

# Mineral Commodity Report 23 – Zeolites

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## Definition

Zeolites are crystalline, porous 3-dimensional aluminosilicates of the alkali (mainly Na and K) and alkaline-earth (mainly Ca) metals. Their crystal structure is based on a three dimensional framework of  $(\text{SiAl})\text{O}_4$  tetrahedra with all four oxygens shared by adjacent tetrahedra (see illustrations in Armbruster and Gunter, 2001). This results in a channel structure with molecular dimensions of 3 to 10 Å. Because some of the  $\text{Si}^{4+}$  is substituted by  $\text{Al}^{3+}$ , there is a net negative charge which is balanced by extra-framework exchangeable cations, mainly  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ . These cations are loosely held within the central cavities and surrounded by water molecules. The water molecules are loosely held in the pores and most zeolites can be reversibly dehydrated, and their cations readily exchanged. Zeolites have an empirical formula of:  $(\text{M}^+, \text{M}^{2+})\text{Al}_2\text{O}_3\text{SiO}_2 \cdot z\text{H}_2\text{O}$ , where  $\text{M}^+$  is usually Na or K,  $\text{M}^{2+}$  is Mg, Ca, or Fe, and g and z are variable multipliers. Rarely Li, Sr, or Ba may substitute for  $\text{M}^+$  or  $\text{M}^{2+}$ . The tetrahedral Si:(Si+Al) ratio is one of the major compositional variables, with some zeolites (e.g. mordenite) being at the silica-rich end and others being more aluminous.

Theoretically, the possibilities for different framework structures are infinite - around 40 are known in nature and more than 150 synthetic zeolites have been manufactured.

## Origin of names

The name zeolite is from the Greek *zein* = to boil, and *lithos* = stone, to describe minerals that frothed when heated. Specific zeolite minerals have been named from the following sources, either from Greek or Latin words or from the names of people or towns connected with the mineral. Analcime from *analkis* (Greek) = without strength as it has a weak electrical charge when heated or rubbed. Chabazite from *chabazios*, *chalazios* or *khalazios* an ancient Greek name for a stone mentioned in the poem *Peri lithos*, ascribed to Orpheus. Clinoptilolite from the Greek *klinein* = to bend or slope or from *clinic* for a wing or down, referring to its lightness, and *lithos* = stone. Erionite from the Greek *erion* = wool, because of its white, fibrous, wool-like appearance. Faujasite for B. Faujas de Saint Fond (1741-1819), a French geologist. Ferrierite for W.F. Ferrier (1865-1950) a Canadian geologist and mining engineer. Heulandite for J.H. Heuland (1778-1834) an English mineral collector. Laumontite for the Frenchman, F.P.N. de Laumont (1747-1834). Mordenite for Morden in Nova Scotia, Canada. Natrolite from the Latin *natrium* or Greek *natron* = native soda and *lithos* = stone. Offretite for A.J.J. Offret, a professor from Lyons, France. Phillipsite for W. Phillips (1775-1829), a British mineralogist and founder of the Geological Society of London. Stilbite from the Greek *stilbe* = lustre, in allusion to the pearly to vitreous luster. Wairakite for Wairakei, New Zealand, where it was first discovered by A. Steiner in 1955 (Steiner, 1955).

## History

Zeolitic tuff has been used as a sculpturing stone since at least 2,800 years ago and as a dimension stone for buildings since 2,700 years ago (Colella, de Gennaro, Aiello, 2001). However, zeolites were first identified as a mineral group in 1756 by Baron A. F. Cronstedt, a Swedish mineralogist, in samples from the Svappavari copper mine, Lappmark, Sweden. Zeolites were regarded as rare mineral curiosities and little commercial interest was shown in the minerals until the 1920s, when Weigel and Steinhoff (1925) found that chabazite when dehydrated can act as a molecular sieve by selectively absorbing smaller organic molecules and rejecting larger molecules.

