
Zeolites

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Zeolites are crystalline, hydrated aluminosilicates that contain alkali and alkaline-earth metals. Their crystal framework is based on a three-dimensional network of SiO_4 tetrahedra with all four oxygens shared by adjacent tetrahedra. The alkali and alkaline earth cations are loosely bound within this structure and can be exchanged by other cations or molecular water. Most zeolites can be dehydrated and rehydrated without any change in volume. More than 48 natural zeolite minerals have been identified (Tschernich 1992), and more than 100 zeolites have been synthesized. Zeolites have unique physical and chemical properties that are utilized in many important commercial applications.

Though zeolites were first identified more than 200 years ago, it was not until the middle of the twentieth century that their widespread occurrence in sedimentary rocks and economic potential were recognized. Since then, thousands of articles have been published in the technical literature. In the past 40 years, the zeolite mineral group has changed from a museum curiosity to an established industrial mineral commodity.

According to Breck (1974), the important physical and chemical properties of zeolites are

- High degree of hydration
- Low density and large void volume when dehydrated
- Stability of the crystal structure of many zeolites when dehydrated
- Cation exchange properties
- Uniform molecular-sized channels in the dehydrated crystals
- Ability to adsorb gases and vapors
- Catalytic properties

Molecular sieves are materials that can selectively adsorb molecules on the basis of their size, shape, or electrical charge (Clifton 1987). Commercial applications of zeolites are based on the following properties: molecular sieving, ion exchange, adsorption, and catalysis. Most zeolites are molecular sieves, but not all molecular sieves are zeolites. Activated carbon, activated clays, aluminum oxide, and silica gels are also molecular sieves. Activated synthetic and natural zeolite molecular sieve products, however, have displaced many of these substances because of their selectivity.

Potential commercial utilization of zeolites includes hundreds of possible applications. The principal uses at this time are

- Ammonium-ion removal from sewage and industrial effluents, aquariums, and commercial fish farms

- Odor control in animal absorbents, floor and carpet cleaning products, and industrial floor absorbents
- Removal of heavy metal ions from nuclear, mine, and industrial effluents
- Agricultural applications as soil conditioners and animal feed supplements
- Desiccants used to adsorb water vapor in sealed containers and packaging
- Carriers for bacteria and enzymes
- Gas separation
- Catalysis

About 3.5 Mt of natural zeolites were produced and consumed worldwide in 2003. Construction and agricultural applications consumed most of the production, especially in developing countries. Consequently, the total production obscures the significant increases in industrial and commercial applications. The estimated production in North America in 2003 was 42 kt. Most of this was consumed in odor mitigation, aquaculture, agriculture, carriers, desiccants, radioactive barriers, effluent treatment, and other ion-exchange applications. Seven companies in the United States and two in Canada produced the zeolite mineral clinoptilolite. Two companies produced the zeolite mineral chabazite from the Bowie, Arizona, deposit (Eyde 2003).

HISTORY

In 1756, Baron A.F. Cronstedt, a Swedish mineralogist, identified zeolites as a new group of minerals. He named the minerals zeolites from the Greek words *zein* and *lithos*, meaning "boiling stones," because of the bubbling and frothing achieved by heating the minerals with a blowpipe. There was no real interest in zeolites until the crystal structure of chabazite was determined, followed by the discovery that chabazite selectively adsorbs smaller organic molecules and rejects larger ones, a property described as *molecular sieving*. Following these discoveries, research on the zeolite minerals began in the laboratory of the Linde Company, a division of Union Carbide Corporation, a producer of industrial gases. Initially the researchers at Linde recognized that molecular sieving could be used to separate gases and that this could be used in their air products business. Later they discovered that zeolites could also separate the components of gasoline.

Although the synthesis of zeolites was reported as early as 1862, Barrer (1938) first successfully synthesized analcime-type

zeolites and confirmed them by x-ray diffraction (XRD). He was unable to synthesize either chabazite or mordenite, but instead produced a synthetic zeolite now designated as Linde type A, which is still one of the most commercially important synthetic molecular-sieve adsorbents. The Molecular Sieve Department of the Linde Company commercialized the technology to manufacture Linde type A as well as other synthetic zeolites.

Historically, natural zeolites were considered mineralogical curiosities that mostly occurred as amygdules in basaltic volcanic flows. Subsequently, Regnier (1960) and others discovered large sedimentary deposits of natural zeolites in the western United States. Later exploration identified other, very large zeolite deposits, particularly of clinoptilolite, in the western states and in more than 40 other countries in sedimentary, volcanoclastic rocks and also in hydrothermal deposits.

Synthetic zeolites have supplied many of the markets that natural zeolite products might have served because the synthetics were available first. Natural zeolite producers attempted to displace synthetic zeolites from uses and applications where natural zeolites would have been a better choice, but they lacked the product development and marketing skills needed to compete with the synthetic producers.

In 2003, worldwide production of synthetic zeolites for all applications was more than 2.2 Mt. Synthetic zeolites can be chemically tailored to meet stringent industrial specifications, whereas natural zeolites have a more fixed range of properties. This is changing with the recent introduction of heat-treated and surface-modified natural products. In many applications, natural zeolites have a significant price advantage over synthetics. Also, in some uses their performance is superior to synthetics, such as the use of chabazite from the Bowie deposit as an adsorbent in the treatment of acidic gases.

Mumpton (1983) described Linde's natural zeolite exploration in North America from 1957 through 1962. Shell Canadian began exploration for natural zeolites that could be used as petroleum catalysts in 1962. Mobil Oil Corporation also had a natural zeolite program and mined erionite from the Jersey Valley, Nevada, deposit. Efforts to develop extensive natural zeolite reserves and new products in North America led Anaconda Minerals Company and Occidental Minerals Corporation into major exploration and product development programs between 1974 and 1983. Tenneco Corporation and Phelps Dodge Corporation were late entrants to the zeolite business. None of these companies, however, generated significant sales, and they left the zeolite business.

Neither the oil nor mining companies understood that millions of tons of reserves were not needed to supply a small but growing industrial business whose sales were less than 5,000 tpy. Their lack of marketing expertise was the major cause of their failure. Dow Chemical Corporation, which acquired the molecular sieve business from UOP (the successor company to Union Carbide Corporation), is now the only major corporation in the natural zeolite business. The products sold by Dow are specialty, high-value-added materials that complement their synthetic molecular sieve product lines. The other producers are small entrepreneurial companies that, to their credit, are rapidly developing the products, applications, and marketing skills needed to sell their zeolite products. The natural zeolite business is an industry in transition.

For more than 40 years, natural zeolite minerals have been described as the industrial mineral of the future. The belief that natural zeolites had a multitude of uses and applications was fostered by an enormous outpouring of research that envisioned zeolites for applications in uses from animal absorbents to zeoionics. The potential applications were oversold. Unfortunately, very little of the

research managed to cross over into product development and then into salable products. The brevity of this chapter is intended to provide more easily accessible, useful information and a more concise bibliography, but readers may wish to consult the Zeolites chapters in the 5th and 6th editions of *Industrial Minerals and Rocks* for more detailed information.

GEOLOGY

Mineralogy

The following discussion on mineralogy, chemical properties, and physical properties reviews the works of Breck (1974), Flanigen (1977), and Mumpton (1978), leaders in the study of these complex silicate minerals. Zeolites occur in a variety of geologic settings, mostly as alteration or authigenic minerals, low temperature-low pressure minerals in metamorphic systems, secondary minerals in weathered zones, or in veins. Commercial zeolite production is currently limited to authigenic and alteration accumulations in finely crystalline sedimentary rocks. Nine zeolites commonly occur in sedimentary rocks: analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. Analcime and clinoptilolite are by far the most abundant. All nine of these show a considerable range in silicon:aluminum (Si:Al) ratios and cation contents. Except for heulandite and laumontite, they generally are alkalic and more siliceous than their counterparts in mafic igneous rocks.

Chabazite, clinoptilolite, erionite, mordenite, and phillipsite are the only zeolite minerals with commercial applications today. Erionite, which has been classified as a human carcinogen, has only limited industrial applications. These five are the only zeolites that are abundant in nature and have adequate ion-exchange, absorbency, or molecular-sieving capabilities. Ferrierite and faujasite may also have economic potential, but they are rare and known to occur at only a few localities in the world. It is possible that new technology may result in applications for other zeolite minerals.

Table 1 lists the chemical composition and selected properties of some possible economic zeolites as adapted from Mumpton (1978) and based on the Breck (1974) classification.

Breck (1974) originally listed 34 natural zeolite minerals. An additional 18 natural zeolite minerals have now been identified. The potential commercial application of both natural and synthetic zeolites is a result of their fundamental chemical and physical properties.

The basic structure of zeolites consists of $(\text{AlSi})\text{O}_4$ tetrahedra, wherein each oxygen is shared by two tetrahedra; thus, the atomic ratio $\text{O}:(\text{Si}+\text{Al})$ is 2. The net negative charge of the structure is balanced by exchangeable cations, which are loosely held within the central cavities and surrounded by water molecules. Although their chemical compositions are similar, each mineral has a unique crystal structure and thereby its own physical and chemical characteristics.

Table 2 shows a classification of natural and synthetic zeolites proposed by Breck (1974). Breck's classification is based on the crystal structure of the zeolites in seven groups. In each group, the zeolites have a common specific array of $(\text{AlSi})\text{O}_4$ tetrahedra. Although the same zeolite mineral from different localities may vary considerably in chemical composition, its crystal structure will be nearly identical. Conversely, zeolite minerals with very different crystal structures can have nearly identical chemical compositions.

The dimensions and orientation of void spaces and the interconnected channels in dehydrated zeolites are important in determining the physical and chemical properties. The three types of channel systems identified are a one-dimensional system, a two-dimensional system, and two varieties of three-dimensional, intersecting systems.

Table 1. Typical formulae and physical properties of zeolite minerals and their synthetic counterparts

Zeolite	Typical Unit-Cell Formula	Crystal System	Void Volume, %	Specific Gravity	Channel Dimensions, Å	Thermal Stability	Ion-Exchange Capacity, meq/g*
Analcime	$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}$	Cubic	18	2.24–2.29	2.6	High	4.54
Chabazite	$(\text{Na}_2\text{Ca})_6(\text{Al}_{12}\text{Si}_{24}\text{O}_{72}) \cdot 40\text{H}_2\text{O}$	Hexagonal	47	2.05–2.10	3.7 × 4.2	High	3.81
Clinoptilolite	$(\text{Na}_4\text{K}_4)(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	Monoclinic	39	2.16	3.9 × 5.4	High	2.54
Erionite	$(\text{Na}_7\text{Ca}_6\text{K})_9(\text{Al}_9\text{Si}_{27}\text{O}_{27}) \cdot 27\text{H}_2\text{O}$	Hexagonal	35	2.02–2.08	3.6 × 5.2	High	3.12
Ferrierite	$(\text{Na}_2\text{Mg}_2)(\text{Al}_6\text{Si}_{30}\text{O}_{70}) \cdot 8\text{H}_2\text{O}$	Orthorhombic	0	2.14–2.21	4.3 × 5.5 3.4 × 4.8	High	2.33
Heulandite	$\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$	Monoclinic	39	2.10–2.20	4.0 × 5.5 4.4 × 7.2 4.1 × 4.7	Low	2.91
Laumontite	$\text{Ca}_4(\text{Al}_8\text{Si}_{16}\text{O}_{48}) \cdot 16\text{H}_2\text{O}$	Monoclinic	34	2.20–2.30	4.6 × 6.3	Low	4.25
Mordenite	$\text{Na}_8(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	Orthorhombic	28	2.12–2.15	2.9 × 5.7	High	2.29
Phillipsite	$(\text{Na}_2\text{K})_{10}(\text{Al}_{10}\text{Si}_{22}\text{O}_{62}) \cdot 20\text{H}_2\text{O}$	Orthorhombic	31	2.15–2.20	4.2 × 4.4 2.8 × 4.8 3.3	Low	3.87
Linde A†	$\text{Na}_{12}(\text{Al}_{12}\text{Si}_{11}\text{O}_{48}) \cdot 27\text{H}_2\text{O}$	Cubic	47	1.99	4.2	High	5.48
Linde X†	$\text{Na}_{66}(\text{Al}_{66}\text{Si}_{106}\text{O}_{364}) \cdot 264\text{H}_2\text{O}$	Cubic	50	1.93	7.4	High	4.73

* Calculated from unit-cell formula.

† Linde A and Linde X are synthetic phases.

The character of the water in hydrated zeolite crystals varies, because it can include molecular clustering or direct bonding between the cations and the framework oxygen molecules. The intercrystalline volume that may be occupied by water constitutes up to 50% of the volume of the crystal. The adsorption capacity of a zeolite is generally related to the free space or pore volume as determined by the quantity of contained water when fully hydrated at a standard temperature and humidity.

Adsorption and ion-exchange capacities in both hydrated and dehydrated zeolites are related to the characteristics of the channel openings. The apertures are bounded by oxygen atoms of the connected tetrahedra. The limiting size of the aperture is governed by the size of the rings, which contain 6, 8, 10, or 12 oxygen atoms.

Gottardi and Galli (1985), as a result of their study of zeolite mineralogy, proposed a classification with 23 types of zeolite framework, each corresponding to a particular species of zeolite, and a more specific classification of five framework groups for the natural zeolites.

Figure 1 illustrates the open structure of chabazite showing the enclosed channels.

Chemical Properties

The applications that use natural zeolites make use of one or more of their chemical properties, which include adsorption, cation exchange, and dehydration or rehydration. These properties are functions of the specific crystal structure of each mineral, its framework, and its cationic composition.

Adsorption Properties

Crystalline zeolites are unique adsorbent materials. The large central cavity and entry channels of the zeolite are filled with water molecules that form hydration spheres around the exchangeable cations. If the water is removed, molecules having cross-sectional diameters small enough for them to pass through the entry channels are readily adsorbed in the channels and central cavities. Molecules too large to pass through the entry channels are excluded, which results in the molecular sieving property of most zeolites.

Table 2. Breck's classification of zeolites*

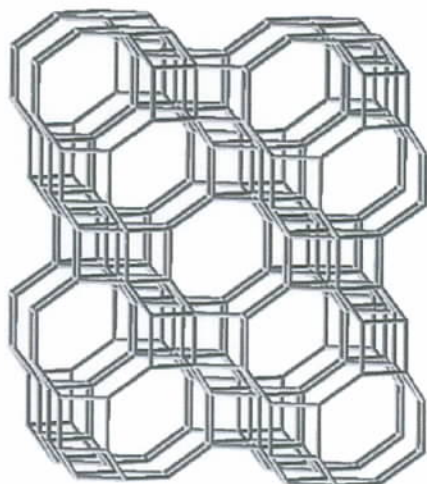
Group 1 (S4R)	Group 5 (T5O10)
Analcime	Natrolite
Harmotome	Scolecite
Phillipsite	Mesolite
Gismondine	Thomsonite
Paulingite	Gonnardite
Laumontite	Edingtonite
Yugawaralite	Group 6 (T8O16)
Group 2 (S6R)	Mordenite
Erionite	Dachiardite
Offretite	Ferrierite
Levynite	Epistibite
Sodalite	Bikitaite
Group 3 (D4R)	Group 7 (T10O20)
A-Type Zeolites	Heulandite
Group 4 (D6R)	Clinoptilolite
Faujasite	Stilbite
X	Brewsterite
Y	
Chabazite	
Gmelinite	

Adapted from Breck 1974.

