	1.97
27123	10.8	14.7	1.72
Clinoptilolite-rich tuff			
M4-22A	8.8	1.5	1.76
27023	9.9	2.8	1.71
AMN-1	10.6	1.6	1.36
27163	10.1	1.7	1.40
W7-36B	6.7	2.0	1.22
HD-2A	9.8	6.8	1.39
DO-54H	6.8	<1.0	1.09
27073	9.6	4.0	1.34
27053	10.3	6.0	1.34
27033	7.6	1.5	1.56
V-1B	3.5	1.1	1.23
27043	4.0	3.1	0.B8
27063	6.9	3.5	1.21
27083	8.0	4.0	1.8B
TX-2	2.5	2.9	0.84
TP-10	6.4	1.4	1.14
Erionite-rich tuff			
27103	15.2	16.1	1.71
SW-26-4B	6.9	13.2	1.41
DO-28B	B.9	14.5	1.21
D1-81	14.6	18.3	1.72
R-13B	13.5	13.2	0.16
E4-1B	16.4	13.9	1.24
27093	9.4	7.7	1.24
Mordenite-rich tuff			
M4-54B	7.5	7.3	1.35
27133	7.9	9.9	1.14
R-5C	4.9	5.1	0.37
E5-11A	5.9	8.7	0.83
27143	7.8	6.9	0.91
Phillipsite-rich tuff			
T4-76A	13.0	<1.0	1.82
T4-85A	5.9	<1.0	1.88
W8-63A	5.3	<1.0	0.48
R-4B	9.2	<1.0	1.39
27153	6.3	1.9	2.05

in the lower part of these ranges include the kind and amount of impurities in the tuff and the cation population and distribution in the constituent zeolites.

CATION-EXCHANGE CAPACITY FOR AMMONIUM ION

Since the cation-exchange property of zeolites was recognized more than a century ago, this behavior of zeolites has led to numerous applications in agriculture and industry. Exchangeable cations of a zeolite are relatively loosely bound to the aluminosilicate framework and can be removed or exchanged easily by washing with an aqueous solution of another cation. The cation-exchange capacity of a zeolite is a consequence of the degree of substitution of aluminum for silicon in the framework. Generally, the greater the substitution is, the greater the number of cations necessary to maintain electrical neutrality. Other factors, however, also affect the cation-exchange behavior of zeolites, such as the nature and concentration of the cation species in solution, the temperature, and the cation population and distribution and structural characteristics of the zeolite.

The removal of ammonia, as ammonium ions, from municipal, industrial, and agricultural wastewater has become increasingly necessary. Certain natural zeolites, particularly clinoptilolite, have shown promise in the treatment of these wastewaters because of their high selectivity for ammonium ions. Clinoptilolite also has many applications or potential applications in agriculture and aquaculture based on its cation-exchange capacity for NH_4^+ (Mumpton and Fishman, 1977). Therefore, NH_4^+ was the ion chosen to characterize the cation-exchange capacity of the zeolitic tuffs.

The cation-exchange capacity for the ammonium ion for the suite of zeolitic tuffs was determined by the Manchester Laboratories, Inc., Manchester, Iowa. This laboratory used a standard procedure that employed ammonium acetate as the source of ammonium ions. The results are reported in table 5 in milliequivalents of NH_4^+ per gram.

The NH_4^+-exchange capacities of the zeolitic tuffs that contain at least 80 percent of the stated zeolite have the following approximate ranges in milliequivalents per gram: analcime, 0.25-0.33; chabazite, 1.57-2.07; clinoptilolite, 1.09-1.88; erionite, 0.16-1.72; mordenite, 0.83-1.14; and phillipsite, 1.39-2.05. Those tuffs rich in chabazite, clinoptilolite, and phillipsite seem to have relatively consistently high exchange capacities for NH_4^+. The range in capacities for tuffs rich in a particular zeolite is due, at least in part, to the kind and abundance of impurities in the tuff and to variations in the chemical composition of the constituent zeolite. No explanation is apparent, however, for the unusually low value for sample No. R-13B, an erionite-rich tuff.