Synthetic zeolites were first reported in 1862. Later, in an attempt to synthesize chabazite and mordenite, Barrer (1938) created a synthetic zeolite called Linde type A zeolite. In the late 1940s, research in zeolite minerals developed in the laboratories of Professor R. M. Barrer at Imperial College, London, T. Sameshima in Japan, and in the Union Carbide Corporation, USA. Most of the natural zeolites have synthetic analogues, commonly with superior properties. Synthetic mordenite has a much more open structure than the natural mineral where the large channels are often blocked by defects in the structure. Synthetic zeolites now have a wide range of commercial applications and can be manufactured to a specific molecular sieve size.

From their initial discovery as rare minerals in hollows and cracks in igneous rocks, natural zeolites have been found in many other geological environments. Bramlette and Posniak (1933) recognised the presence of zeolites as alteration products of vitric ash in fine-grained sedimentary rocks. Coombs (1954) identified zeolite minerals in low-grade metamorphic rocks in Southland, New Zealand. Deposits of natural zeolite minerals have now been identified in many countries, including: Japan, Russia, Italy, Greece, Turkey, Mexico, USA, Kenya and Australia.

## Minerals and properties

The most common natural zeolites are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, phillipsite and wairakite (Table 1). The most commercially important synthetic zeolites are zeolites A, X, Y and ZMS-5.

Zeolites are colourless, white crystals, with a hardness generally between 3 and 6 (Table 1). Zeolites have a number of characteristic properties that are important for commercial applications, including:

- 1) High degree of hydration and easily dehydrated
- 2) Low density and large void volume when dehydrated
- 3) Stability of the crystal framework structure when dehydrated
- 4) Cation exchange properties
- 5) Uniform molecular-sized channels in the dehydrated crystals