* Expressions in parentheses refer to types of zeolite frameworks (e.g., D4R = double 4-ring, T5O10 = a unit of 5 tetrahedra).

Cation Exchange Properties

The exchangeable cations of a zeolite are loosely bonded to the tetrahedral framework and can be easily exchanged and removed by washing with a strong solution of another cation. Crystalline zeolites are very effective ion exchangers. The ion-exchange capacity is basically a function of the degree of substitution of aluminum for silicon in the framework structure. The greater the substitution, the



Adapted from *International Zeolite Association Atlas 2004*.

Figure 1. Open molecular structure of the zeolite mineral chabazite viewed along [010]

greater the charge deficiency, and the greater the number of alkali or alkaline earth cations required for electrical neutrality. Cation-exchange behavior also depends on other factors, including (1) the concentration of the specific cation in the solution, (2) the temperature, (3) the nature of the cation species (e.g., size, charge), and (4) the structural characteristics of the particular zeolite.

Cations can be trapped in structural positions that are relatively inaccessible, thereby reducing the effective ion-exchange capacity. Cation sieving may also take place if the cation in solution is too large to pass through the entry ports into the central cavities. Unlike most noncrystalline ion exchangers, the framework of a zeolite defines its selectivity toward competing ions, and different structures offer different sites for the same cation. The hydration strength of some ions prevents their close approach to the seat of charge within the framework. In many zeolites, ions having a low field strength are more tightly held and are more selectively taken up from solutions than the other ions.

Dehydration/Rehydration

Zeolites exhibit no major structural changes during dehydration; they do exhibit continuous weight loss as a function of temperature and will rehydrate. If the temperature required for complete dehydration is exceeded, the zeolite structure collapses and rehydration cannot occur. Most natural zeolites are thermally stable from 250°C to 400°C (482°F to 752°F). Zeolites with higher silica contents, such as mordenite and clinoptilolite, collapse at temperatures greater than 650°C (1,202°F).

Physical Properties

A zeolite can also be described by its physical properties and performance. The physical properties include morphology, crystal habit, specific gravity, density, color, grain or crystal size, degree of crystallinity, presence of corrosion or etching, presence of contaminants or diluents, and any other descriptive features.

Performance, which is the evaluation of the zeolite for any specific application, entails such characteristics as brightness, color, Brookfield viscosity, Hercules viscosity, surface area, internal volume, particle size and morphology, hardness, abrasion resistance,

wet abrasion durability, thermal expansion, resistance to weathering, and also cation exchange capacity (CEC).

Characterization of any zeolite requires an assessment of the mineralogical properties and the performance characteristics that are believed to be required for the specific use or application. When a specific zeolite is chosen for a commercial application, it must be tested in the environment of the planned use. The efficacy of the zeolite chosen for a use cannot be accurately predicted from properties such as bulk chemistry, zeolite content, or CEC. It is imperative to realize that "one size doesn't fit all," meaning that clinoptilolite from deposit A may react differently than clinoptilolite from deposit B.

Origin

Zeolite minerals occur in several geologic settings and can be formed from a variety of starting vitric or lithic materials within an extended range of physiochemical conditions. They occur in rocks deposited in diverse geologic settings and ages. Nearly all the productive deposits in North America occur in sedimentary and volcanoclastic formations of Tertiary age.

Volcanic glass of acid to intermediate composition is the most common precursor for zeolite minerals. Less common precursors include microcrystalline quartz, opal, and feldspars. Nearly all the minable zeolite deposits in the world occur as zeolitized ash fall tuffs interbedded with lacustrine sediments, zeolitized vitroclastic tuffs in volcanic rocks, and zeolitized vitrophyres and vitroclastic tuffs as a result of hydrothermal alteration.

The development of a specific zeolite mineral depends on interrelated physical and chemical factors. Pressure, temperature, and time are three important factors that produce zeolitic alteration of the vitric precursor. The composition of the vitric component and the composition of the reactive pore water that contains cations such as H^+ , Na^+ , Ca^{++} , K^+ , and H_4SiO_4 are important factors needed to produce zeolitic alteration.

Most zeolites in sedimentary rocks formed from volcanic ash or other pyroclastic material by reaction of the aluminosilicate glass with saline-alkaline pore water. Others originated from the alteration of preexisting feldspars, feldspathoids, biogenic silica, or poorly crystalline clay minerals. Zeolites in sedimentary rocks probably formed by means of dissolution-precipitation reactions.

Earlier formed zeolite minerals can be altered to other zeolite minerals both in near-surface and in deeply buried environments. This is generally a result of changes in the physical parameters within the host rock or changes in the chemistry of the pore water. Natural zeolites have long been known to occur in basaltic rocks as veins and fillings of vugs and cavities. Only much later, because of the introduction of XRD for mineral identification, were they recognized as one of the most common groups of authigenic silicates in sedimentary rocks of volcanic origin.

Based on zeolite geologic setting, mineralogy, and genesis, Sheppard (1973) classified zeolite deposits into the following types:

- Closed system: Deposits formed from volcanic materials in hydrologically closed, saline/alkaline lake systems
- Open system: Deposits formed in hydrologically open, freshwater lake or groundwater systems
- Burial metamorphic: Deposits formed by low-grade, burial metamorphism
- Hydrothermal or hot spring: Deposits formed by hydrothermal or hot spring activity
- Deep marine: Deposits formed in deep marine environments
- Weathered zone: Deposits formed in soils, most commonly from volcanic materials

Closed System

Closed-system zeolite deposits formed in closed or partially closed hydrologic systems that had restricted movement of water out of the basin. The zeolite deposits that formed from accumulations of vitric ash fall tuffs in saline or alkaline lakes are the highest purity sources of the zeolite minerals clinoptilolite, chabazite, and erionite. Sheppard and Gude (1968, 1969b, 1973), starting with the study of a playa lake near Tecopa, California, found that tuffs deposited in such hydrologically closed basins are characterized by a later zonation: fresh ash near the margins of a basin, succeeded inward by a zone of almost complete zeolitization, a zone of analcime, and finally a central core of authigenic potassium feldspar.

The alteration to zeolites depended on high alkalinity and lake brines rich in HCO_3 . Ash falls of glassy tuff into an alkaline-saline playa or rift lake provided the ideal setting for the formation of high-grade, closed-system deposits. Erionite, chabazite, and phillipsite characterize the saline, alkaline-lake deposits. Zeolitic tuffs in saline-lake deposits generally are from a few centimeters to a few meters thick. They commonly contain monomineralic or mixed zones of the larger pore zeolites erionite and chabazite, which are relatively uncommon in other types of deposits.

Open System

Open hydrologic systems are those in which percolating groundwater moved freely through the host rock. As the groundwater circulated, it was chemically modified by dissolution of reactive materials or hydrolysis. Clinoptilolite and mordenite are the principal zeolites of open-system deposits. The Campanian Tuff and Neapolitan Yellow Tuff near Naples, Italy, are examples of thick, open-system zeolite deposits. These deposits were formed by alteration of volcanic ash by descending groundwater.

Burial Metamorphic

Zeolites may form in thick volcanoclastic sequences affected by metamorphism. Burial metamorphic deposits, also known as burial diagenetic deposits, are widespread in the Green Tuff region of Japan. With increasing depth, the deposits usually contain zones of (1) fresh ash, (2) alkali clinoptilolite, (3) clinoptilolite-mordenite, (4) analcime, and (5) albite that correlate with the depth of burial and related increases in temperature, pressure, and degree of metamorphism.

Hydrothermal or Hot Spring

The hot spring type includes zeolites associated with hydrothermal alteration, such as those at the East Tintic District, Utah, and especially those associated with hot springs. These occurrences show a vertical zonation and a downward succession of mineral assemblages that appears to correlate with an increase in temperature.

Deep Marine

The most common marine zeolites are clinoptilolite and phillipsite, formed from siliceous tephra and in low-silica basaltic tephra, respectively. Marine zeolites form at low temperatures and may replace as much as 80% of the marine sediments. Deep-sea drilling has found abundant clinoptilolite and phillipsite in cores from many localities in the Atlantic, Pacific, and Indian oceans.

Weathered Zone

Zeolite occurrences within weathered zones are scattered and of little economic significance. Analcime has been reported in alkaline, saline soils in the eastern San Joaquin Valley, California.



Figure 2. Locations of the producing zeolite deposits in the western United States

DISTRIBUTION OF MAJOR DEPOSITS

United States

The western United States has several hundred known occurrences of natural zeolites, including all the zeolite minerals having commercial potential. Resources of clinoptilolite, mordenite, and erionite are extensive, whereas sources of chabazite and phillipsite are more limited. Ferrierite occurrences are restricted to two sites in Nevada; there are, however, no present uses or applications for this mineral. Figure 2 is a map of the western United States showing the locations of producing deposits, important explored but undeveloped deposits, and the principal zeolite minerals that occur in each of them.

Alabama-Mississippi

Low-grade clinoptilolite occurs in the Tallahatta, Nanafalia, Clayton, and Lisbon formations, the Porter Creek Beds, and the Meridian Sand in Alabama and eastern Mississippi (Reynolds 1970). Occurrences in the Porter Creek Beds and the Meridian Sand typically have less than 50% clinoptilolite. Their commercial potential is limited to soil amendments, animal absorbents, and floor sweep products.

Alaska

Mordenite, heulandite, and laumontite deposits occur in the vicinity of Sheep Mountain and Horn Mountain in the Upper Matanuska Valley of Alaska. Zeolitization is the result of burial diagenesis and regional metamorphism of volcanic rocks and related sediments of the Lower Jurassic Talkeetna Formation and the lower units of the Upper Cretaceous Matanuska Formation (Hawkins 1973).

Arizona

Forty-six natural zeolite occurrences have been identified in Arizona; they include open, closed, and hydrothermal deposits. In western Arizona, hydrothermal alteration modified some of the open-system deposits. Most of the open-system zeolites are in Cretaceous to Late Tertiary rocks. Generally, the open-system mordenite and clinoptilolite deposits are in thick sections of vitroclastic ash-flow tuffs and breccias, or clastic tuff units. These zeolite deposits are highly variable in quality because of their high content of fragmentary lithic material.



Figure 3. Chabazite "chains" and clinoptilolite crystals, Bowie, Arizona

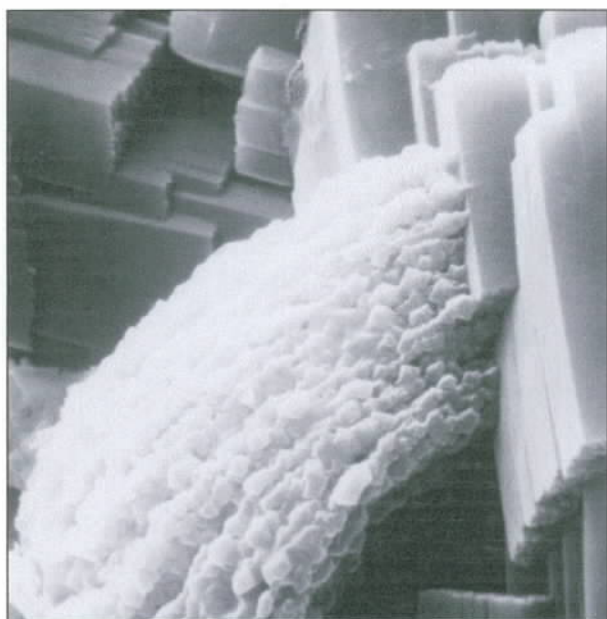


Figure 4. Chabazite "chains" and nonfibrous erionite crystals, Bowie, Arizona

Closed-system zeolite deposits occur in many of the Plio-Pleistocene intermontane basins in the Basin and Range Province of Arizona. These lacustrine deposits extend from the Wickieup clinoptilolite deposit in the Big Sandy Basin in the northwest, through the Horseshoe Dam clinoptilolite deposit and the Dripping

Spring chabazite deposit in the central part, to the Bowie chabazite deposit in the San Simon Basin in southeastern Arizona.

Hydrothermal open-system mordenite and mordenite-clinoptilolite occur in Tertiary volcanic rocks in the Oatman and Union Pass areas and the Black Mountains in Mohave County. Mordenite and clinoptilolite occur in the alteration halo surrounding the Oatman gold deposit. This suggests that the zeolitic alteration was produced by the hydrothermal solutions that also transported the gold.

Union Pass Mordenite Deposit. The mine is about 32 km west of Kingman, Arizona, on State Highway 68 at the summit of Union Pass. Union Carbide Corporation shipped several carloads containing 70% mordenite from this deposit (Eyde 1977). A pink mordenite that breaks with a conchoidal fracture replaced a bed of vitrophyre and vitroclastic ash-flow tuff that contains almost no lithic fragments. The mordenite was ground, extruded, and thermally activated. It was sold as Linde AW 300 for the separation of acid gas streams.

Bowie Chabazite Deposit. A series of small strip mines produce chabazite from what was once a nearly continuous, northwest-trending, 15-km outcrop along the San Simon River, 24 km north of Bowie, Arizona. It is the largest known high-purity deposit of chabazite in North America (Sheppard et al. 1987).

The report of Lowe (1875) appears to be the earliest reference to a bedded zeolite deposit in the United States. Lowe reported an outcrop of what appears to be the marker tuff and described it as being composed of the zeolite mineral chabazite. The marker tuff bed was an airborne vitric ash that fell into a saline-alkaline lake and was subsequently altered to zeolite minerals. It is present in a section of Plio-Pleistocene lacustrine beds composed of unconsolidated clays, sand, and gravel.

The marker tuff, which ranges from 22 to 155 cm thick, is composed of varying amounts of chabazite, erionite, and clinoptilolite. It consists of a lower massive bed ranging from 10 to 20 cm thick, overlain by 4 to 135 cm of thin beds. The lower bed, designated as the ore or high-grade bed, contains nearly 100% zeolite minerals. At the northwest end of the deposit, the lower bed is more than 90% chabazite and less than 10% clinoptilolite (see Figure 3). In the central part of the deposit, the lower bed is about 80% chabazite and 10% erionite (see Figure 4). At the southeast end, the lower bed contains 90% chabazite and 10% clinoptilolite. The chabazite in the northwestern part contains more calcium than sodium; in the central part, the percentages of calcium and sodium are about equal; and at the southeastern end, sodium greatly exceeds calcium. The upper thin beds contain 60% to 70% zeolite minerals, principally chabazite and erionite.

