Clinoptilolite of Possible Economic Value in Sedimentary Deposits of the Conterminous United States

GEOLOGICAL SURVEY BULLETIN 1332-B

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By RICHARD A. SHEPPARD

CONTRIBUTIONS TO ECONOMIC GEOLOGY

GEOLOGICAL SURVEY BULLETIN 1332-B

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON:1971

UNITED STATES DEPARTMENT OF THE INTERIOR

ROGERS C. B. MORTON, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

Library of Congress catalog card No. 78-610524

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 20 cents

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CLINOPTILOLITE OF POSSIBLE ECONOMIC VALUE IN SEDIMENTARY DEPOSITS OF THE CONTERMINOUS UNITED STATES

By RICHARD A. SHEPPARD

ABSTRACT

Clinoptilolite is a very common zeolite, and it has formed in sedimentary rocks of diverse lithology, age, and depositional environment. Extensive and nearly monomineralic beds of clinoptilolite are especially common in Cenozoic rocks that originally contained silicic vitric material. Clinoptilolite is potentially valuable for many industrial and agricultural processes, and it may find extensive use in the control of water pollution by the removal of ammonia from wastewater.

INTRODUCTION

This report summarizes the chemical and physical properties of the zeolite clinoptilolite and briefly discusses its occurrence in sedimentary deposits of the conterminous United States. Clinoptilolite is potentially valuable for many industrial processes, and it may find extensive use in the control of water pollution as an agent for the removal of ammonia from wastewater (Mercer, 1969).

Zeolites are among the most common authigenic silicate minerals that occur in sedimentary rocks. They have formed in rocks that are diverse in lithology, age, and depositional environment (Hay, 1966). Authigenic zeolites are especially common in Cenozoic sedimentary rocks that originally contained silicic vitric material. Nearly monomineralic beds of zeolite are known from many areas of the United States, but most zeolitic sedimentary rocks consist of two or more zeolites as well as clay minerals, silica minerals, and feldspars of authigenic origin. Zeolitic rocks also commonly contain relict vitric material and pyrogenic or detrital grains.

Clinoptilolite is probably the most abundant authigenic zeolite that occurs in sedimentary rocks. The original description of clinoptilolite was of material from amygdales in a basaltic rock from Wyoming (Pirsson, 1890; Schaller, 1932). Occurrences of this zeolite, however, have subsequently been reported chiefly from sedimentary rocks, especially those originally rich in silicic vitric material.

ACKNOWLEDGMENT

Grateful appreciation is expressed to those colleagues in the U.S. Geological Survey who contributed to this assembly of data on occurrences of clinoptilolite.

CHEMICAL AND PHYSICAL PROPERTIES

Clinoptilolite is a member of the heulandite structural group. Although there is still some disagreement on the distinction between the closely related zeolites of this group, most workers agree that clinoptilolite is the Si-rich (Hey and Bannister, 1934; Mumpton, 1960) and alkali-rich member (Mason and Sand, 1960). The compositions of clinoptilolite and heulandite from various rock types are presented in figure 1. Except for a slight overlap in the Si:Al+Fe^{+3} and Na+K:Na+K+Ca+Mg ratios, plots of the compositions form two clusters. Heulandite characteristically has a Na+K:Na+K+Ca+Mg