**Table 1:** Properties of natural zeolite minerals (modified after Table 192 of Harben and Kuzvart, 1996).

Minerals	Formula	Colour	Tranparency	Lustre	SG	H	Crystal system	Habit	Occurrences
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	Colourless, white, grey, yellowish, pink greenish	Transparent-translucent	Vitreous	2.2-2.3	5-5.5	cubic	Trapezohedrons or modified cubes; massive, granular; compact with concentric structure	Basalt and other igneous rocks; alteration product of nepheline & sodalite; siltstone, sandstone and other sedimentary rocks
Chabazite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$	Colourless, white, yellowish, pinkish, reddish white, greenish	Transparent-translucent	Vitreous	2.1	4-5	trigonal	Simple rhombohedrons; complex tabular	Cavities in basalt, andesite and other igneous rocks in assoc with other zeolites, calcite, quartz; fractures in schist & crystalline limestone; certain hot springs
Clinoptilolite	$(\text{Na}, \text{K}, \text{Ca})_6 (\text{Si}, \text{Al})_{36} \text{O}_{72} \cdot 20\text{H}_2\text{O}$	Colourless, white	Transparent to translucent	Vitreous	2.1-2.2	3.5-4	monoclinic	Platy, minute xls, often clustered	Bedded deposits; volcanoclastic sediments and altered vitric tuff; basalt
Erionite	$(\text{K}_2, \text{Ca}, \text{Na}_2)_2 \text{Al}_4 \text{Si}_{14} \text{O}_{36} \cdot 15\text{H}_2\text{O}$	White, green, grey or orange	Transparent to translucent	Vitreous to silky	2.1	3.5-4	hexagonal	Minute xls, prismatic; radiating groups, finely fibrous	Fractures in rhyolitic tuff
Faujasite	$(\text{Na}_2, \text{Ca}) \text{Al}_2 \text{Si}_4 \text{O}_{12} \cdot 8\text{H}_2\text{O}$	Colourless, white or stained by impurities	Transparent thin section	Vitreous	1.9	5	cubic	Octahedral xls	With other zeolites
Ferrierite	$(\text{Na}, \text{K})_2 \text{MgAlSi}_{15} \text{O}_{36} (\text{OH}) \cdot 9\text{H}_2\text{O}$	Colourless, white	Transparent translucent	Vitreous to pearly	2.0-2.1	3-3.5	Orthorhombic	Thin tabular; in radiating groups	In cavities in andesitic breccia
Heulandite	$\text{Ca}(\text{Al}_2\text{Si}_7\text{O}_{10}) \cdot 6\text{H}_2\text{O}$	Brick red, light pink	Translucent	Pearly, vitreous, dull	2.1-2.2	3.5-5	Monoclinic	Tabular xls, rose shaped aggregates	In druses, vesicles, cracks in basalt
Laumontite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$	White, grey, yellowish, pink, brownish	Transparent to translucent	Vitreous to silky	2.2-2.4	3-4	Monoclinic	Squarish prism xls; fibrous, columnar, radiating, divergent	Veins and cavities, mainly in basalt and related rocks; decomposed granite and pegmatite; metamorphic and sedimentary rocks; metallic vein deposits
Mordenite (Ptilolite)	$(\text{Ca}, \text{Na}_2, \text{K}_2) \text{Al}_2 \text{Si}_{10} \text{O}_{24} \cdot 7\text{H}_2\text{O}$	Colourless, white or stained yellowish or pinkish	Transparent to translucent	Vitreous to silky	2.1	4-5	Orthorhombic	Prismatic xls, acicular, cottony aggregates	Veins and cavities in igneous rocks; hydration product of glasses; authigenic deposits in sediments
Natrolite	$\text{Na}_2 \text{Al}_2 \text{Si}_3 \text{O}_{10} \cdot 2\text{H}_2\text{O}$	Colourless, white, grey, yellowish, reddish	Transparent to translucent	Vitreous to pearly	2.2	5-6	Orthorhombic	Short, columnar, needle-shaped capillary crystals	Cavities in basalt and related rocks; alteration product of nepheline/sodalite in nepheline syenite, phonolite, related rocks; alteration product of plagioclase in aplite, dolerite
Offretite	$(\text{K}_2, \text{Ca})_5 \text{Al}_{10} \text{Si}_{26} \text{O}_{72} \cdot 30\text{H}_2\text{O}$	Colourless to white	Transparent to translucent	Vitreous	2.1	-	Trigonal	Prismatic xls, vertically striated	In basalts
Phillipsite	$(\text{K}, \text{Na}, \text{Ca})_{1.2} (\text{Si}, \text{Al})_8 \text{O}_{16} \cdot 6\text{H}_2\text{O}$	Colourless, white, yellowish, reddish	Transparent to translucent	Vitreous	2.2	4-4.5	Monoclinic	Isolated xls or druses; spherulites	Cavities in basalt, phonolite, and related rocks; saline lake deposits; calcareous deep-sea sediments; hot spring deposits
Stilbite	$\text{NaCa}_4 \text{Al}_8 \text{Si}_{28} \text{O}_{72} \cdot 30\text{H}_2\text{O}$	White, red, brown, yellow, cream	Transparent to translucent	Vitreous to pearly	2.1-2.2	3.5-4	Monoclinic	Prismatic, sheaf-like aggregates, fibrous, globular	Cavities in basalts, druses
Wairakite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	Colourless	Transparent to translucent	Vitreous - dull	2.3	5.5-6	Monoclinic	Prismatic crystals	Tuffaceous sst, breccia, ignimbrite, vitric tuff in geothermal fields and low grade metamorphic rocks

**Table 2:** Properties and uses of commercial zeolites (modified after Vaughan 1978; Harben and Kuzvart, 1996, Table 193).