The Linde Company acquired the deposit in 1961 and made the first shipment to its molecular-sieve manufacturing plant in North Tonawanda, New York, that same year. This was the first zeolite deposit brought into production in the United States. Several companies have produced more than 20 kt of 80% chabazite from the deposit over the past 42 years. All the production was from the lower massive bed.

The ore bed, which has been explored by more than 3,000 drill holes, has an average thickness of 20 cm. It is mined and carefully cleaned to ensure that all the upper bed and underlying clay have been removed.

The chabazite mined by Dow Chemical from the old UOP and Union Carbide property is processed into extrudates that are activated at 425°C (797°F). The chabazite products are used for natural gas purification, acid-gas drying, hydrogen drying, chlorinated and fluorinated hydrocarbon purification, hydrochloric acid (HCl) removal from by-product hydrogen streams, and the treatment of nuclear effluents. Chabazite from the Bowie deposit was

used to clean up the radioactive effluent from the damaged Three Mile Island nuclear reactor near Middletown, Pennsylvania (King and Opelka 1982; Bostick and Guo 1996).

GSA Resources crushes, screens, and thermally activates chabazite granules at a production plant in Tucson, Arizona. These products are used to remove thallium and heavy metals from mine water. As desiccants, the chabazite products maintain the motility of enzymes and bacteria used to inoculate silage and clean up sites contaminated by hydrocarbons. The upper thin-bedded unit has been used as a lightweight oil-well cement additive.

Horseshoe Dam Clinoptilolite Deposit. This deposit crops out on the east side of the Verde River near Horseshoe Dam, 89 km northeast of Phoenix, Arizona. The principal clinoptilolite bed ranges from 2.6 to 5.3 m thick and crops out continuously for 1.6 km. Most of the deposit is more than 90% white, high-brightness clinoptilolite. The clinoptilolite contains more strontium than calcium and, unlike the clinoptilolite from other deposits, adsorbs oxygen. A 5-t bulk sample was evaluated in a papermaking machine pilot plant.

California

Stinson (1988) described the more than 100 known zeolite occurrences in California. Most are in Late Tertiary rocks in open or closed systems in an east-west belt in the Mojave Desert, extending from Mojave-Rosamond easterly about 190 km to Hector and Midway. A second belt of zeolite occurrences extends about 60 km from Tecopa and Shoshone north to the Ash Meadows deposit, northeast of Death Valley Junction.

Zeolite deposits of burial metamorphic or sedimentary origin are present in San Luis Obispo County, where mordenite with clinoptilolite replaced volcanic glass in tuffs of the marine Obispo Formation. Alteration by hydrothermal processes is represented by zeolitization of rhyolitic tuffs and pumice by hot-spring activity near Casa Diablo Hot Springs in Mono County.

Ash Meadows Clinoptilolite Deposit. This deposit is northeast of Death Valley Junction near the California-Nevada border. The zeolitized tuff occurs in an 8-km-long belt in unnamed Late Tertiary sedimentary rocks and extends north into Nye County, Nevada. White to yellowish-white zeolitized ash-flow tuffs and lapilli tuffs typically contain 80% or more clinoptilolite and exhibit high ammonia cation-exchange capacity. The exposed, altered tuff beds strike north-south, generally dip 25° east, and range in thickness from 100 to 130 m. Zeolitization is irregular, leaving some zones unaltered or weakly altered, which requires careful mining control (R.M. Colpitts, personal communication).

Anaconda Minerals Company drilled and developed this deposit with a small open pit, removing and stockpiling about 18 kt of material for bulk-sample testing to initiate production of the clinoptilolite (Santini and Knostman 1979). American Resource Corporation purchased the deposit from Anaconda. Their sources of clinoptilolite were the stockpile and the open pit at the California site. It was processed at the plant at Ash Meadows Rancho in Nevada, where it was crushed, screened, and bagged.

Badger Mining Corporation purchased the deposit, plant, and the assets of American Resource Corporation after the bankruptcy of the parent company, Rea Gold. The company constructed a new processing plant, purchased a packaging company, and began selling products including materials for swimming pool and spa filtration, absorbents, and deodorizers. Clinoptilolite from the Ash Meadows Deposit continues to be used at several sewage treatment plants and nuclear waste processing facilities.

Lake Tecopa Phillipsite Deposit. The Lake Tecopa phillipsite deposit is in the Pleistocene Lake Tecopa basin, between the towns



Figure 5. Phillipsite, Tecopa, California

of Shoshone and Tecopa. The Pleistocene sediments consist mostly of interbedded mudstones and altered to unaltered rhyolitic ash-fall tuffs. These interfinger with coarser clastic sediments toward the margin of the basin. Sheppard and Gude (1968) discovered that a fresh-glass facies occurs along the lake margin, succeeded basinward by a zeolite facies, and then by a central zone of potassium feldspar with sparse amounts of searlesite ($\text{NaBSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), reflecting the changes in the chemical environment of the lake. Phillipsite is the predominant mineral in the zeolite facies, with lesser clinoptilolite, erionite, and minor analcime and chabazite (see Figure 5). Anaconda Minerals Company conducted an extensive drilling and sampling program on this deposit.

Hector Clinoptilolite Deposit. The Hector deposit is 65 km east of Barstow and 5 km west of Hector siding. The sodium-rich clinoptilolite is light green in color and attrition resistant, which makes it suitable for ion-exchange applications. This deposit produced high-purity clinoptilolite used in the treatment of radioactive effluent at the Hanford, Washington, Nuclear Test Station. Millions of liters of low-level cesium-137 have been processed through the zeolite ion exchangers at Hanford since the 1960s. At the National Reactor Testing Station at Arco, Idaho, steel drums filled with granular Hector clinoptilolite were used in ion columns to recover the radioactive isotopes of strontium and cesium.

Mud Hills Clinoptilolite Deposit. This deposit is about 13 km north of Barstow. It occurs in the Skyline Tuff unit of the Miocene Barstow Formation. Sheppard and Gude (1969b) described extensive clinoptilolite mineralization in the Skyline Tuff unit, which was mined at the Mud Hills open pit operated by Occidental Minerals Corporation. In 1982 the mine supplied British Nuclear Fuels Ltd. (BNFL) with high-purity clinoptilolite for ion-exchange applications. Two thousand tons of carefully mined and processed clinoptilolite were shipped to Sellafield, United Kingdom, for use in the BNFL nuclear fuel reprocessing facility. The Skyline Tuff is 3 to

5 m thick at the Mud Hills mine site and typically contains 70% to 90% clinoptilolite that has a high cation-exchange capacity. Since 1982, several successive owners have operated the mine, intermittently supplying clinoptilolite for use as adsorbents and cation-exchange media.

Colorado

The several clinoptilolite deposits in the state include the Creede deposit and the Sand Wash deposit near Craig. The latter is the stratigraphic extension of the Robin's Egg Blue clinoptilolite tuff member of the Washakie Formation in Wyoming (described in that section).

Creede Clinoptilolite Deposit. This deposit is in the Oligocene Creede Formation, about 3 km south of Creede. Altered ash-fall tuff units up to 7 m thick consist of white to light-gray, dense, massive clinoptilolite. The tuffs were deposited in a structural moat around the periphery of the Creede Caldera. Intermittent mining operations have tapped this deposit as a source for regional absorbent markets.

Idaho

Southern Idaho has several large clinoptilolite deposits in production.

Bear River Clinoptilolite Deposit. The Bear River deposit is 10 km from Preston, Idaho. Bear River Zeolite Company, a wholly owned subsidiary of U.S. Antimony Corporation, produces clinoptilolite from a green zeolitized tuff in the Eocene Salt Lake Formation that crops out over a large area in southeastern Idaho. These beds are equivalent in age and physical properties to those at the Mountain Green clinoptilolite deposit in the Salt Lake Formation east of Provo, Utah.

The company produces granular clinoptilolite products for several applications. These include a soil conditioner, cat litter, an algae control product for ponds, and preloaded zeolite fertilizers containing 2.5% nitrogen for use on turf. An absorption product manufactured by the company was successfully used to clean up an anhydrous ammonia spill from a ruptured railroad tank car. Bear River Zeolite continues to expand their customer base, both in the United States and in foreign countries (Anon. 2003, 2004).

Castle Creek Clinoptilolite Deposit. This deposit is 71 km south of Boise, Idaho. Discovered in 1962, it is the largest high-purity deposit of clinoptilolite found by the Union Carbide zeolite exploration program. The soft, fine-grained, ash-fall tuff unit in the Miocene Chalk Hills Formation is altered to fine-grained, white, high-brightness clinoptilolite. Double Eagle Petroleum and Mining Company acquired the deposit in 1976. A paper company evaluated several bulk samples of the clinoptilolite in 1982.

Sheppard (1993a) and Teague Mineral Products subsequently identified an extension of the clinoptilolite bed to the east and southeast along Castle Creek. Teague Mineral Products is actively mining and processing the clinoptilolite for sale in industrial and agricultural applications (G.A. Teague, personal communication).

Chrisman Hill Clinoptilolite Deposit. The Chrisman Hill deposit is 30 km north of Jordan Valley, Oregon. A thick, massive to thin-bedded zeolitized tuff bed occurs in the Miocene Sucker Creek Formation. The deposit consists of high-quality, white to light-gray clinoptilolite, similar in appearance to the Sheville, Oregon, deposit 11 km to the south. The zeolitized zone is 20 m thick. It contains millions of tons of potential zeolite resources. The deposit, which straddles the Idaho-Oregon border, is mined by Teague Mineral Products to supply its processing plant in Adrian, Oregon. The Chrisman Hill deposit is on a weak hydrothermal alteration trend and shows evidence of hydrothermal alteration as well as obliteration of sedimentary structures (G.A. Teague, personal communication).

Montana

Clinoptilolite is reported from 14 localities in southwestern Montana, all in tuffaceous beds thought to be of Tertiary age and deposited in intermontane basins (Berg and Cox 2001). Clinoptilolite and mordenite occur in Cretaceous tuffs in Beaverhead County.

Grasshopper Creek Clinoptilolite Deposit. This deposit is 16 km southwest of Dillon, Montana. A section of Cretaceous tuffaceous beds is altered to clinoptilolite and minor amounts of mordenite. The cation-exchange capacity of 12 samples collected from the deposit ranges from 0.68 to 1.29 meq/g. Detailed mapping, surface sampling, and three drill holes indicate that this is a minable deposit (Berg and Cox 2001).

Nevada

Nevada has huge resources of zeolites, primarily in two geologic settings: Late Tertiary erionite-clinoptilolite-phillipsite-chabazite ash-fall tuff occurrences of closed system origin in northern Nevada; and thick Tertiary zeolitized ash-flow tuff occurrences of clinoptilolite and mordenite in central and southern Nevada.

Papke (1972) described four Late Tertiary closed-system deposits in north-central Nevada: Eastgate, Jersey Valley, Pine Valley, and Reese River. All the deposits occur in silicic ash-fall tuffs as thick as 5 m in sections of lacustrine sedimentary rocks. The principal zeolite minerals are erionite, clinoptilolite, phillipsite, and chabazite. Mordenite is less common in lacustrine tuff beds. The zeolites were formed by postdepositional diagenesis of vitric volcanic ash that fell into saline, alkaline lakes (Papke 1972).

Pine Valley Erionite Deposit. The Pine Valley deposit is 55 km south of Carlin, Nevada (Regnier 1960). Erionite and phillipsite occur in altered ash-fall tuffs in a thick sequence of Pliocene lacustrine rocks of the Hay Ranch Formation. The principal erionite bed strikes north-south, and dips 2° to 3° east. Union Carbide Corporation has operated the deposit intermittently since 1959 (Papke 1972). The principal zeolitized tuff bed is as much as 2 m thick and typically contains 80% to 90% erionite. Three to five thin beds of high-purity phillipsite occur in bentonitic sediments at the south end of the deposit.

Eastgate Clinoptilolite-Erionite Deposit. This deposit is 88 km east of Fallon, Nevada, and 5 km east of the junction of U.S. Highway 50 and Nevada Highway 2. The beds occur in the Monarch Mill Formation, an Early to Middle Pliocene sedimentary sequence (Papke 1972).

The zeolite beds are of closed-system origin in air-fall tuffs. One or more zeolite beds are present in a zone ranging in thickness from a few centimeters to as much as 5 m. The beds strike north to northwest, are exposed intermittently, and dip easterly at low angles. The most common zeolite associations are erionite and erionite-clinoptilolite accompanied by varying amounts of unaltered glass. Locally, chabazite, phillipsite, erionite-phillipsite, and mordenite are also present.

Union Carbide Corporation staked claims on the deposit in 1957 and dropped them after the Bowie, Arizona, chabazite deposit went into production in 1961. Anaconda Minerals Company staked mining claims on this deposit in 1970 and undertook a detailed exploration program. East-West Minerals, Ltd. later acquired the deposit and built a processing plant nearby. The company attempted to mine the southern part of the deposit, a short distance south of State Highway 2, and process the material for pet litter and absorbent uses. The venture was unsuccessful and the plant was dismantled and removed. In 1997 American Colloid built a state-of-the-art processing plant to produce animal absorbents at the site. Erionite was discovered in the zeolite and the plant was shut down. Badger Mining

Corporation purchased the plant and moved it to Ash Meadows (Eyde 2003).

Jersey Valley Erionite Deposit. The Jersey Valley deposit is 67 km southwest of Battle Mountain, Nevada. Ash-fall tuff beds within Late Tertiary lacustrine sediments are altered to erionite, erionite-clinoptilolite, and erionite-phillipsite-clinoptilolite in the deposit. Papke (1972) described the deposit, which has two zeolitic tuff beds that have minable thicknesses of 2 to 3.5 m. Mobil Oil Corporation mined these zeolites by underground and open-pit methods from 1965 to 1970 to produce raw material for catalysts used in oil refining and natural gas purification.

Reese River Chabazite Deposit. This deposit is 56 km north of Austin, Nevada. Deffeyes (1959) identified chabazite, clinoptilolite, erionite, and phillipsite occurring in ash-fall tuffs within Miocene or Pliocene lacustrine beds. Eight zeolite beds thicker than 33 cm are present; one is as much as 2.5 m thick (Papke 1972). Union Carbide staked claims on the deposit in 1959 but dropped them after mapping and sampling the deposit.

Lovelock Ferrierite Deposit. This deposit is 17 km northwest of Lovelock, Nevada. Ferrierite-mordenite-clinoptilolite and ferrierite-mordenite occur in altered Miocene or Pliocene ash-fall tuffs. Clinoptilolite is a relatively minor constituent, occurring principally in the upper part of the stratigraphic section.

A remarkable concentration of ferrierite is present in the central part of the deposit. Here, a unit with an exposed thickness of about 17 m contains 75% to 95% ferrierite and minor amounts of mordenite and clinoptilolite. Apparently, this is the largest known deposit of ferrierite in the world (K.G. Papke, personal communication).