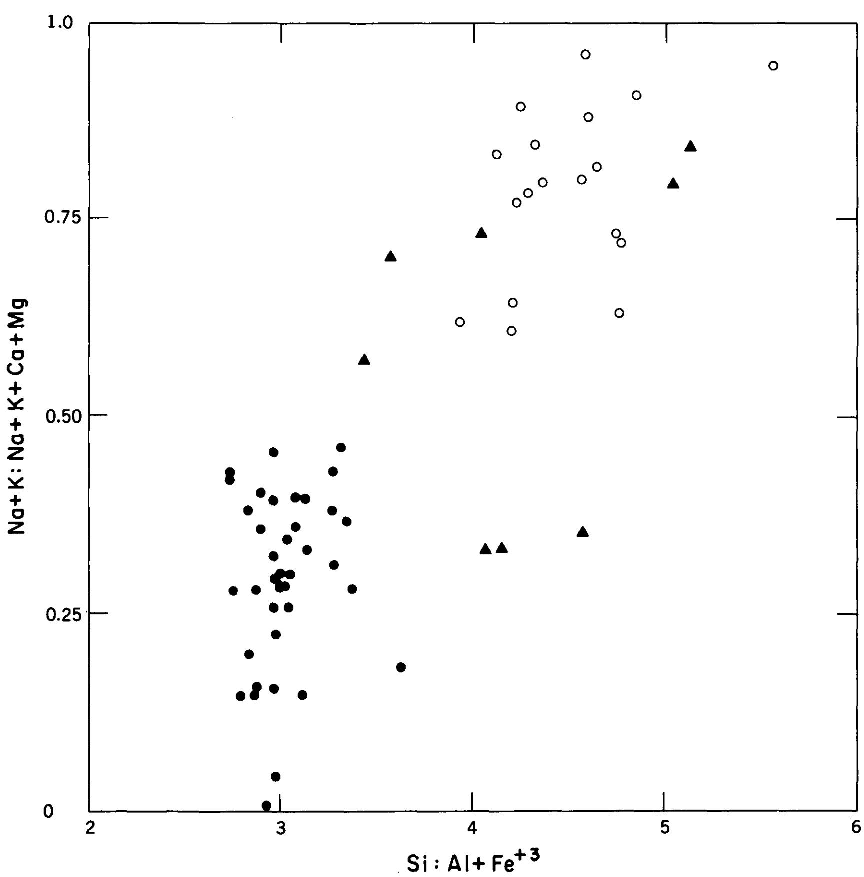

FIGURE 1.—Plot showing the compositional variation of clinoptilolite and heulandite. ○, clinoptilolite from sedimentary rocks; ▲, clinoptilolite from volcanic rocks; ●, heulandite from igneous rocks.

ratio less than 0.5 and a Si:Al+Fe^{+3} ratio near 3, whereas most clinoptilolites have a Na+K:Na+K+Ca+Mg ratio greater than 0.6 and range in Si:Al+Fe^{+3} ratio from about 4.0 to 5.0. The clinoptilolites from sedimentary rocks show a range in Si:Al+Fe^{+3} ratio of about 3.9–5.6. Sodium is the predominant cation in most clinoptilolites; however, potassic clinoptilolites are known in California (Sheppard and others, 1965) and in Japan (Minato and Takano, 1964). The few analyzed clinoptilolites that have a Na+K:Na+K+Ca+Mg ratio less than 0.6 are calcic specimens from volcanic rocks in Bulgaria (Kirov, 1965) and in Italy (Alietti, 1968).

Indices of refraction and thermal treatment have also been used to distinguish clinoptilolite from heulandite. Mason and Sand (1960) suggested that clinoptilolite can be identified by a β index of refraction of 1.485 or lower and that heulandite can be identified by a β index of 1.488 or higher. Most clinoptilolites from sedimentary rocks have a mean index of refraction of 1.471–1.483 and a low birefringence of about 0.003. Heulandite is thermally unstable above about 250°C, whereas clinoptilolite is stable to at least 750°C (Mumpton, 1960; Shepard and Starkey, 1964). However, some members of the heulandite structural group from sedimentary rocks display anomalous optical properties and exhibit anomalous thermal behavior, and these members cannot be conveniently classified as clinoptilolite or heulandite (Hay, 1963; Shepard, 1961).

Clinoptilolite occurs as platy or prismatic crystals that are 0.005–0.3 mm (millimeter) long; however, most clinoptilolite crystals are 0.01–0.02 mm long. Some of the large clinoptilolite crystals show progressive or oscillatory zoning (Sheppard and Gude, 1969b, p. 13). Because of the relatively small crystal size and the optical and physical properties that are similar to the other authigenic zeolites, X-ray powder diffraction techniques are generally used for positive identification of clinoptilolite. A typical X-ray diffractometer trace of clinoptilolite is shown in figure 2.

OCCURRENCES

Clinoptilolite is the zeolite most often reported from sedimentary deposits in recent years, and it occurs in many rock types from lacustrine, fluviatile, and marine environments (table 1, fig. 3). Although clinoptilolite is most abundant in rocks of Cenozoic age, it has been found in rocks as old as Jurassic in New Mexico (E. S. Santos, oral commun., 1970). Occurrences of clinoptilolite are especially common in the Western United States. Clinoptilolite is also a common and locally abundant constituent in Tertiary sedimentary rocks of the Coastal Plain from southeastern Texas to North Carolina and northward to western Kentucky (fig. 3).