Zeolite	Void volume	Pore size Å	Ion exchange capacity meq/g	Composition		Sorption capacity (wt%)			Selected end uses
				Si/Al	Cation	H <sub>2</sub> O	NC <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>12</sub>	
<b>Large pore (maximum 7.5 ?)</b>									
X		7.4		1.0-1.5	Na	28	14.5	16.6	Catalytic cracking (FCC) and hydrocracking; selective catalytic reduction of NO and NO <sub>2</sub> ; CO <sub>2</sub> removal, fructose-glucose separation; air and N <sub>2</sub> separation; drying refrigerants, natural gas, air; monosaccharide separation
Y		7.4		1.5-3.0	Na	26	18.1	19.5	
US-Y		7.4		>3	H	11	15.8	18.3	
Heulandite	39	4.0 x 5.5 4.4 x 7.2 4.1 x 4.7		2.91					
Mordenite	28	6 x 7 (2.9 x 5.7)	2.29	5.5	"N"	6	2.1	2.1	Hydroisomerisation; dewaxing; selective catalytic reduction of NO and NO <sub>2</sub> ; I <sup>129</sup> removal from air
Mordenite		6 x 7		5-6	Na	14	4	4.5	Drying acid gas; removal of H <sub>2</sub> S; nuclear waste treatment
Mordenite		6 x 7		5-10	H	12	4.2	7.5	Municipal waste water treatment; pet litter and odour control
<b>Medium pore (maximum 6.3 ?)</b>									
Ferriite		5.5 x 4.8	2.33	5-10	H	10	2	1	Dewaxing
L type		6		3-3.5	K	12	8	7	Reforming catalyst
Offertite		6		4	K, H	13	6	2	
Silicalite		6		Infinity	H	1	10	0	Removal of SO <sub>x</sub> , NO <sub>x</sub> , Kr <sup>85</sup> from air, trace organics from water
ZSM-5		6		10-500	H	4	12	6	Dewaxing; benzene alkylation; xylene isomerisation; FCC; selective catalytic cracking; synfuel production (methanol to gasoline); toluene disproportionation; ethylbenzene synthesis
Laumontite	34	4.6 x 6.3	4.25						
<b>Small pore (maximum 4.3 ?)</b>									
Chabazite	47	4	2.54	4	"N"	15	7	1	Radioactive waste treatment; catalyst
Clinoptilolite	39?	4 x 5 3.9 x 5.4	2.54	6	"N"	10	2	0	Municipal waste water and nuclear waste treatment; paper filler; animal feed additive
Erionite	35	4 3.6 x 5.2	3.12	4	"N"	9	2	0	Selective catalytic cracking; metal removal from water
Phillipsite	31	3 4.2 x 4.4	3.87	2	"N"	15	1	0	Metal removal from water
A		3		1	K, Na	22	0	0	Olefin drying; concentrating alcohols
A		4		1	Na	23	13	1	Detergent builder; drying natural gas, air and refrigerants; removing CO <sub>2</sub> from air; concentrating alcohols; N <sub>2</sub> production from air
A		5		1	Ca, Na	23	7	0	Iso/n-paraffin separation; O <sub>2</sub> production from air

"N" = mineral zeolite, cations variable but usually Na, K, Ca, Mg.

- 6) Ability to adsorb gases and vapours
- 7) Catalytic properties with H<sup>+</sup>-exchanged forms
- 8) Special electrical properties.

Many zeolites lose water fairly continuously over a temperature range of 150 to 400°C without collapse of the framework structure and resorb it from the atmosphere at room temperature. All zeolites are molecular sieves that can selectively adsorb molecules on the basis of their size, shape, or electrical charge.

Erionite and mordenite are fibrous minerals, whereas most zeolites crystallise as blocky crystals. Erionite has been found to be a carcinogenic health hazard (Ross et al., 1993), but limited studies on mordenite indicated that it was at most only mildly active as a potential carcinogen (Klein, 1993; Bish and Guthrie, 1993).

### Uses

The ion exchange, catalytic and molecular sieve properties of zeolites makes them useful in a wide range of applications.

Environmental applications include water and sewage treatment, pollution control including heavy metal adsorption, and air and gas purification. Other applications include pet litter, aquaculture, soil conditioning, animal feed supplements, carriers for slow release insecticides, fungicides and herbicides, and industrial applications including catalysis, selective adsorption and fillers in paint, paper and plastics.

The presence of large channels and cavities, with their associated extra-framework cations, facilitate cation exchange. Natural zeolites have cation-exchange capacities between 200 to 400 meq/100g, superior to most other inorganic cation exchangers. In general, natural zeolites that are open and silica-rich are highly selective for large univalent cations, such as  $\text{Cs}^+$  or  $\text{NH}_4^+$ .

The catalytic properties of zeolites are due to their large surface areas (internal and external) and their Si-Al frameworks. The  $\text{Si} \rightarrow \text{Al} + \text{H}^+$  exchange is widely used for catalysis, because the Al-tetrahedra can function as proton donors or acceptors. Synthetic zeolites are preferred for industrial applications, although natural zeolites may be important in catalysing biochemical reactions in biological systems (Bish and Guthrie, 1993).