Many large deposits of clinoptilolite and mordenite occur in ash-flow tuffs, tuff breccias, and lithic tuffs in Nevada. Most of these occurrences are open system in origin, though some appear to be related to hydrothermal alteration as well. Typically, a large vitroclastic ash-flow zeolite deposit contains 30% to 80% zeolite and has abundant lithic fragments and unzeolitized crystalline and vitric material. Ammonia cation-exchange capacities are usually significantly lower than those in closed-system ash-fall tuffs.

Ash Meadows Clinoptilolite Deposit. An ash-flow zeolite deposit with large resources of high-quality clinoptilolite crops out at Ash Meadows, Nevada. The deposit straddles the Nevada-California border, northeast of Death Valley Junction, California. The deposit is described more fully in the section on California zeolites. The Nevada portion of the deposit includes a large resource of green clinoptilolite in Pliocene ash-flow and lapilli tuffs.

Beatty Mountain Mordenite Deposit. This deposit crops out on the west side of Beatty Mountain. Thick greenish-white mordenite beds are interbedded in a section of Pliocene ash-flow tuffs. Samples collected by Union Carbide contained from 70% to 85% mordenite.

New Mexico

There are two productive clinoptilolite deposits in New Mexico.

Buckhorn Clinoptilolite-Chabazite Deposit. This deposit is 58 km north of Silver City, New Mexico, and 2.5 km south of the community of Buckhorn on the west side of Duck Creek Valley. Two clinoptilolite beds crop out in the Plio-Pleistocene Cactus Flat beds. The lower bed is 1 to 1.6 m thick with 70% to 90% clinoptilolite and chabazite. The upper bed is about 30 cm thick and contains 60% clinoptilolite and a trace of erionite (Eyde 1982; Sheppard et al. 1987). Zeotech Corporation mined and shipped a few truckloads of clinoptilolite to their processing plant at Tilden, Texas.

Cuchillo Negro Clinoptilolite Deposit. The most productive clinoptilolite deposit in New Mexico is about 300 km south of Albuquerque and 6.5 km south of Winston. The deposit is in a 180-

to 240-m-thick section of interbedded tuffaceous and conglomeratic rocks that are 29 million years old (McIntosh, Kedzie, and Sutter 1991); it crops out along Cuchillo Negro Creek at the south end of the Winston graben. The zeolite bed being mined by the St. Cloud Mining Company is 4.4 to 10.7 m thick and contains 50% to 85% clinoptilolite that is more attrition resistant and has higher potassium content than most other clinoptilolite. In 2002 St. Cloud Mining Company mined and processed 14.5 kt of clinoptilolite products. These were sold into consumer, industrial, and agricultural markets throughout North America (Barker et al. 2003).

Oregon

Several natural zeolite deposits with economic potential occur in eastern Oregon. The zeolite occurrences in marine sedimentary rocks in western Oregon have no obvious commercial potential.

Durkee Chabazite Deposit. This deposit is in a closed basin near the community of Durkee, Oregon, 165 km northwest of Boise, Idaho. An area of about 18 km² is underlain by chabazite, clinoptilolite, erionite, and authigenic feldspar. Vitric ash fell in a Miocene saline alkaline lake and formed zeolite minerals at low temperature and pressure. The zeolitized ash-fall and reworked tuffs and one ash-flow tuff are interbedded with diatomite, mudstone, sandstone, siltstone, and conglomerate. The U.S. Geological Survey made several investigations of the deposit (Sheppard and Gude 1969a, 1980; Gude and Sheppard 1986, 1993).

Anaconda Minerals Company, Occidental Minerals Corporation, and Filtrol Corporation explored the deposit and identified several promising target areas containing possible large tonnages of chabazite, but their exploration results remain unknown.

The Harney Basin Clinoptilolite Deposits. The Harney-Malheur Basin is about 40 km south of Burns, Oregon. Near-surface Miocene tuffaceous rocks constitute an enormous zeolite resource. The principal mineral is clinoptilolite with lesser erionite, chabazite, phillipsite, and mordenite on the basin margins. The principal mineralized zone underlies an area of more than 20 km² (Sheppard 1993c). A massive clinoptilolite bed 20 m thick underlies much of the basin. Toward the southern margin of the basin, the clinoptilolite-rich tuff interfingers with thinner beds of erionite, chabazite, and phillipsite. The zeolite deposits of the Harney Basin formed as a result of diagenetic alteration of ash-fall tuffs and reworked tuffaceous fluvial sediments within a closed hydrologic system.

Rome Erionite Deposit. The Rome deposit is 60 km west of Jordan Valley, Oregon, near the Owyhee River and Crooked Creek in an area dissected by steep-walled canyons (Sheppard and Gude 1983, 1993b). The deposit has an extensive resource of high-purity erionite, mordenite, and mixed mordenite-clinoptilolite. The zeolites occur in several tuffaceous members of the Rome beds, a 130-m-thick Miocene fluvio-lacustrine sequence. Two zeolitized beds in the lower member initially appeared to have significant commercial potential. Each bed is about 3 m thick and contains 50% to 70% erionite. The fibrous morphology precludes its use in commercial and consumer applications.

Sheaville Clinoptilolite Deposits. The Sheaville deposits are 19 km north of Jordan Valley, Oregon, between U.S. Highway 95 and the Oregon-Idaho border. These deposits are present in at least 10 km² where the westward-flowing Succor Creek crosses the state border and the axis of a north-south trending anticline. The Sheaville District has large resources of high-quality clinoptilolite available for mining.

The Sheaville clinoptilolite sequence is in the Miocene Sucker Creek Formation, a lacustrine unit of interbedded tuff, zeolitized tuff, bentonite, and carbonaceous siltstone (Almner and Grim 1990; Sheppard and Gude 1983, 1993c).

As many as five thick, massive units of white to light gray, zeolitized ash-fall tuff crop out in the area. Clinoptilolite is the predominant zeolite, with trace amounts of mordenite. Zeolitization is most intense near the axis of the anticline (Holmes 1990).

Zeolite production by the Norton Company has been confined to the uppermost clinoptilolite bed on the western flank of the anticline. The bed is well exposed several hundred meters east of U.S. Highway 95, near the western edge of the zeolitized area. The lowest clinoptilolite bed is the thickest in the district and crops out on the south side of Succor Creek. It is as much as 22 m thick and consists of white to light-gray massive clinoptilolite. Occidental Minerals Corporation drilled this bed between 1977 and 1981 and opened a large test pit near the anticline axis in 1982.

Succor Creek Clinoptilolite Deposits. These deposits are 13 km north of Rockville, Oregon, and just south of Succor Creek State Park. Several deposits of white to light gray, massive, and sandy zeolitic tuff occur in the Miocene Sucker Creek Formation along the lower part of Sucker Creek, both within and downstream from the state park (Almner and Grim 1990).

The beds contain 30% to 70% clinoptilolite and are up to 26 m thick. These occurrences have a hydrothermal alteration overprint and generally are more variable and less altered than the Sheaville and Chrisman Hill deposits (Altaner and Teague 1993). Teague Mineral Products operates an open pit in the lower Succor Creek area to extract clinoptilolite for pet litter and odor control uses.

South Dakota

The only important occurrence of natural zeolites in South Dakota is the Sheep Mountain Table clinoptilolite deposit.

Sheep Mountain Table Clinoptilolite Deposit. This deposit is on the Pine Ridge Indian Reservation near Rockyford, South Dakota. An extensive resource of clinoptilolite occurs in zeolitic tuff in the Rockyford Member of the Miocene Sharps Formation, which caps hills and mesas in the badlands on the Pine Ridge Indian Reservation and adjacent Badlands National Monument to the north (Raymond 1986). The zeolite-rich tuffs are as much as 33 m thick and are of open-system genesis. The clinoptilolite content is in the 50% to 60% range, with ammonia cation-exchange capacity values of 0.6 to 1.40 meq/g (Desborough 1989). The deposit is not developed.

Texas

Texas has large resources of clinoptilolite in two regions (Walton, et al. 1972). In south Texas, a belt of zeolitized ash-fall tuff in the Wellborn and Yegua formations of the Eocene Jackson Group of Gulf Coast sediments extends from Zapata County on the Rio Grande River northeasterly, cropping out west of Tilden in McMullen County, and extending east toward the Gulf of Mexico.

Large resources of clinoptilolite also occur in zeolitized ash-fall tuff beds and tuffaceous sediments in the Oligocene Tascotal Formation in the Trans-Pecos region between Presidio and Marfa (Bostros 1976; Walton and Henry 1979).

Tilden Clinoptilolite Deposits. A cluster of clinoptilolite deposits is located 8 to 13 km west to northwest of Tilden. The Buck Martin pit has a flat-lying, white, flaggy, zeolitized ash-fall tuff 3 m thick containing as much as 80% clinoptilolite. The nearby Kuykendall pit has a 4-m-thick bed containing 90% clinoptilolite. The Tilden Area zeolite resources are large, but they occur in scattered deposits. Zeotech Corporation mines and processes clinoptilolite into pet litter, swimming pool filtration media, a turf treatment product, material for ion-exchange applications, and other generic absorbent products (Eyde 2003).

Utah

Zeolite occurrences have been identified at 56 localities in Utah. Six sedimentary clinoptilolite deposits may be minable.

Trenton Clinoptilolite Deposit. The Trenton deposit is located along the west side of Cache County about 35 km north-northwest of Logan, Utah, and extends northward into Idaho. It is a zeolitized air-fall tuff in the Tertiary Salt Lake Formation. (See the description of the Bear River Clinoptilolite Deposit in the Idaho section [Mayes and Frupp 1991].)

The zeolitized green, fine-grained tuffs constitute a very large potential resource, containing as much as 70% clinoptilolite. It is a high-potassium clinoptilolite deposit, similar to the Mountain Green occurrence to the south.

The Mountain Green Area in Morgan County contains estimated zeolite resources greater than 240 Mt. The clinoptilolite content commonly is 50% to 80%.

Wyoming

Natural zeolites have been described at 88 locations in Wyoming. Potentially minable zeolites, in order of importance, include clinoptilolite deposits in the Washakie Basin, along Beaver Rim, and on Lysite Mountain (Harris and King 1990).

Washakie Basin Clinoptilolite Deposits. This deposit is about 73 km east of Rock Springs, Wyoming. Roehler (1973) discovered and described the Washakie Basin clinoptilolite. The report identified clinoptilolite and mordenite in tuffs of the Laney Shale Member of the Green River Formation and in tuffs in the Robin's Egg Blue tuff bed of the Adobe Town Member of the Washakie Formation. The Robin's Egg Blue bed is a light blue to greenish-blue zeolitized ash-fall tuff altered to 50% to 90% clinoptilolite. Extensive drilling and testing indicate that the clinoptilolite is suitable for a wide range of applications, including nuclear waste cleanup.

Rocky Mountain Energy Corporation (now Union Pacific Resources-Minerals) attempted to develop clinoptilolite in its check-board sections on the north rim of the Washakie Basin between 1978 and 1983. The venture also produced limited tonnages of the blue-green clinoptilolite for cat litter and other deodorant applications (Hulbert 1987).

U.S. Zeolite Corporation subsequently leased the Rocky Mountain Energy fee lands and claims and obtained state mineral leases covering other promising clinoptilolite occurrences along the rim. The company is now doing testing and marketing studies and has produced small tonnages of clinoptilolite for absorbent and industrial uses (T. van Fleet, personal communication). Addwest Minerals International acquired U.S. Zeolite and now controls the deposit.

Beaver Rim Clinoptilolite-Chabazite Deposit. The Beaver Rim deposit is near Riverton, Wyoming. Several beds of clinoptilolite, mixed clinoptilolite-chabazite and clinoptilolite-erionite occur in ash-fall tuffs in the Eocene Wagon Bed Formation in the district, in Fremont County (Boles 1968; Van Houten 1964). U.S. Energy Corporation produced and sold small tonnages of clinoptilolite during the 1980s to western aquacultural markets and to an experimental sewage treatment plant developed by ATEC Inc. in Riverton.

Zeolites Outside the United States

Natural zeolites are being produced in 37 countries and occur in another 28. Production is intermittent and figures are unreliable (Harben and Bates 1990). The major producing countries are China, Cuba, Japan, the United States, Hungary, and Bulgaria. Smaller tonnages come from Australia, Germany, New Zealand, Italy, and South Africa. More new discoveries of natural zeolite minerals are being reported. Most of the discoveries are minor

occurrences that will never be put into production because of their impurities or size. Many of the deposits being mined in developing countries supply crushed and quarried products used in agriculture and construction. Only the deposits that are in production or are being explored are described here. For more comprehensive information on the distribution of zeolites, refer to the 5th and 6th editions of *Industrial Minerals and Rocks*.

The following countries are also known to have zeolite deposits that are not being explored or developed:

- Algeria
- Austria
- Chad
- Denmark
- Egypt
- Iran
- Israel
- Jamaica
- Kenya
- Malawi
- Mali
- Mauritania
- Mongolia
- Namibia
- The Netherlands
- Pakistan
- Papua New Guinea
- Philippines
- Puerto Rico
- Senegal
- Spain
- Switzerland
- Taiwan
- Tunisia
- Uganda
- United Kingdom

Cuba has done extensive research on the agricultural applications for natural zeolites. In fact, most of the natural zeolite research was done in the communist Eastern bloc countries before the collapse of the Soviet Union. Since then there has been a significant transfer of technology from these countries to entrepreneurial companies based in the capitalist countries for commercialization. One of the best examples is the ZELfloc technology for sewage treatment developed in Hungary and licensed by Zeolite Australia. The company now has 14 wastewater treatment plants in operation using the process (Eyde 2000).

In the case of China, Russia, and many other countries, the information is incomplete and possibly inaccurate. Some of the information has been provided verbally, and may be lacking in credible documentation. It is presented here, nevertheless, to provide the most complete reference on natural zeolite mineralogy, occurrences, uses, and applications. Certainly, in the future, other deposits will be discovered and brought into production from deposits in countries that are not mentioned in this chapter.

Argentina

Cristamine SA processes and sells clinoptilolite from local sources for use in animal feeds.

Australia

Natural zeolites occur in Paleozoic rocks in the Drummond Basin, Queensland, and in rocks from Late Carboniferous to Tertiary age in New South Wales. Production of zeolite from New South Wales is limited to two producers with a total production of about 7 ktpy. Zeolite Australia Ltd. has produced and sold clinoptilolite from sources in New South Wales since 1988. Zeolite Australia operates the Escott mine and processing plant, 5 km southwest of Werris Creek, New South Wales. Zeolites from this deposit are being used in many parts of Australia and some are being exported. The production is about 4 ktpy (Anon. 2004).

A number of reports have been published on the occurrence of natural zeolites in New South Wales (Holmes and Pecover 1987; Crossley 2002; Cullen 2004).

Currumbin Sand and Gravel Pty Ltd. operates a zeolite mine at Willows, in central Queensland. Currently, production is 3 ktpy.

Supersorb Environmental NL processes zeolite through its crushing and screening plants at Springvale and Duaringa, central Queensland (Anon. 2004).

Bulgaria

Extensive zeolite deposits occur in Bulgaria. The principal deposits are in the Srednogorian zone south of the Balkan Mountains and the Eastern Rhodopes (Gottardi and Obradovic 1978).