At the localities listed in table 1 the clinoptilolite content of the rock samples ranges from less than 1 percent to nearly 100 percent.

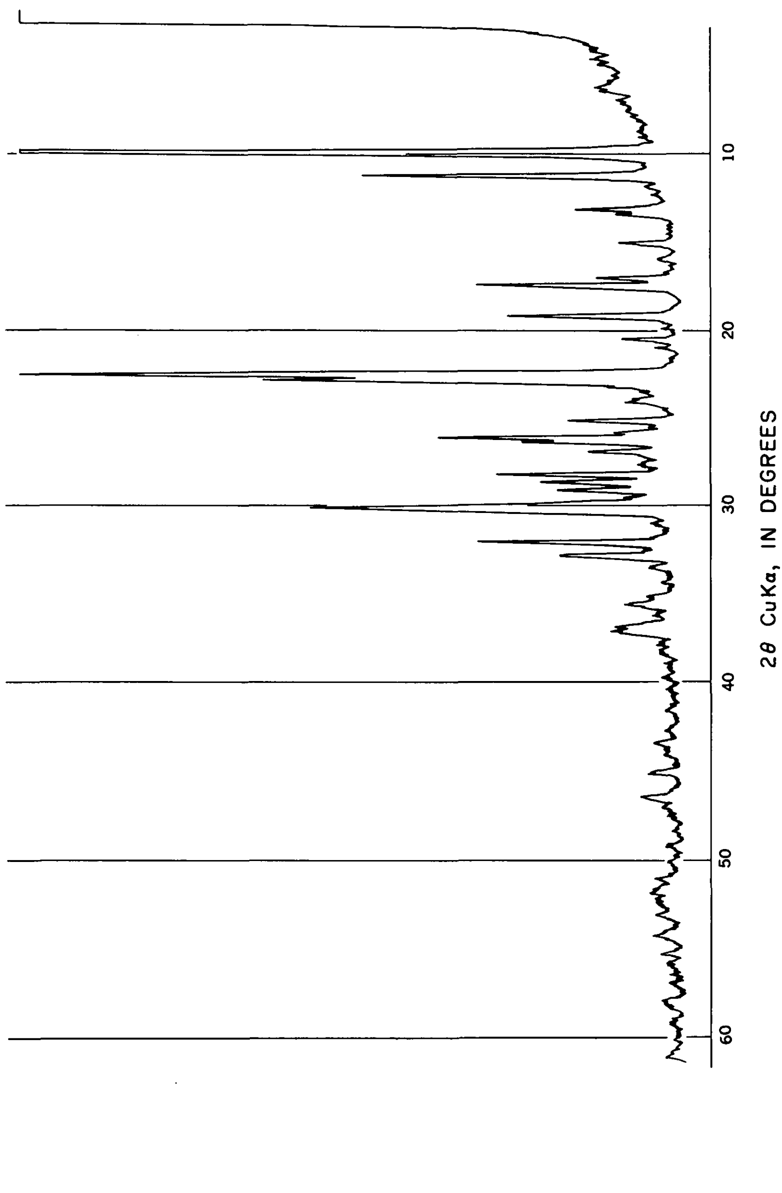

FIGURE 2.—X-ray diffractometer trace of clinoptilolite from a tuff bed in the Barstow Formation of California.

TABLE 1.—*Occurrences of clinoptilolite in sedimentary rocks of the conterminous United States*

[Locality numbers are shown in figure 3. Asterisk (*) indicates localities where beds are at least 1 foot thick and contain at least 75 percent clinoptilolite]