The NH_4^+-exchange capacity for clinoptilolite-rich tuffs seems to be related to the potassium content of the zeolite. Figure 2 is a plot of the NH_4^+-exchange capacity versus the K_2O content of those tuffs that contain at least 80 percent clinoptilolite. Although there is much scatter, an inverse relationship is obvious, and those samples having a low K_2O content have a high NH_4^+-exchange capacity. Other investigators have also noted the low mobility of potassium in the clinoptilolite structure. Munson (1973) found that less than 6 percent of the potassium could be removed by cation exchange

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from a clinoptilolite-rich tuff from California, and Galabova (1979) removed only less than 3 percent of the potassium from a clinoptilolite-rich tuff from Bulgaria. Potassium apparently is not easily removed from clinoptilolite by cation exchange because it is strongly bonded in structural positions (Galabova, 1979). Thus, clinoptilolites having a low-potassium content seem best suited for those industrial and agricultural applications that require a high NH_4^+-exchange capacity.
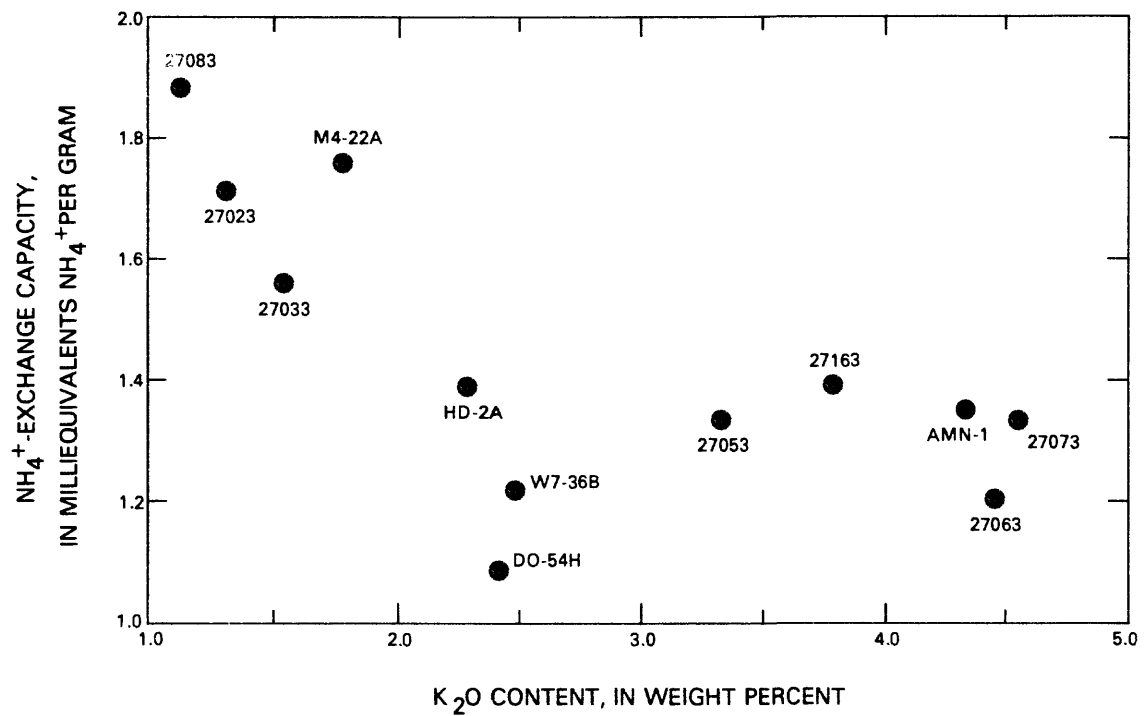
Figure 2.--Plot showing the variation in the NH_4^+-exchange capacity versus the K_2O content for clinoptilolite-rich tuffs.

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