In the Rhodopes, large deposits of clinoptilolite and mordenite occur in the Oligocene rhyolitic pyroclastic rocks. A bed of white clinoptilolite 35 m thick crops out near the village of Perperek. A clinoptilolite bed 110 m thick occurs in a section of Oligocene tuffaceous sediments between the villages of Beli Plast and Mest.

Clinoptilolite has been produced from the deposits in the Eastern Rhodopes for many years. Bentonite EAD in Kardjali operates a surface mine at White Hill that has a capacity of 50 ktpy. Clinoptilolite production over the past 10 years has ranged from 2 to 45 ktpy. The clinoptilolite products are used in detergents, water filtration, food additives, and gas treatment, and as soil conditioners and fertilizer carriers.

Canada

Sedimentary zeolites that were discovered in Tertiary basins in interior British Columbia during the 1980s are now being brought into production. Clinoptilolite and heulandite occurs in Tertiary sedimentary rocks in the Cache Creek, McAbee, and Battle Creek areas. The rhyolitic tuffs of Eocene age contain clinoptilolite beds that range from 1 m to 6 m thick (Read 1987).

Several companies produce clinoptilolite from deposits in the Princeton and Cache Creek basins in British Columbia. Canmark International Resources explored and began clinoptilolite production from a deposit in the Princeton Basin. Highwood Resources produces clinoptilolite–heulandite from a deposit in Cache Creek. The zeolite is processed into agricultural products at Rocky Mountain House, Alberta.

China

Clinoptilolite and mordenite deposits occur at a number of locations throughout China. Six producers are reported in the country. Most of the production is from deposits in altered volcanic rocks of open-system origin. Most of the estimated 3 Mtpy of zeolite produced in China goes into pozzolanic applications. The balance goes into agricultural and industrial applications. Chabazite, phillipsite, and erionite are reported in closed-system settings in interior desert playas.

The U.S. Geological Survey estimates that the worldwide (not including China) production of zeolites in 2002 was 3.5 Mtpy. Thus, the estimated Chinese zeolite production is nearly equal to production in the rest of the world. Assuming that the production estimate is close to being correct, China is the world's largest producer of zeolite minerals.

Cuba

Exploration for natural zeolites that began in the 1970s has developed resources of more than 300 Mt, principally clinoptilolite–heulandite and mordenite (Griffiths 1987; Fuentes and Gonzales 1991). Cuba may be the world's second largest producer of zeolites. In 1994 the Cuban International Marketing Firm for Industrial Minerals SA (CIMTEC) reported exports of 100 kt for agricultural applications.

There are at least 25 zeolite deposits in Cuba. Most deposits consist of altered volcanic tuffs within volcanogenic sedimentary rocks of Lower Cretaceous and Middle Eocene age.

Clinoptilolite–heulandite resources include the Tasajeras-Piojillo, San Antonio, Najasa, and La Pita deposits. The Palmarito and San Cayataro deposits are nearly pure mordenite. Five plants having an overall annual production capacity of 500 kt are currently processing zeolites mined from four deposits (Anon. 1988).

France

Exploration in France for economic zeolite deposits began in 1989, principally in the Massif Central region. Three areas of promising discoveries include clinoptilolite and heulandite in ash-fall sediments of the Limagne Bourbonnaise Basin and phillipsite in ash-pumice tuffs originating from stratovolcanoes of the Cantal and Mont-Dore regions (Rocher et al. 1991).

Clinoptilolite occurs in Upper Cretaceous marls and chalks in the Anjou District on the west side of the Paris Basin. It has also been detected in Paleogene marine sediments of that basin. Analcime and clinoptilolite are present in sediments containing volcanic debris in the Limagne de Clermont-Ferrand (Gottardi and Obradovic 1978).

No production has been reported from these deposits, although Materials de la Mediterranee SA processes zeolites and Poortershaven processes zeolites for animal feed at its plant in Poissy, France.

Germany

Rocks containing zeolite minerals are mined from several deposits in Germany. Nearly all the production is used as pozzolan. Clinoptilolite occurs in Upper Cretaceous marls and marly limestone. It is used in the manufacture of cement at plants near Hannover and surrounding areas in northwest Germany.

Quaternary volcanic rocks in the Bonn and Laacher See areas of the Rhine region contain zeolitized pumiceous tuffs that are mined for pozzolans. The zeolite minerals include chabazite, phillipsite, and analcime.

The largest producer of zeolites in Germany is Hans G. Hauri Mineralstoffwerk in Botzingen-Oberschaffhausen. The company produces 150 ktpy of a zeolitically altered phonolite that contains 40% zeolite. The principal minerals are natrolite, skolezite, and lesser amounts of mesolite, thompsonite, and phillipsite. Nearly all the production is sold as a pozzolan. The fines are sold to vineyards in the Rhine and Mosel valleys where they are used as a highly effective nontoxic fungicide. The fines are also used in personal care products.

Franke & Schulte GmbH, H.J. Schmidt Mineraltechnik GmbH & Co., and Carl Spaeter GmbH custom process and sell zeolite products.

Greece

The Institute of Geology and Mineral Exploration and the Institute of Geological and Mining Research identified zeolitically altered tuffs on the islands of Milos and Polyaeos, and also in the Evros Area in mainland Greece (Tsirambides, Filippidis, and Kassoli-Fournaraki 1993; Tsolis-Katagas and Katagas 1990).

Silver & Baryte Mining Company SA began producing zeolite from the Evros deposits in 1996. The deposits are estimated to contain 6 Mt of 75% clinoptilolite. The company produces five clinoptilolite products that are used as supplements in animal feeds, soil amendments and conditioners, water treatment, animal litter, and absorbents.

Hungary

Major deposits of clinoptilolite and mordenite occur in the zeolitically altered Sarmatian rhyolitic tuffs and ignimbrites in the Tokay

Mountains. The zeolite deposits contain 65% to 95% clinoptilolite (Gottardi and Obradovic 1978).

Clinoptilolite is mined from the Ratka deposit and mordenite is mined from the Bodrogeresztur deposit. Hungarian production of natural zeolites was estimated to be 40 to 50 kt in 1987 (Griffiths 1987). In 1997 the production was estimated to be 15 kt.

The principal markets for the clinoptilolite products are feed supplements, products for ammonia–nitrogen removal from aquariums, and cat litter. The specialty products sold in Hungary include a deodorizer for wineries, a kitchen scrubbing compound, and a bathroom cleaning and deodorizing product.

Indonesia

Altered volcanic rocks hosting natural zeolites have been identified on several islands in Indonesia. Several recently developed clinoptilolite deposits are providing zeolite products to regional agriculture and aquaculture industries.

Eastmet Ltd. is developing a clinoptilolite deposit at Mt. Ratai and Tarahan in Lampung Province, Sumatra. Another zeolite deposit 20 km south of Panjung, the major port in Lampung Province, is currently producing crushed and screened clinoptilolite product for use in local aquaculture markets. Clinoptilolite and mordenite are produced from a mine on Java and made into products for sale throughout the eastern Pacific Rim.

Italy

Italy has a great number of zeolite occurrences, ranging from the extensive Neapolitan and Campanian zeolitic tuff systems in central Italy near Naples and Rome to zeolites of marine origin in Sicily. Burial metamorphic and hydrothermal origin zeolitic tuffs occur in the Apennines in northern Italy.

The Neapolitan Tuff, the Campanian Tuff, and equivalent volcanic formations crop out over extensive areas around Rome and the Gulf of Napoli. The deposits in these tuff beds are the economically important ones in Italy. Both tuffs contain phillipsite and chabazite in beds from 20 to 120 m thick and have been used since Roman times as dimension stone (Aiello 1993). Both are sources of raw materials used in a wide range of industrial and agricultural applications. Coarse pyroclastic rocks from the Roccamonfina Volcano, about 50 km northwest of Naples, contain significant amounts of chabazite and analcime and are quarried as building stone.

Tuff layers in a thick Quaternary pyroclastic sequence from the calderas of the Vulcano Laziale, about 20 km east of Rome, contain chabazite and phillipsite. Chabazite occurs in altered zones in tuffs and ignimbrites within Quaternary calderas in the Latium region near Rome. Lenzi and Passaglia (1975) described chabazite occurrences at Bracciano Lake that constitute more than 50% of the tuff.

Mineraria del Mediterraneo Italia Srl. produces 4 ktpy of chabazite and phillipsite from its mine in Sorano, Grosseto, about 100 km north of Rome. Its zeolite products are used in water treatment and animal feeds.

Japan

As a leading producer of natural zeolites, Japan is also a world leader in development and application of zeolite technology. It utilizes zeolites for a wide range of agricultural, industrial, and consumer uses. Annual production has ranged from 60 to 100 kt since the mid-1960s. Torii (1978) and others studied Japanese natural zeolite deposits and described their uses and applications. Zeolites occur in rocks ranging from Triassic to Quaternary in age, but the majority is in Miocene pyroclastic and volcanogenic

sedimentary rocks. Most zeolite occurrences in Japan are related to low-grade metamorphism. Many occurrences show zonation typical of burial metamorphism; others show zoning caused by hydrothermal alteration related to igneous intrusion.

Clinoptilolite and mordenite are the only zeolite minerals mined in Japan. Both minerals have been used for industrial and agricultural applications since 1949. Both minerals occur in the Green Tuff belt of metavolcanic rocks, but clinoptilolite is the most important zeolite mineral in Japan.

Eighteen companies produce between 140 and 160 kt per year of natural zeolites in Japan. Only eight produce significant quantities, and only three produce more than 10 ktpy. Clinoptilolite is produced at the Itaya mine in Yamagata Prefecture, Honshu, and processed by the Zeaklite Chemical & Mining Company, Ltd. for use in agricultural and other applications. The company produces at least 60 ktpy and is Japan's largest zeolite producer. Sun Zeolite Ind. Co., Ltd. produces clinoptilolite from its deposit in Akita Prefecture for agricultural use (Griffiths 1987). Nippon Kasseihakudo Co., Ltd. produces by-product clinoptilolite from its calcium-bentonite operations. The company also produces synthetic zeolite A using clinoptilolite as the raw material.

Smaller Japanese producers include Shinshin Development Co., Ltd. (mordenite and montmorillonite), Hamamich Kohsan Co., Ltd. (zeolite and montmorillonite), and Asahi Kasei Kogyo Co., Ltd. (mordenite) (Griffiths 1987). Other markets for Japanese zeolites are adsorption and water treatment.

Korea

Clinoptilolite-heulandite and mordenite deposits occur in both countries on the Korean peninsula. In the Democratic People's Republic of Korea, zeolites occur in Pliocene acid volcanic rocks in the Kilcho-Mjong Chong Province, which is in the northeastern part of the Korean peninsula. Clinoptilolite- and mordenite-rich tuffs also occur in the northeastern part of the province, near the villages of Han Zin and Pho Ha. Two clinoptilolite deposits in the southwestern part of the province contain clinoptilolite, heulandite, phillipsite, and chabazite (Han et al. 1985).

Clinoptilolite and mordenite occur within altered Miocene tuffs and tuffaceous sediments in the Guryongpo Area in the Republic of Korea (Noh and Kim 1982). The Kuryong mine at Kuryong and the Dalsin mine at Tonghai, both in Kyongsangbuk Province, produce 110 ktpy of clinoptilolite products.

Mexico

Natural zeolites occur in altered Tertiary volcanics and lacustrine beds in Mexico. A chabazite-erionite bed 12 to 14 cm thick occurs in Plio-Pliocene lacustrine beds in the extension of the Santa Barbara Valley south of Agua Prieta, Sonora. The deposit is nearly identical to the Bowie, Arizona, chabazite deposit 120 km to the north, both in extent and mineralogy. The erionite from the deposit was tested for use in petroleum-cracking catalysts and radioactive waste treatment.

A clinoptilolite-mordenite deposit near Rancho Tetuache, 20 km south of Arizpe, Sonora, is a zeolitized vitroclastic tuff more than 200 m thick that contains 80% to 90% combined clinoptilolite and mordenite. A 20-ton bulk sample was used to treat the runoff from cattle feed lots. There are several other zeolite occurrences in the state of Sonora.

Zeolite deposits occur at Etlá and San Antonio, Oaxaca, and in the states of San Luis Potosí, Puebla, and Guanajuato. Over four centuries, large buildings in southern and central Mexico, including a cathedral at Oaxaca, have been built of clinoptilolite-mordenite-rich tuffaceous rocks because of its strength, workability, and durability.

Geoexplorers International began processing test lots of clinoptilolite at a toll-processing facility in the city of San Luis Potosí. The clinoptilolite is mined from the Escalera deposit in the state of San Luis Potosí and the Almandina deposit in the state of Guanajuato (Eyde 2000).

New Zealand

Natural zeolites are abundant in the Waitemata Group, an Early Miocene sedimentary sequence in Auckland Province. The main part of the group consists of sediments where clinoptilolite and chabazite occur in interbedded volcanoclastic rocks. NZ Natural Zeolite has begun producing zeolite products. It supplies a range of products used as adsorbents in ion-exchange applications and fertilizer carriers (Eyde 2000).

Republic of South Africa

Clinoptilolite is produced from altered Jurassic volcanic rocks at the Pratley Perlite Mining Co. Pty. Ltd. mine at Hluhluwe in what is now the province of KwaZulu-Natal. Both clinoptilolite and mordenite are associated separately with perlite and white calcium bentonite, which are also mined and processed (Griffiths 1987).

Romania

Large deposits of clinoptilolite and mordenite occur in Late Tertiary tuffs in the Transylvanian Basin and in the Precarpathian zone. These tuffs are commonly tens of meters thick and have been used for hundreds of years as building stone. They are of open-system origin and offer significant economic potential (Istrate 1980).

Russia

Research done in the former Soviet Union developed a wealth of potential applications for zeolite minerals. In fact, the Soviet Union was probably ahead of Japan in technological capability to develop new zeolite-based products, but the Soviets, unlike the Japanese, did not have the product development and marketing expertise needed to sell their products. Most of the Russian zeolite production is used in agricultural applications. The widespread radioactive contamination of soil and water caused by the Chernobyl nuclear reactor disaster required the development of decontamination techniques that utilized natural zeolites (Chelishchev 1993).

Gottardi and Obradovic (1978) presented a cursory overview of Soviet natural zeolite occurrences and geology. Tsitsishvili (1988) summarized earlier information on Soviet zeolite research and commercial application, including zeolite synthesis.

Salavatnefteorgsintez and Bashneftekhinzavody Ishimbay Special Chemical Catalysts produce zeolites in Russia. Both of these plants are in the Bashkortostan region. Production at Bashneftekhinzavody is about 8 ktpy of clinoptilolite used as a pozzolan in cement.

Serbia

Zeolites occur in open, hydrothermal, and burial metamorphic deposits in Serbia. Clinoptilolite and mordenite are present in altered pyroclastic rocks of Triassic to Late Tertiary age. Clinoptilolite is mined for local use, mostly agricultural, from several deposits.