Locality	Occurrence	References
Montana		
1. Near Vaughn, Cascade County	Tuff and tuffaceous siltstone and sandstone in the Taft Hill, Vaughn, and Bootlegger Members of the Blackleaf Formation of Cretaceous age.	Cobban (1955, p. 110); Fox (1966, p. 13); R. E. Van Loenen (written commun., 1968).
2. Near Big Sandy, sec. 22, T. 29 N., R. 14 E., Chouteau County.	Sandstone in the Wasatch Formation of Eocene age.	J. D. Vine (oral commun., 1970).
3. Near Harlem, Blaine County	Bentonite in the Bearpaw Shale of Cretaceous age.	Berg (1969).
4. Near Turner, Blaine County	do	Do.
5. Near Livingston, Park County	Tuffaceous mudstone, siltstone, and sandstone in the Livingston Group of Cretaceous age.[1]	Roberts (1963); Sims (1969).
6. Near Joliet, Carbon County	Bentonite in the Claggett Formation of Cretaceous age.	Berg (1969).
7. Near Bridger, Carbon County	Bentonite in the Thermopolis Shale of Cretaceous age.	Do.
8. Near Acton, Yellowstone County	Bentonite in the Bearpaw Shale of Cretaceous age.	Do.
Idaho		
9. Near Preston, Franklin County*	Tuff in the Salt Lake Group of late Tertiary age.	Deffeyes (1959a).
Washington		
10. Near Renton, King County	Sandstone and conglomerate in unnamed marine formation of Oligocene age.	D. R. Mullineaux (oral commun., 1969).
Oregon		
11. Near Bearbones Mountain, Lane County.*	Tuff and lapilli tuff in the Little Butte Volcanic Series of Oligocene and Miocene age.	Moore and Peck (1962, p. 188); Peck and others (1964, p. 15, 40).
12. Near Stein's Pillar, Crook County	Tuff in the John Day Formation of Oligocene and Miocene age.	Waters (1966).
13. Near the Painted Hills, Wheeler County.*	Tuff and claystone in the lower part of the John Day Formation of Oligocene and Miocene age.	Hay (1962, 1963).
14. Near Deep Creek, Wheeler County.*	Tuff in the lower part of the John Day Formation of Oligocene and Miocene age.	Fisher (1962, 1963); Wilcox and Fisher (1966).
15. Swayze Creek, near Durkee, Baker County.	Tuff in unnamed lacustrine formation of Pliocene age.	A. J. Gude 3d (oral commun., 1970).
16. Sucker Creek, Malheur County*	Tuff and tuffaceous sandstone in the Sucker Creek Formation of Miocene age.	Kittleman and others (1965).
17. Near Sheaville, Malheur County*	Tuff probably equivalent to part of the Sucker Creek Formation of Miocene age.	Sheppard and Walker (1969).
18. Near Rome, Malheur County	Tuff and tuffaceous sandstone in unnamed lacustrine formation of Pliocene age.	Regis and Sand (1966); Studer (1967); Sheppard and Gude (1969a).
19. East face of Steens Mountain, Harney County.	Tuff in the Pike Creek Formation of Oligocene(?) and Miocene age.	Walker and Repenning (1965).
20. Near Harney Lake, Harney County.*	Tuff and tuffaceous sedimentary rocks in the Danforth Formation of Pliocene age.	Walker and Swanson (1968a).
21. West face of Hart Mountain, Lake County.*	Tuff and tuffaceous sedimentary rocks of late Oligocene or early Miocene age.	Walker and Swanson (1968b).

[1] Zeolite identified as heulandite.

TABLE 1.—*Occurrences of clinoptilolite in sedimentary rocks of the conterminous United States*—Continued

Locality	Occurrence	References
	Wyoming	
22. Near Pedro, Weston County*	Bentonite in the Sharon Springs Member of the Pierre Shale of Cretaceous age.	Bramlette and Posnjak (1933); J. R. Gill (oral commun., 1970).
23. Southeast flank of North Butte, Campbell County.	Sandstone in the Wasatch Formation of Eocene age.	J. D. Vine (oral commun., 1970).
24. Near Lysite Mountain, Hot Springs County.*	Tuff in the Tepee Trail Formation of Eocene age.	J. D. Love (written commun., 1964).
25. Snake River Canyon, Lincoln County.	Shale in the Aspen Formation of Cretaceous age.[1]	Heinrich (1963).
26. Near Cameron Spring on Beaver Rim, Fremont County.	Tuffaceous sandstone in the White River Formation of Oligocene age.	Van Houten (1964, p. 65).
27. Beaver Rim, Fremont County*	Tuff in the Wagon Bed Formation of Eocene age.	Van Houten (1964); Boles (1968).
28. Near Split Rock, Natrona County.*	Tuff in the Moonstone Formation of Pliocene age.	Love (1970).
29. Near Green River, Sweetwater County.	Tuff in the Tipton Shale Member of the Green River Formation of Eocene age.	Goodwin and Surdam (1967).
30. Near Twin Buttes, Sweetwater County.*	Tuff and tuffaceous sandstone in the Bridger Formation of Eocene age.	R. A. Sheppard (unpub. data).
	South Dakota	
31. Near Chamberlain, Buffalo County.	Bentonite in the Sharon Springs Member of the Pierre Shale of Cretaceous age.	Schultz (1963).
32. Sheep Mountain Table, Shannon County.*	Tuff in the Arikaree Formation of Miocene age.	Schultz (1961).
	Colorado	
33. Near Vermillion Cliffs, sec. 30, T. 10 N., R. 98 W., Moffat County.*	Tuff in the Bridger Formation of Eocene age.	A. J. Gude 3d (oral commun., 1966).
34. Near Como, sec. 11, T. 8 S., R. 76 W., Park County.	Tuff and tuffaceous sandstone in the Denver Formation of Late Cretaceous and Paleocene age.	D. G. Wyant (oral commun., 1970).
35. Near Creede, Mineral County*	Tuff in the Windy Gulch Member of the Bachelor Mountain Rhyolite of Oligocene age.	Ratté and Steven (1967, p. H7).
	Utah	
36. Near Mountain Green, sec. 24, T. 5 N., R. 1 E., Morgan County.*	Tuff in the Salt Lake Formation of Tertiary age.	R. A. Sheppard (unpub. data).
37. Eastern flank of Topaz Mountain, sec. 5, T. 13 S., R. 11 W., Juab County.*	Tuff in unnamed formation of Pliocene(?) age.	D. A. Lindsey (oral commun., 1970).
38. Gunnison Plateau, sec. 12, T. 16 S., R. 1 E., Juab County.	Sandstone in the Colton Formation of Eocene age.	J. D. Vine (oral commun., 1970).
39. Northern part of the Markagunt Plateau, Iron County.	Tuffaceous sandstone of Oligocene and Miocene(?) age.	Anderson (1969).
	Nevada	
40. Near Elko, Elko County	Oil shale in unnamed formation of Oligocene age.	Deffeyes (1959a).
41. Near Carlin, Eureka County*	Tuff in the Safford Canyon Formation of Oligocene(?) or Miocene(?) age and the Carlin Formation of Pliocene age.	Deffeyes (1959a); Regnier (1960).
42. West flank of the Shoshone Range, Lander County.	Tuff in unnamed lacustrine formation of Pliocene age.	Deffeyes (1959b).
43. Reese River, Lander County	do	Do.
44. Jersey Valley, Pershing County*	do	Do.

[1] Zeolite identified as heulandite.

TABLE 1.—*Occurrences of clinoptilolite in sedimentary rocks of the conterminous United States*—Continued