Slovakia

Natural zeolites were discovered at Nizny Hrabovec in eastern Slovakia in 1976. Reserves of more than 7 Mt ranging in grade from 40% to 60% clinoptilolite have a mean cation-exchange capacity of 0.78 meq/g. K.S.K. (Kosice) mines between 7,000 and 12,000 ktpy of clinoptilolite from a deposit at Bystra Nad Toplou.

Slovenia

Zeolites are mined and processed at Zaloska Gorica. The operation produces ground and micronized clinoptilolite for pozzolan and agricultural use.

Spain

Mordenite occurs in an Upper Miocene bentonite sequence near Cabo de Gata, about 14 km from Almeria. Montmorillonite is the major component of the bentonite, with mordenite the next most common mineral. Minas Volcan SA has capacity to mine 10 ktpy of zeolites from quarries in Almeria Province. Bentonitas Especiales SA mines and processes zeolites in Madrid Province in conjunction with its bentonite mining operations.

Turkey

There are several very large deposits of clinoptilolite in the central part of the Bigadic Basin. The largest deposit is reported to have an extensive reserve of 82% clinoptilolite. About 9,000 tpy are produced by Yapi Insaat ve Ticaret AS and Zeolitas Turizm Yapi Ticaret ve Sanayi AS (C. Turner, personal communication).

Ukraine

Several large clinoptilolite deposits are present in the Ukraine. The Sokimitsa deposit in the Transcarpathian Ukraine contains 60% clinoptilolite that has a cation-exchange capacity of 1.44 meq/g. The Zatsyansky Chemical plant at Zakarpaty produces about 15 ktpy of clinoptilolite.

TECHNOLOGY

Exploration Techniques

Most productive deposits occur in zeolitized vitroclastic tuffs or tuffaceous sediments of Tertiary or, to a much lesser extent, Mesozoic age. Though deposits in other geologic settings may be developed in the future, it is almost certain that bedded deposits will remain the principal source of natural zeolites.

Exploration for zeolite deposits is a challenge. When the Union Carbide exploration program began in 1958, no one had ever explored for zeolite deposits. In fact, almost no one except for company geologists knew where zeolite deposits occurred, much less what the outcrop of a zeolite deposit looked like.

Union Carbide used a simple but effective technique to locate the white to yellowish-white outcrops of zeolite deposits in the intermontane valleys of the western United States. Geologic maps of the Tertiary formations in the valleys were nonexistent. The geologists flew in light aircraft at an altitude of about 150 m above the terrain and posted the light-colored outcrops on 1:250,000 scale topographic maps. The outcrops were sampled, and if the sample adsorbed carbon dioxide in the portable field adsorption unit, the outcrop was extensively sampled and mapped. The samples were then sent to the Linde Company laboratory in Tonawanda, New York, for oxygen adsorption and XRD analysis.

The exploration program based on visual analysis from aircraft was effective. The program discovered every zeolite deposit now in production. Unfortunately, the Molecular Sieve Department of the Linde Company was interested only in chabazite, erionite, and mordenite—the zeolite minerals that adsorbed oxygen and could be used as adsorbents. Therefore, there was no interest in clinoptilolite, which is now the zeolite with the greatest commercial potential.

This kind of exploration program for zeolites would still work well in undeveloped areas without undertaking a costly grassroots exploration program. Zeolites are difficult to identify in the outcrop

because they are so finely crystalline they cannot be identified with a hand lens. Zeolites resemble fine-grained tuffaceous rocks, bentonite, diatomite, freshwater limestone, and fine-grained sediments. Nevertheless, with a little experience, zeolites can easily be identified in hand specimens, but XRD analysis is needed to identify the specific zeolite minerals.

One exploration technique is to examine and sample known zeolite occurrences and then examine adjacent areas for outcrops that appear to be similar in appearance. Many of the known zeolite deposits in the world, especially in North America and Europe, have not been sampled and characterized adequately, so there are many opportunities to develop new zeolite deposits without undertaking a costly exploration program.

As the uses and applications of natural zeolites are expanded, new and innovative exploration methods may be required to locate new sources. Exploration programs will be developed that identify exploration targets based on the geology of the region, known zeolite occurrences, and the desired characteristics of a deposit that might yield specific zeolite products.

Field exploration for zeolites depends on careful geologic examination and sampling. Zeolitized tuffs usually appear to be altered rocks, but locally may not be distinguishable from unaltered rocks. Outcrops of zeolitized tuffs are commonly yellowish-white to gray, massive and blocky, and generally resistant to weathering; they may also exhibit distinctive surface textures. Natural zeolites may contain iron oxides or other minerals that produce outcrops with various shades of red, brown, yellow, or green.

XRD analysis of outcrop and drill samples is the most effective technique available to identify zeolite minerals. Specific zeolite minerals or mixtures of minerals may be identified, and semiquantitative estimates can be made of their abundance. Ammonia CEC determination of samples is also a very effective early screening technique for zeolitized tuffs believed to contain clinoptilolite, chabazite, erionite, or phillipsite. This screens out heulandite and analcime, which have similar appearances but almost no commercial potential.

Samples of mordenite, chabazite, and erionite require XRD and adsorption or separation tests to determine their zeolite content. The least expensive method of determining the purity of a zeolite mineral is to measure its adsorption capacity for water vapor at the standard temperature 25°C (77°F) and 40% relative humidity. The sample is heated to about low red heat in a porcelain crucible, then cooled and weighed. It then is placed in a desiccator overnight at the standard temperature and humidity and weighed again. The weight gain is compared to the increase of weight of a standard sample of known purity of the same zeolite mineral.

Once a zeolite deposit is identified, it must be sampled, mapped, and drilled to determine its consistency in mineralogy and purity and its vertical and horizontal extent. With this information, the geologic and minable reserves can be calculated. The deposit must then be bulk sampled. These samples are used for pilot-plant testing and also to provide samples for customer acceptance of the suitability of the product for specific uses and applications. If all these are satisfactory and a market has been established, the deposit can be brought into production.

Mining Methods

Both bedded sedimentary and thick vitroclastic zeolites deposits are mined by surface methods. Conventional earth-moving equipment, including scrapers and loaders, are used to mine the zeolite bed. Selective mining and blending during removal or stockpiling controls any variations in the purity of the ores. Sampling drill holes, the area being mined, the haulage truck, and the process stream are all used for quality control.



Figure 6. EZ chabazite mine, Bowie, Arizona

Zeolites for special, high-value applications require selective open-pit mining. Dow Chemical Corporation, which now owns and operates the deposit in Bowie, Arizona, manufactures high-value molecular sieve and ion-exchange products mined from the 15-cm-thick chabazite bed (see Figure 6). Before mining, the deposit is drilled on 15.25-m or 7.62-m centers. Overburden is stripped from the bed with self-loading scrapers. All the overlying thin-bedded chabazite waste is scraped off with a road grader. The bed is then pulled up with a backhoe. Any clay adhering to the bottom of the chabazite is scraped off by hand.

The chabazite from each pit is stored in a separate stockpile. Chabazite is blended from the stockpiles to guarantee that every shipment contains no less than 85% chabazite. Each railroad car shipment is sampled. The samples are sent to the processing plant so that the chabazite content of the car is known prior to its arrival at the plant.

Mining at the Mud Hills clinoptilolite deposit in Southern California recovered ore with strict specifications in 30-cm slices from a 4.6-m-thick deposit to yield a very high value product for ion-exchange media used by BNFL.

Processing

Natural zeolites are crushed and screened into granules that range from coarse to fine. Some zeolites are micronized to products with a particle size of less than 5 μm . The granules are used in soil conditioners, aquarium filters, feed supplements, animal absorbents, or cat litter. Chabazite granules used in desiccant applications are double activated at 260°C (500°F) and shipped to the customer in sealed containers. The chabazite produced for adsorption applications is ground, mixed with a binder, extruded, and activated at 424°C (795°F) (see Figure 7).

Natural zeolites can be enhanced in performance by washing them with acid or NaCl (sodium chloride) solutions to raise the H^+ or Na^+ content, respectively. Clinoptilolite products are particularly enhanced in ion-exchange capacity by washing to replace the slower reacting K^+ ions with Na^+ ions. Thermal treatment of clinoptilolite slows calcium from blocking exchange sites (Eyde 2000).

Specifications

Specifications are based on the end use application of the zeolite product. The user almost always sets the specifications. The pro-



Figure 7. Zeolite processing plant at the Ash Meadows Deposit near the California-Nevada border

ducer must guarantee that the zeolite product will meet or exceed the user's specifications. A chabazite product used in a desiccant application would specify the weight percent of water adsorbed at a specific temperature and humidity. Clinoptilolite used in cation-ion exchange would have to exchange a specific amount of the ion being exchanged.

Natural zeolites must have a specification sheet that provides information on the chemical and physical properties of the product. The American Society for Testing and Materials (ASTM) Committee No. D-32 was established to set testing methods and standard specifications for zeolites in the United States. Unfortunately, the committee has not been successful in setting testing standards for natural zeolites.

Industrial mineral producers deal with specifications in two ways—either by selling products on a custom basis to the specifications negotiated with the buyer or selling them on a product-line basis where each product has a name or number designation and specific physical or chemical standards. In the United States and Europe, zeolite products are commonly sold under a trade name rather than a mineral name. Tables 3 and 4 are sample specification sheets for chabazite and clinoptilolite products.

Testing for Zeolite Mineral Identification

Natural zeolite minerals are identified primarily by their crystal habit. Chemical analyses alone are not a satisfactory method of identification because they all have similar chemical compositions. The same zeolite from different localities or even from different parts of the same deposit may not have exactly the same chemical composition. Macroscopic zeolites, particularly those occurring in vesicles and fractures in basaltic rocks, can be identified by careful visual examination. In virtually all the deposits being mined, the minerals are of microscopic grain size. Positive identification and semiquantitative determination of such fine-grained materials can be done only by laboratory methods. The principal methods of identification are XRD and scanning electron microscopy (SEM). Neither optical microscopy nor differential thermal analysis (DTA) is particularly useful for identifying zeolite minerals.

X-ray Diffraction

XRD is the most reliable and widely used method for identifying zeolite minerals and providing a semiquantitative estimate of the

Table 3. Chabazite* properties

Typical Properties	
Form	Powder or granules
Color	Light brown (dry brightness 43)
Ring members	8
Crystal size—chabazite	Less than 1 μm
Crystallinity	+90%
Density	1.73 g/cm ³
Pore size	4.1 \times 3.7 \AA
Effective pore diameter	4.3 \AA
Cavity size	11.0 \times 6.6 \AA
Total pore volume	0.468 cm ³ /g
Surface area	520.95 m ² /g
Crystal void volume	0.47 cm ³ /cm ³
Packing density	Approximately 577 kg/m ³ (36 lb/ft ³)
SiO ₂ :Al ₂ O ₃ ratio	Approximately 4:1
Mohs hardness	4–5
Moisture as packaged	Less than 10% by weight
Stability	pH 3–12
Ion-exchange capacity	2.50 meq/g

Typical Chemical Analysis

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	LOI [†]	Dominant Cation
54.6	14.9	2.28	0.22	0.60	6.67	0.90	19.4	Na

Exchange Selectivities

$\text{Ti}^+ > \text{Cs}^+ > \text{K}^+ > \text{Ag}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{Pb}^{2+} > \text{Na}^+ = \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Li}^+$

Exchange of Heavy-Metal Ions[‡]

Ag		Pb		Cu		Co	
pH	wt %	pH	wt %	pH	wt %	pH	wt %
5.30	21.65	3.80	5.27	3.43	3.17	2.91	2.82

* Hydrous sodium aluminosilicate, natural herschelilite-sodium chabazite (CHA)

[†] LOI = loss on ignition

[‡] Weight percent of heavy metals retained in chabazite after ion exchange from a 0.10 mg/mL solution $\text{AgNO}_2 + \text{Pb}(\text{NO}_3)_2^{2+}$, CoSO_4 , and a 0.025 mg/mL solution of CuSO_4 at the initial pH indicated for each solution.

percent present in the sample (Papke 1972). This method has a high degree of accuracy and can readily be used to identify individual minerals in mixtures of zeolite and nonzeolite minerals. A skilled technician is required to operate the XRD equipment, which may be automated and able to run multiple determinations unattended, and to interpret the results. XRD analysis is a nondestructive method, and the powder used for the analysis can be further tested. The method is least reliable in mixtures of minerals; the lower detection limit for an individual zeolite is about 1%. An experienced mineralogist is needed to interpret the diffraction trace. Papke (1972) and Slansky (1987) give more detailed descriptions of the XRD method.

Scanning Electron Microscopy

The scanning electron microscope is effective in identifying zeolite minerals and establishing their size, morphology, genesis, and mineralogic setting. Magnifications of several thousand times or more allow a visual examination of the zeolite minerals in small samples mounted on a specimen holder. Representative samples must be used to avoid misleading results. SEM analysis is relatively slow and costly.

Table 4. Clinoptilolite properties

Typical Properties*	
Silica:alumina ratio	5.8:1–6.4:1
Silicon:aluminum ratio	5.1:1–5.7:1
Bulk density (dry solid)	87 lb/ft ³ (1,394 kg/m ³)
Bulk density (dry, loose)	51–60 lb/ft ³ (817–961 kg/m ³)
Mohs hardness	5.1
Nominal channel size	4.0 \times 4.6 \AA
Porosity	15%
Specific surface area	1,357 yd ² /oz (43.8 m ² /g)
Alkali stability (pH)	7–13
Acid stability (pH)	1–7
Thermal stability	1,292°F (700°C)
Crushing strength	2,500 lb/in. ² (176 kg/cm ²)
Wet attrition (average)	6%–7%
G.E. brightness (N.C. State University)	71.5

Chemical Analysis, % (The Mineral Lab, Inc.)

	Major Exchangeable Cations (USBM) [†]	
	X-ray Fluorescence Results	Normalized to 100%
SiO	66.9	76.7
Al ₂ O ₃	10.5	12.0
CaO	1.15	1.32
MgO	0.57	0.65
Na ₂ O	2.95	3.38
K ₂ O	4.12	4.72
Fe ₂ O ₃	0.92	1.05
TiO ₂	0.11	0.13
MnO	0.03	0.03
LOI [†]	9.00	NA [§]

Heavy Metal Cations (USBM)[†]

$\text{Pb}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Ca}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$

Primary Adsorbed Gases

NH_3 CO CO_2 SO_2 H_2O N_2
Freon, formaldehyde, mercaptans, benzene, methanol

Adapted from Ash Meadows Zeolite L.L.C.

* Total cation exchange capacity (CEC) 1.4 to 2.1 + meq/g; average clinoptilolite content >85%

[†] In order of selectivity for exchange

[‡] LOI = loss on ignition

[§] NA = not applicable

Optical Microscopy

Optical microscopes are generally ineffective in identifying zeolite minerals in zeolitized tuffs because of the very small grain size of the zeolite minerals, their low birefringence, and variation of their indices of refraction with changes in chemical composition.