Locality	Occurrence	References
	Nevada—Continued	
45. Near Lovelock, sec. 20, T. 28 N., R. 30 E., Pershing County.*	Tuff in unnamed lacustrine formation of late Tertiary age.	R. A. Sheppard (unpub. data).
46. Near Eastgate, sec. 28, T. 17 N., R. 36 E., Churchill County.*	do	Do.
47. Teels Marsh, Mineral County	Tuff in lacustrine deposit of Quaternary age.	Hay (1964, 1966); Cook and Hay (1965).
48. Near Silver Peak, Esmeralda County.*	Tuff in the Esmeralda Formation of Miocene and Pliocene age.	Moiola (1964a, 1964b); Robinson (1966).
49. Near Goldfield, Esmeralda County.	Tuffaceous sandstone in the Siebert Formation of Tertiary age.	R. J. Moiola (written commun., 1964).
50. Nevada Test Site, Nye County*	Tuff and lapilli tuff of Tertiary age.	Gibbons and others (1960); Hoover (1966, 1968); Hoover and Shepard (1965).
51. Near Bullfrog Hills, Nye County	Tuff of Tertiary age	Cornwall (1962).
	California	
52. Death Valley, sec. 2, T. 26 N., R. 2 E., Inyo County.*	Tuff in the Furnace Creek Formation of Pliocene age.	J. F. McAllister (written commun., 1965).
53. Lake Tecopa, Inyo County*	Tuff in lacustrine deposit of Pleistocene age.	Sheppard and Gude (1968).
54. Owens Lake, Inyo County	Tuff and tuffaceous sediments of Pleistocene age.	Hay (1964, 1966).
55. Mojave Desert, eastern Kern County and San Bernardino County.*	Tuff and tuffaceous rocks in numerous formations of late Tertiary and Quaternary age.	Kerr and Cameron (1936); Ames and others (1958); Sheppard and Gude (1964, 1965, 1969b).
56. Near Branciforte Creek, Santa Cruz County.	Tuffaceous sandstone in the Santa Margarita Formation of Miocene age.	Gilbert and McAndrews (1948).
57. Near Nipomo, San Luis Obispo County.*	Tuff in the Obispo Formation of Miocene age.	Bramlette and Posnjak (1933); Surdam and Hall (1968).
58. Near Oakview, Ventura County	Bentonite in the Modelo Formation of Miocene age.[1]	Kerr (1931).
59. Near San Pedro, Los Angeles County.	Dolomitic sandstone in the Monterey Formation of Miocene age.	Spotts and Silverman (1966).
	Arizona	
60. Near Wikieup, Mohave County*	Tuff in unnamed lacustrine formation of Pliocene age.	Sheppard (1969).
61. Near Dome, Yuma County*	Bentonite and tuff in unnamed lacustrine formation of late Tertiary age.	Bramlette and Posnjak (1933).
62. Near Horseshoe Reservoir, sec. 3, T. 7 N., R. 6 E., Maricopa County.*	Tuff in the Verde Formation of Pliocene(?) or Pleistocene age.	R. A. Sheppard (unpub. data).
63. Near Nutrioso, Apache County	Tuff and sandstone in unnamed formation of Tertiary age.	Wrucke (1961).
64. Near Morenci, Greenlee County	Tuff and lapilli tuff in unnamed formation of Tertiary age.	Sheppard (1969).
65. Along San Simon Creek, Cochise and Graham Counties.*	Tuff in unnamed lacustrine formation of late Cenozoic age.	Sand and Regis (1966); Regis and Sand (1967).
	New Mexico	
66. Near Bayard, Grant County*	Tuff in the Sugarlump Tuff of Oligocene age.	Jones and others (1967, p. 104).
67. Near Cuba, sec. 25, T. 20 N., R. 1 W., Sandoval County.	Tuff and tuffaceous sandstone in the Brushy Basin Member of the Morrison Formation of Jurassic age.	E. S. Santos (oral commun., 1970).

[1] Zeolite identified as heulandite.

TABLE 1.—*Occurrences of clinoptilolite in sedimentary rocks of the conterminous United States*—Continued

Locality	Occurrence	References
	Texas	
68. Near Coy City, Karnes County	Tuff and tuffaceous sandstone in the Jackson Group of Eocene age.	Weeks and others (1958); Weeks and Eargle (1963).
69. Near Tilden, McMullen County*	Tuff in Jackson Group of Eocene age and the Gueydan Formation of Oligocene or Miocene age.	Eargle (1968, p. D24); McBride and others (1968).
	Mississippi	
70. Near Meridian, Lauderdale County.	Tuffaceous sandstone in the Meridian Sand of Eocene age.	Wermund and Moiola (1966).
	Alabama	
71. Near Nettleboro, Clarke County	Tuffaceous sandstone in the Meridian Sand of Eocene age.	Wermund and Moiola (1966).
72. Near McKenzie, Butler County*	Tuff and tuffaceous claystone in the Tallahatta Formation of Eocene age.	Reynolds (1966).
	Kentucky	
73. Near Paducah, McCracken County.	Claystone in the Clayton(?) Formation of Paleocene age and clay in the Porters Creek Clay of Paleocene age.	Sohn and others (1961); Finch (1966).
	Tennessee	
74. Near Jackson, Madison County	Fossiliferous rock of Paleocene age.[1]	Switzer and Boucot (1955).
	Florida	
75. Near Caryville, Washington County.	Suwanee Limestone of Oligocene age.[1]	Switzer and Boucot (1955).
	South Carolina	
76. Near Coosawhatchie, Jasper County.	Clay in the Hawthorn Formation of Miocene age and the Santee Limestone of Eocene age.	Heron and Johnson (1966).
77. Central South Carolina	Mudstone in the Black Mingo Formation of Paleocene and Eocene age.	Heron (1969).
	North Carolina	
78. Near Eward, Beaufort County	Phosphorite in the Pungo River Formation of Miocene age.	Rooney and Kerr (1964); Cathcart (1968).