Differential Thermal Analysis

DTA can be used to identify zeolite minerals, but the method is not effective when several zeolites or certain other minerals are present or when only a small quantity of a mineral is available. Variations in the exchangeable-cation content may also cause differences in the differential thermal curve. The method is very useful in distinguishing clinoptilolite from the closely related mineral heulandite. Gottardi and Galli (1985) published a comprehensive collection of DTA curves for natural zeolites.

Other Methods

Other analytical methods can be used in special circumstances but they are generally complex, very costly, and not currently practical for exploration or quality control. Such methods include infrared

absorption spectrography, Mossbauer spectroscopy, electron spin resonance spectroscopy, electron spin echo spectrometry, solid-state nuclear magnetic resonance, neutron diffraction, and synchrotron XRD (Slansky 1987).

Testing for Characterization

In characterizing zeolitic materials for commercial uses, it is important to quantify other physical and chemical properties required by the specific application. The following are physical and chemical properties and tests that may typically be required: wet chemical analysis; CEC; specific gravity and bulk density; brightness, whiteness, and color; hydration/dehydration; gas adsorption; attrition in water; internal and external surface area; pore size; and volume.

By-products and Coproducts

Deposits containing two or more zeolites may yield several individual varietal products or mixtures of the zeolite minerals. For example, zeolite products from the Itaya mine in Japan, a clinoptilolite and mordenite deposit, include mordenite, clinoptilolite, and mixed mordenite-clinoptilolite products depending on the selectivity of mining and processing.

Zeolite mining may yield bentonite as a by-product or coproduct. Bentonite commonly occurs in the same geologic setting as natural zeolites. At the Teague Mineral Products operation in Oregon, both minerals are mined from nearby pits and processed in the same grinding plant.

USES

Agricultural Products

Zeolites are used as soil conditioners and fertilizer extenders, particularly in Japan, Cuba, and the former Soviet bloc countries in Eastern Europe. Zeolites increase the cation-exchange capacity, improve moisture retention, and, because of their high pH, buffer acidic soils. Zeolites act as a slow-release media for ammonia and to a lesser extent potassium. Zeolite soil conditioners preloaded with nitrogen are now available. The zeolite crystal structure shields the ammonium ion from rapid consumption by nitrifying bacteria (Ferguson 1984), allowing a reduction in the amount of nitrogen fertilizers applied to the soil. Chabazite and clinoptilolite are effective carriers of herbicides, pesticides, fungicides, enzymes, and bacteria because of their high ion-exchange and adsorption capacities.

Zeolite-polymer blends are being used to improve water retention in sandy soils. In fields watered by pivot irrigation systems, the production of corn increased by 30% and water consumption decreased by nearly an equivalent percentage (R. Salestrom, personal communication). A test plot on tailings from a large open-pit copper mine in Arizona was treated with a mixture of clinoptilolite-polymer blend and dry municipal sewer sludge. Native desert vegetation established itself on the test plot without being either seeded or irrigated (S.A. Bengston, personal communication).

Zeolites also act as scavengers for heavy-metal ions such as cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) in soils, particularly those contaminated by industrial wastes. Clinoptilolite added to soils contaminated with strontium-90 and cesium-137 reduces the uptake of these radioisotopes by plants in areas contaminated by radioactive fallout, such as around the damaged Chernobyl reactor.

Animal Nutrition

Adding clinoptilolite to animal feeds in controlled amounts increases utilization of feed and decreases ammonia stress in animal digestive systems. Controlled feeding of clinoptilolite to chickens,

turkeys, and swine has increased growth rates, improved feed efficiency, reduced the incidence of diarrhea and related health problems, and produced a drier and less odoriferous excrement. Also, excrement and sewer sludge treated with zeolites are more effective fertilizers because their slow-release properties prevent fertilizer burns on the plants. The zeolite-treated manure is drier and less odoriferous than composted manure.

Feeding clinoptilolite, and to a lesser extent mordenite, to animals is an accepted practice in Japan, Cuba, Bulgaria, and Hungary (Griffiths 1987). The use is growing slowly and steadily in the United States and in Russia, but it is still not widely accepted (Pond 1993).

Clinoptilolite fed to broiler chickens in amounts of 1% to 3% of the total feed increases feed efficiency and lowers the time required to reach a marketable size. Laying chickens fed supplemental zeolite took fewer days to the first egg, had increased numbers of eggs, and had general improvement in health through a reduction in fecal bacteria (Griffiths 1987).

Clinoptilolite also reduces the incidence of post-weaning diarrhea when added to the starter diet of young pigs. A zeolite used as a feed supplement may also reduce the levels of antibiotics needed in feeds, particularly for swine.

Aquaculture

Zeolites are used in aquariums, fish farms, and fish hatcheries to avoid the buildup of ammonia to toxic levels. Fish hatcheries are using self-contained systems that recycle water to reduce downstream contamination from their effluent. Clinoptilolite is highly effective in the removal of ammonia from recirculating fish culture systems. In oxygen-poor environments, concentrations of less than 1 ppm ammonia can damage gill tissue, increase the incidence of gill disease, reduce the rate of growth, and increase mortality (Mumpton 1977).

In Alabama and Mississippi, clinoptilolite is being used to remove ammonia from catfish ponds (Williford, Reynolds, and Quiros 1991). Ammonia-removal kits containing granular clinoptilolite as the ion-exchange media are available in many pet supply stores for home aquarium use. The U.S. Fish and Wildlife Service has also successfully used clinoptilolite-charged systems for recirculating water in tank trucks transporting live fish.

Catalysis and Petroleum Refining

Zeolites with large channel sizes have large internal surface areas and can catalyze many types of reactions (Dwyer 1984). Though natural zeolites have been used in sorption applications in the petroleum and petrochemical industries, synthetic zeolites are generally used because of their larger channel sizes, greater adsorption capacities, and uniformity. Chabazite is used to remove water, carbon dioxide, and hydrogen sulfide from gaseous hydrocarbons, to remove HCl from gas streams, and to dry hydrogen and chlorine.

Desiccants

Activated chabazite is used as a carrier and desiccant in packaged enzymes and bacteria used to inoculate silage. Partially activated clinoptilolite and chabazite are used as anticaking agents in cattle feeds containing mineral and organic supplements and other bulk agricultural and chemical products shipped in pneumatic containers. Small amounts of zeolite desiccant are blended with animal feed, fertilizers, and hygroscopic chemicals before sealing the products into bags.

Dimension Stone

Zeolitic tuffs have been used for thousands of years as lightweight, durable dimension stone. The physical properties of such stone are

important. Zeolitic tuffs have low bulk densities, are weather resistant, have superior insulating properties, and can be easily cut into attractive stone.

Many buildings in ancient and modern Rome and Naples have been constructed from local zeolite sources, particularly from the Neapolitan Yellow Tuff (Aiello 1993). In central Europe, many buildings and cathedrals were constructed with blocks of zeolitic tuff. Quarries in the Laacher See Area in Germany, Kurdzali in Bulgaria, and Tokaj in Hungary produced blocks of zeolitic tuff for dimension stone used in building construction.

Several sources in Japan have produced zeolitic dimension stone for centuries, particularly from pumiceous marine tuffs in the Green Tuff region, Tochigi Prefecture. The principal source is a quarry near Otsunomiya City, where a green tuff bed 108 m thick has been mined for hundreds of years (Mumpton 1978).

In the United States, the use of zeolitic tuff dimension stone has been limited to a few areas in Nevada and Oregon, where several structures were constructed from blocks of zeolitic tuff from local quarries. The old Nye County courthouse, St. Patrick's Catholic Church, and several commercial buildings in Tonopah, Nevada, were built with blocks of zeolitic tuff.

Gas Separation

Zeolites are used to separate nitrogen and oxygen to produce a gas stream containing up to 95% oxygen. Mordenite appears to be the best natural zeolite for oxygen generation, although clinoptilolite and chabazite have also been used; pressure swing adsorption (PSA) plants using synthetic zeolites have displaced the compression-expansion air-separation systems.

PSA plants that use mordenite were designed and used principally in Japan to supply oxygen for basic oxygen furnaces in steel mills. PSA plants supply oxygen to municipal wastewater treatment plants, hospitals, and other users. Perhaps the most important application is the small oxygen generators used in homes to provide continuous oxygen to patients with pulmonary diseases. Natural zeolites have been displaced in virtually all the industrial and medical applications by synthetic zeolites, which have significantly higher adsorption capacities than natural mordenite.

Ion-Exchange Applications

The ability to exchange cations is one of the most important properties of zeolites. Cation-exchange capacity is a measure of the number of cations per unit weight available for exchange, usually expressed as milliequivalents per gram or milliequivalents per 100 grams of zeolite. The ammonia ion is most commonly used for CEC testing. The result is referred to as the ammonia ion-exchange capacity.

Both chabazite and clinoptilolite are used to treat mine water and metallurgical effluents. Because chabazite has a higher selectivity for thallium than any other natural zeolite or ion-exchange resin, it is used to remove thallium from mine water. Sodium chabazite modified with ferrous iron removes arsenic from solution without first converting it to arsenate (Eyde 2000). The ZELfloc technology uses clinoptilolite to treat municipal sewage (Eyde 2000).

NSF International approved clinoptilolite for use in swimming-pool filtration systems. In these systems, granular clinoptilolite replaces the sand in the filter. Clinoptilolite is superior to sand because it removes chloramines, heavy metals, urea, and organic matter from the pool water.

Synthetic zeolites are used in detergents. This is because natural zeolites are not uniform in purity and composition; are inferior in color, brightness, and CEC; and have smaller channel sizes and higher percentage of iron and other impurities. Natural zeolites are superior to synthetic ones for uses such as the treatment of radio-

active waste or the removal of metals from low-pH solutions because of their hardness and resistance to attrition and degradation by intense radiation.

Fine grinding of zeolitic materials can improve their CEC by increasing their surface area, especially when the zeolite (usually mordenite) has a low permeability. Zeolite minerals with high CEC include clinoptilolite, erionite phillipsite, chabazite, and mordenite. Minerals with low CEC include heulandite, laumontite, and analcime.

Medical and Personal Care Applications

The U.S. armed forces uses zeolite products that stop bleeding from wounds by promoting clotting (Healy 2003). Clinoptilolite has been used successfully as a polishing agent in fluoride-containing toothpaste by allowing a higher level of fluoride to remain in anionic form (Kato et al. 1970). Clinoptilolite is encased in tampons to control odor and reduce the incidence of sepsis. Because of its ability to absorb ammonia ions from air and water, clinoptilolite has been used in products such as baby powder and filler in disposable baby diapers, and as an ammonia control product in diaper pails.

Natural Gas Purification

Chabazite has been used to separate carbon dioxide, hydrogen sulfide, and other gases from methane produced from natural gas and oil wells (Mumpton 1978). Other sources of methane that use either synthetic or natural zeolites to remove noncombustible gases and contaminants include municipal wastewater treatment plants, sanitary landfills, and animal waste treatment facilities. NRG Corporation constructed two gas treatment plants in the Los Angeles, California, area that used the NuFuel PSA process to produce pipeline quality methane. The Palos Verdes Landfill plant treated gas containing about 50% methane and 40% carbon dioxide to produce about 30,000 m³ of methane per day. The other NRG Corporation plant treated casing head gas at the Farmers Market oil field. Both plants used activated extrudates produced from chabazite mined at the Bowie, Arizona, deposit (Anon. 1975).

Nuclear Waste Treatment and Handling

Chabazite and clinoptilolite are used in the treatment, handling, and containment in engineering structures for the storage of nuclear wastes (Grant, Skriba, and Saha 1987; Grant et al. 1988, 1989). Natural zeolites have the unique ability to selectively remove Sr⁹⁰, Cs¹³⁷, and other dangerous isotopes from solutions containing high concentrations of competing ions. Natural zeolites are less expensive than organic ion-exchange resins and much more resistant to degradation from radiation. Zeolites melt at low temperature into a stable silicate glass, which greatly reduces the volume of the radioactive waste. By encapsulating the radioactive glass in concrete, the radioactive cations can be safely stored in a secure disposal site.

The Hanford Laboratories of Battelle Pacific Northwest Laboratory in Richland, Washington, initially demonstrated the high efficiency of clinoptilolite from Hector, California, in removing radioactive Cs¹³⁷ and Sr⁹⁰ from low-level waste streams at nuclear facilities. Radioactive solution treatment at Hanford has processed millions of gallons of solutions. A comparable Sr⁹⁰/Cs¹³⁷ waste treatment is used at the National Reactor Testing Station at Arco, Idaho; West Valley, New York; and other nuclear facilities. Chabazite products IE-95 and IE-96 from the Bowie deposit were used in the cleanup of the Three Mile Island nuclear power plant site (King and Opelka 1982; Bostick and Guo 1996).

Ion-exchange treatment utilizing clinoptilolite has also been used for nuclear-waste treatment in other countries, including Russia, Ukraine, Japan, Hungary, Bulgaria, Canada, Italy, the United

Kingdom, France, and Germany. Large tonnages of clinoptilolite were used in direct application to contaminated soils at the devastated Chernobyl nuclear power plant to contain radioactive contaminants spilled during the accident (Griffiths 1987; Chelishchev 1993).

Mixed clinoptilolite and mordenite have been used for Cs¹³⁷ removal in Japan (Kato 1974). Clinoptilolite from the Tokaj District in Hungary has been used to encapsulate Sr⁹⁰ for solid waste disposal and removal of Sr⁹⁰ and Cs¹³⁷ from effluent waste streams (Adam, Kakasy, and Pallos 1971). In Canada, clinoptilolite was used to recover Sr⁹⁰ and Cs¹³⁷ from waste solutions in underground disposal sites at Chalk Run, Ontario (Mathers and Watson 1962).

Chabazite and phillipsite from the Neapolitan Yellow Tuff at Naples, Italy, have been used to remove Cs¹³⁷ and Sr⁹⁰ from nuclear effluents. The zeolite minerals loaded with the radioactive cesium and strontium were stored in secure underground disposal sites at Cassaccig, Italy (Anon. 1972).

BNFL uses clinoptilolite from the Mud Hills deposit near Barstow, California, to selectively exchange Sr⁹⁰, Cs¹³⁷, and other radioisotopes from effluent waste streams at its nuclear fuel reprocessing plant at Sellafield, U.K. (Anon. 1990). Levels of Sr⁹⁰ and Cs¹³⁷ in the clinoptilolite-treated plant effluent, which is discharged into the Irish Sea, have dropped to very low levels.

Battelle Pacific Northwest Laboratory uses clinoptilolite in engineered sorbent barriers in containment and waste storage structures for low-level nuclear wastes (Freeman and Jones 1989).

Odor Control

Natural zeolites, particularly clinoptilolite, adsorb ammonia ions. This process suppresses odors from fecal matter and urine. Hydrated zeolites adsorb ammonia vapor; when the gas enters the zeolite pores, it bonds to or replaces crystalline water (Frederickson 1987).

In Europe and the United States, clinoptilolite is used as pet litter and to suppress odors in horse stalls (Eyde 1987). In Japan, clinoptilolite and mordenite are used to control odors from poultry and swine. Crushed and sized zeolites, principally clinoptilolite, have proven effective in controlling the pungent odor of ammonia fumes produced when animal excrement dries (Griffiths 1987). Granular clinoptilolite is applied directly to the floors in pens and stables and in litter trays for cats and small pets. Adding clinoptilolite as a supplement to animal feeds has a nutritional benefit in addition to reducing the odor from fecal matter and urine.

Natural zeolites, notably clinoptilolite, chabazite, and phillipsite, have also been used for odor control in personal products (e.g., in athletic shoes). Room air cleaners with zeolite filters have also been used in living quarters and to remove high-ammonia urine odors in nursing homes and similar facilities. Ground clinoptilolite is effective as a dry carpet cleaner, particularly to remove pet odors.

Paper Fillers

Natural zeolites have been used as fillers in some specialty paper products. Clinoptilolite and the crystalline quartz that occurs as an impurity in the zeolitic tuffs are abrasive. In addition, clinoptilolite has a low brightness and a poor color (Kobayashi 1970). Clinoptilolite is not competitive with kaolin and calcium carbonate for either coating or filling most paper products.

Pozzolan and Cement

Pozzolan is a naturally occurring cementaceous material that can replace up to 25% of the portland cement in concrete. Pozzolans both improve the quality and reduce the cost of concrete. Zeolitic tuffs have been used as pozzolan in many places in the world. The Romans employed pozzolanic materials in aqueducts, public buildings, and highways using the Neapolitan Yellow Tuff near Poz-

zuoli, Italy. In Europe, zeolites are being mined in Serbia, Germany, Bulgaria, and other countries for use as pozzolan. The minerals used include clinoptilolite, natrolite, skolezite, and phillipsite.

Monolith Portland Cement Company mined zeolitic ash-flow tuffs near Tehachapi, California, for pozzolan in cement. The use of pozzolanic cements in the construction of the 400-km-long Los Angeles aqueduct in 1912 saved several million dollars by enabling a 25% reduction in the amount of cement consumed.

GSA Resources and C2C Corporation developed a light-weight, oil-well cement additive that Halliburton Energy Services is evaluating. The additive is based on the chabazite in the thin-bedded horizon that overlies the high-purity ore bed at the Bowie Arizona, deposit. The additive is blended with the portland Class G cement to optimize placement within a well bore. The technology is based on research done at the Institute of Architecture, Slovak Academy of Sciences (Janotka, Krajčič, and Dzivák 2003).

Sewage Treatment

Clinoptilolite and chabazite remove ammonia and some heavy metals from sewage and other effluent streams. The ammonia removed can be discharged into the atmosphere, recovered as a gas by-product, or converted to an ammonium sulfate fertilizer. Plants in Truckee, California; Rosemont, Minnesota; and Manassas, Virginia, have operated successfully for many years using clinoptilolite in tertiary sewage treatment processes to remove ammonia.

Zeolite Australia licensed the ZELfloc technology that uses zeolites for municipal wastewater treatment. The company has 14 wastewater treatment plants using the technology (Eyde 2000). Supersorb, another Australian company, has undertaken full-scale trials of an activated zeolite technology at the Water Corporation of Western Australia Kwinana Wastewater Treatment Plant in Queensland (Crossley 2000).

An improved environment is the incentive behind the increased use of zeolites in tertiary wastewater treatment. Ammonia ions should be removed because they are toxic to fish and other aquatic life and contribute to rapid growth of algae and the eutrophication of streams and lakes.

Solar Energy and Heat Exchange

Chabazite and clinoptilolite absorb and release heat from solar radiation for air conditioning, refrigeration, and water heating applications. The dehydration of the zeolite during the day and its rehydration at night result in the exchange of several hundred BTUs per kilogram of zeolite, sufficient to operate refrigerators or to cool small buildings (Tchernev 1993). The study estimated that 1 t of zeolite in solar panels spread over 19 m² of roof surface will produce 1 t of air conditioning. Recreational uses such as in beverage coolers, and use in less developed countries where power is not available to refrigerate medical supplies and food, are important applications.

Stack Gas Cleanup

Natural zeolites can be used to remove sulfur dioxide from the stack gases of coal-burning power plants. Clinoptilolite and mordenite can adsorb as much as 200 mg of SO₂ (sulfur dioxide) per gram of zeolite under static conditions and as much as 40 mg under dynamic conditions, even in the presence of high percentages of carbon dioxide. These zeolites are especially suited to the low-pH and high-temperature conditions of exhaust gas systems

ECONOMIC FACTORS

Markets

Synthetic zeolites were produced and used for many years before Union Carbide discovered large deposits of chabazite, clinoptilolite,

erionite, and mordenite. In fact, their Linde Company subsidiary that developed and sold the first 5A molecular sieve products marketed the Bowie chabazite as their AW500 synthetic zeolite product in 1961. AW500 was sold into applications where the adsorption bed was exposed to an acidic environment in which the 5A synthetic molecular sieve quickly deteriorated.

Union Carbide was not interested in the mineral clinoptilolite because at that time it had no adsorption applications. Had the company been interested in clinoptilolite, it could have acquired all of the major deposits in the western United States. Although W.R. Grace and Company acquired the eastern part of the Bowie chabazite deposit in 1965, no major mining or oil companies acquired large zeolite reserves until they entered the natural zeolite business about 10 years later.

Natural zeolites are still an undeveloped facet of the zeolite business. Synthetic zeolite sales worldwide total several billion dollars, whereas natural zeolite sales are only a few million dollars. No formal commodity markets exist, and sales for lower value products are confined mostly to countries with zeolite resources. Higher value products may be sold internationally, but their total value worldwide is still small. Synthetic zeolites have established major, growing markets through silicate chemical manufacturers, mostly in North America, Western Europe, and Japan.

Because of their very wide range of applications, natural zeolites sell into diverse markets. Japan has a particularly wide range of zeolite markets for agricultural, industrial, and consumer uses. North American sales are principally for agricultural, ion-exchange, and pet litter applications. Markets in Western Europe, the former Eastern bloc countries, and Cuba are primarily for agricultural products, with a growing industrial market sector.

The fastest growing market sector is for ion-exchange applications. Clinoptilolite is a superior swimming pool filtration product that will displace sand as the preferred media. The new tertiary wastewater treatment systems will experience continuing strong growth.

Steady growth is anticipated for agricultural, industrial, and consumer applications. The strongest areas of market growth in North America are expected to be in water treatment, deodorants, pet litter, soil treatment, and nuclear waste treatment and containment.

Values and Costs

The cost of zeolite products depends on the type and degree of processing that must be done to satisfy targeted market specifications. Mining costs are generally fairly low, typically \$3 to \$6/t, unless very selective mining is done.

Most natural zeolites are sold into low-value industrial or agricultural markets, commonly selling for \$30 to \$70/t for granular products down to 40 mesh, and \$50 to \$120/t for ground materials in a range of -40 to -325 mesh. Consumer products such as pet litter, fish-tank media, or deodorant materials commonly sell for \$0.50 to \$4.50/kg at the retail level.

Products for specialty industrial applications, such as radioactive waste filtration media, specialty adsorbents, and surface modified products, are sold for several dollars per kilogram or thousands of dollars per ton. Specialty materials with products developed for specific markets are highly profitable even though the market for these products may be very limited.

Transportation

Zeolite products are generally transported by highway or rail carriers in bulk, in 1-t "supersacks," or in multiwall paper bags, usually

palletized. The products are not hazardous and present no special problems, subject to proper labeling and handling. Chabazite and clinoptilolite, which have been stored at high temperatures or low humidity, can adsorb several weight-percent water if their destination has a high humidity. Zeolites prepared as dimension stone are shipped as any other stone products, generally palletized and by truck.

Transportation costs strongly affect the distance a lower-value zeolite can be hauled to reach markets. Agricultural-grade clinoptilolite from the western United States can reach markets in the eastern half of the country.

Future imports from Greece, Italy, China, and other tidewater sources with low ocean freight rates could make some materials produced in the western United States uncompetitive. High-value-added zeolites can generally be shipped nationwide and even to international destinations because the freight is such a small incremental cost in relation to the cost of the product.

Alternate Materials

Natural zeolites are competitive on the basis of price and performance with other mineral products. It is difficult for a new product to displace one with performance characteristics that are known and are satisfactory to the user. There are many established alternate materials for most zeolite applications. Market entry of a natural zeolite product requires equivalent or superior performance or a significant cost advantage over the product being used.

Synthetic zeolites (molecular sieves) are natural zeolites' principal competitor. Synthetic zeolites often can be modified in physical and chemical properties to enhance their performance in specific applications. The synthetics are more uniform in quality than their natural equivalents. Natural zeolites have an advantage over synthetic materials in some applications (e.g., cesium and strontium adsorption in radioactive waste cleanup) and are also able to function at lower pH levels. They are also generally less expensive than synthetic zeolite products, which gives them a superior price performance ratio.

Activated carbon, synthetic ion-exchange resins, and similar materials can be more effective than zeolites for many ion-exchange applications. Activated bentonite, silica gel, calcium oxide, calcined gypsum, and other minerals also can be competitive adsorbents and desiccants in a comparative price range.

GOVERNMENTAL CONSIDERATIONS

Taxes, Subsidies, and Depletion Allowance

No specific taxes are related to zeolites, and the material is not subject to any government subsidies in the United States and Canada. The depletion allowance is 14% for natural zeolites mined in the United States.

Zoning and Land Use

Natural zeolite deposits experience zoning and land use restrictions similar to most other fine-grained minerals such as kaolin or diatomite. Most zeolite deposits are located in rural areas, so their utilization seldom interferes with urban development. The very large zeolite deposits around Naples, Italy, are a conspicuous exception, but the deposits are so extensive that many other sites in the region are available where disturbing residential or industrial lands is not an issue.

Environmental Regulations

Environmental regulations are always a matter of concern. Excessive regulation is always a source of conflict between government

regulators and mine operators. Natural zeolite mines and processing facilities generally present no serious environmental problems, with two possible exceptions:

1. Erionite and mordenite may be fibrous. Fibrous erionite is a Class I carcinogen. Mordenite is not known to be a carcinogen.
2. Crystalline silica commonly occurs in zeolite deposits, and the finely ground products may contain more than 0.1% respirable silica.

Natural zeolites are dusty materials when crushed and ground. Therefore, air quality standards should be maintained carefully during mining and processing.

Fugitive dust from mining and plant facilities may be considered a local environmental pollutant. Most zeolite deposits contain silica minerals in the form of amorphous silica such as opal or opal-CT, cristobalite, or crystalline silica. Processing plants therefore must have air-pollution control systems ranging from standard bag-house dust collectors to electrolytic precipitators to minimize worker exposure to fugitive dust at grinding mills or bagging stations and to comply with local air quality control requirements. Most zeolite production uses dry processing methods.

Zeolite processing will inevitably use water-washing and wet classification methods, requiring proper handling of plant effluent and tailings pond discharges. Zeolite minerals are generally considered to be chemically inert, and most are nonfibrous. Erionite is classified as a fibrous, acicular mineral and has been labeled a human carcinogen on the basis of medical studies of the large number mesothelioma cases in the Capadoccia District of Turkey. Mordenite is also a fibrous mineral but is currently not regarded as a potential carcinogen.

FUTURE TRENDS AND PROBLEMS

Future Trends

The zeolite industry continues to develop new applications in both industrial and consumer markets. Most of this activity and growth, however, has been in synthetic zeolites. Most natural zeolites uses are in commodity and lower-value applications such as agriculture or pozzolan. This is changing. Specialty and consumer applications are the fastest growing segments of the natural zeolite market.

Chabazite and clinoptilolite are the only ion-exchange products that do not degrade when exposed to radiation. The zeolites used to clean up radioactive waste streams sell from \$2/kg to as much as \$14/kg. Clinoptilolite is displacing sand as a filtration media in swimming pool filters. These are applications where the physical and chemical properties of natural zeolites are superior to synthetic zeolites or other ion-exchange media.

Although the production of natural zeolites in North America is growing slowly, the value of this production is increasing more rapidly. This has occurred because of the shift from commodity to specialty and performance products. This trend will continue as more specialty products such as clinoptilolite coated with the quaternary amine hexadecyltrimethyl-ammonium are developed. (Bowman 2003). These organophilic zeolite products are now available for removing organic chemicals from ground- and surface waters. The coated zeolite products do not swell in water and therefore can displace organoclay products that swell and block circulation.

The producers of natural zeolite have characterized their products and provide specification sheets that document the physical and chemical properties. Still, no high-purity-beneficiated zeolite products are available. The technology is available to beneficiate zeolites by air separation, wet processing, or flotation. Until beneficiated clinoptilolite products become available as powders, beads,

or extrudates, natural zeolite products will be unable to gain access to many high-value-added specialty and performance uses and applications.

The highest purity zeolite product available in North America is the chabazite from the Bowie, Arizona, deposit. This unique deposit was formed when airborne volcanic ash from a distant volcanic eruption was deposited in a saline alkaline lake. By the time the ash arrived at the lake, virtually all the other minerals had been removed by natural air separation and only the glass fraction remained.

Problems

The use of inclusive generic mineral names for both the fibrous and nonfibrous varieties of erionite, phillipsite, and mordenite is inaccurate and has resulted in the designation of the nonfibrous varieties of these minerals as carcinogens. Nonfibrous erionite, phillipsite, and mordenite were identified in samples being studied for the U.S. Bureau of Mines report on size and shape characterization of fibrous zeolites by electron microscopy (Shedd, Virta, and Wylie 1982). The erionite in the Bowie deposit was judged to be nonfibrous. Yet the *Sixth Annual Report on Carcinogens* classifies all erionite as fibrous and as a carcinogen (Eyde 1996).

Because erionite has been classified as a carcinogen, it cannot be used in consumer products. The presence of even trace amounts of erionite may prevent its use or consideration for some applications. Mordenite has also been designated as a fibrous mineral but has not been classified as a carcinogen. Figures 8 and 9 illustrate the differences in the crystal morphology between fibrous and non-fibrous erionite (Eyde 1996). Natural zeolites usually contain some crystalline silica, which must be listed on the Material Safety Data Sheet.

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The zeolite chapter in the 6th edition of *Industrial Minerals and Rocks* was a carefully researched and referenced chapter that accurately summarized the content of the four outstanding individual papers in the 5th edition. This chapter has relied heavily in places on the data in the 6th edition (Holmes 1994), using some sections with no or very little change. The goal in the 7th edition is to update the previous chapters and to place more emphasis on the productive deposits and the end-use applications of the zeolites being produced. As a result, the bibliography has been updated and significantly reduced in size, a difficult task because each reference is important, and any of the references could be the inspiration for the development of a world-class natural zeolite product.

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Figure 8. Fibrous erionite, Eastgate, Nevada



Figure 9. Nonfibrous erionite, Bowie, Arizona

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