[1] Zeolite identified as heulandite.

Localities where beds are at least 1 foot thick and consist of at least 75 percent clinoptilolite (table 1) are marked by an asterisk. Some beds that have a relatively low content of clinoptilolite probably originally contained a high content of crystal and rock fragments. Other clinoptilolite-poor beds contain much relict vitric material or authigenic clay minerals and opal. Tuff beds rich in clinoptilolite are commonly white to pale gray, are very well indurated, and are low in porosity, and they generally break with a blocky to conchoidal fracture.

ECONOMIC CONSIDERATIONS

Clinoptilolite is used on a very limited scale in the United States in the extraction of radioactive cesium from atomic-energy waste effluent (Brown, 1962). The ion exchange and molecular sieve properties of clinoptilolite coupled with a seemingly low cost of mining suggest a much wider and more varied application in future years. Barrer and Makki (1964) showed that a wide range of sorbents could be produced from clinoptilolite by acid treatment. Thus, the potential uses of clinoptilolite are considerably increased by chemical and structural modifications of the natural material.

Clinoptilolite is currently mined and used for a variety of industrial and agricultural processes in Japan. Minato and Utada (1969) described the following uses: desiccant for gases, separator of oxygen from air, adsorbent for obnoxious odors in farm yards, filler and whitening agent for paper, and a soil conditioner to increase the effectiveness of chemical fertilizers. More clinoptilolite is mined in Japan for the last use than for any of the other uses listed.

Laboratory and pilot-plant studies by Pacific Northwest Laboratory, Battelle Memorial Institute, Richland, Wash. (Mercer, 1969; Mercer and others, 1970), indicate that clinoptilolite is effective in the removal of ammonia from wastewater. Clinoptilolite used in these studies was obtained from Hector, Calif. (Ames and others, 1958). Recent legislation in some States and cities has made the removal of ammonia a necessary step in the treatment of wastewater in many parts of the United States. Although more research is needed on the durability, reliability of different sources, and methods of regeneration (Holcomb, 1970), large quantities of this zeolite would be required for wastewater treatment. Mercer (1969, p. 210) estimated on the basis of a pilot-plant study that 480,000 cubic feet of clinoptilolite would be required to treat the wastewater presently discharged from Detroit, Mich.

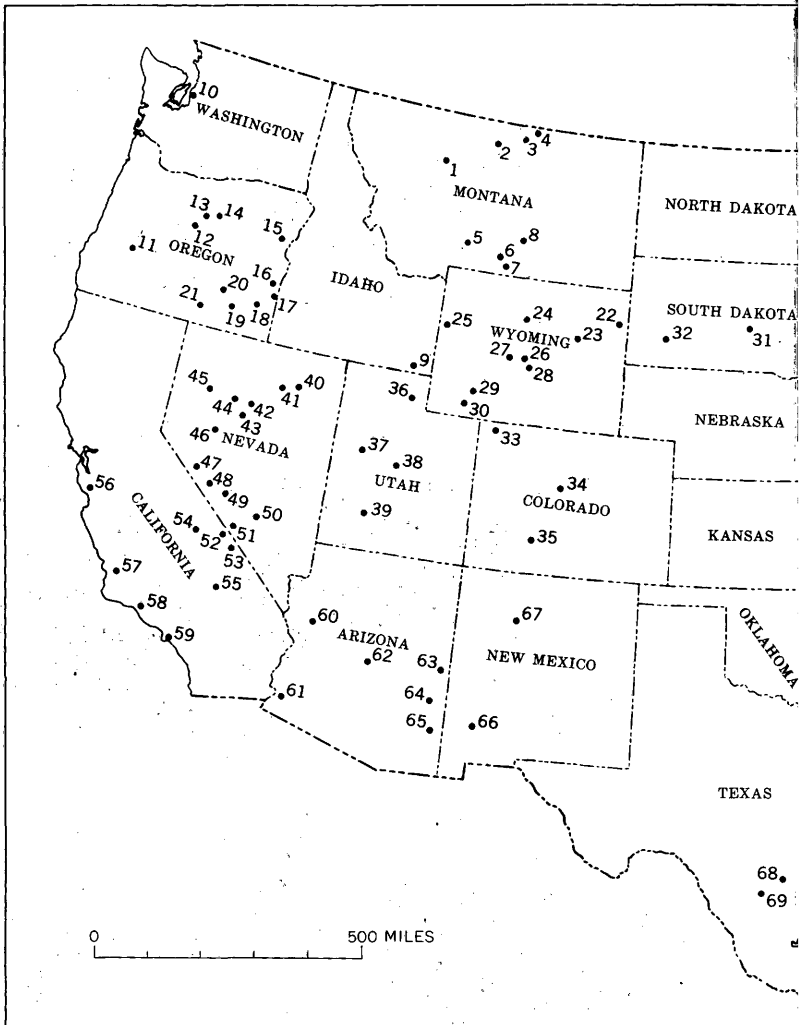

FIGURE 3.—Map showing occurrences of clinoptilolite in sedimentary rocks of the

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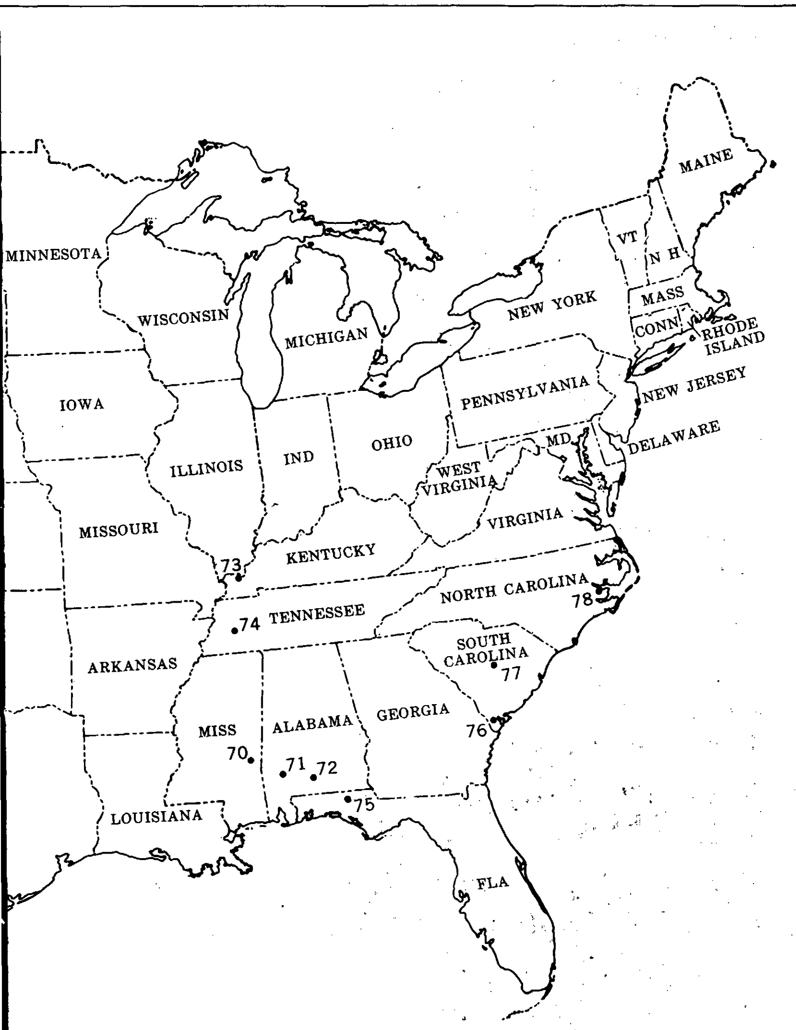

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☆ GPO : 1971 O - 417-587

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