The molecular sieving properties vary among the different zeolite minerals according to the pore size of the mineral structure and the sizes of channels and cavities. Typically, a zeolite is useful as a molecular sieve only after it has been completely dehydrated. Natural zeolites in this category include: mordenite, erionite and chabazite.

Pore size determines their general usage. Mordenite and the synthetic faujasites (zeolite X and zeolite Y) are examples of large pore size (maximum free diameter 7.5 Å) zeolite minerals. The faujasites contain a large central cavity known as a supercage. The large surface area of the large pores and cavities is the key to their use as catalysts or as catalyst carriers, particularly for petroleum cracking to produce the lower boiling point, lighter fractions such as fuel oil, petroleum and kerosene. They are also used in isomerisation, hydrogenation and dehydrogenation, methanation and in  $\text{NO}_x$  gases control. They are used in the collective removal (adsorption and the reverse case desorption) of water and gases and in the selective molecular sieves according to molecule and pore size.

Synthetic medium pore size (maximum free diameter 6.3 Å) zeolites (e.g. ferrierite, ZSM-5) are used in the petroleum industry for the removal of high melting point waxes, or for converting low octane paraffins/naphthalenes into higher-octane isoparaffins and aromatics. Extra-framework cations in zeolites can be exchanged for other ions, such as in the adsorption of ammoniacal nitrogen, some radioactive waste ( $\text{Sr}^{90}$ ,  $\text{Ca}^{137}$ ), and to increase the dryness of animal waste. ZSM-5 zeolite was used to convert methanol to synthetic gasoline at Motunui, near New Plymouth and is widely used for selective cracking and alkylation.

Small pore size (maximum free diameter 4.3 Å) zeolites, such as chabazite, clinoptilolite and zeolite A, are used in the radioactive waste, municipal water treatment, and odour control industries. Clinoptilolite (and mordenite) are added to animal feed to reduce health problems, improve feed efficiency and to dry excrement. Synthetic zeolite A is an important builder in the manufacture of detergent because of its ion exchange properties, and in the oxygen and

nitrogen separation industries. In its dehydrated state it is widely used as a desiccant.

Zeolitic tuffs have been used for thousands of years as a light-weight, durable dimension stone (e.g. Neapolitan yellow tuff used in ancient buildings of Rome and Naples) and as pozzolanic materials in blended cements. Expanded, lightweight aggregate similar to perlite has been prepared by calcining or "popping" zeolitic tuffs at temperatures between 1200 and 1400°C.

## Formation of natural zeolites

Naturally occurring zeolites are formed at temperatures below 200°C from volcanic glass, poorly crystallised clay, and feldspar or silica in wet situations, where there is a high ratio of  $\text{Mg}^{++}$  and  $\text{H}^+$  to  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{++}$ . They are commonly found in a variety of sedimentary and igneous rocks and in soils. The main geological occurrences are in tuffs, tephra and volcanoclastic rocks in lakes or deep sea basins that have been subjected to relatively low temperature (<200°C) hydrothermal alteration or burial diagenesis (Hay and Sheppard, 2001). Hay (1978) identified six geological environments in which natural zeolites are commonly formed:

1. Zeolites formed in tephra beds in hydrologically closed, saline/alkaline lake systems, in which water is unable to move freely in and out (Langella et al., 2001). Common zeolites include analcime, chabazite, clinoptilolite, erionite and phillipsite. Examples include: Tecopa lake, California, USA; the Green River Formation of Wyoming, Utah, and Colorado, USA; Lake Magadi, Kenya; Samos Island, Greece; and Werris Creek, NSW, Australia.
2. Zeolites formed in hydrologically open systems by meteoric water flowing through tephra and tuff beds in nonmarine or shallow marine environments (Sheppard and Hay, 2001). Common zeolites include clinoptilolite and mordenite. Examples include: John Day Formation, Oregon, USA; Campanian Tuff, Neapolitan Yellow Tuff, Italy; and Ngakuru Formation, Taupo Volcanic Zone, New Zealand.
3. Zeolites formed in saline, alkaline soils (Ming and Boettinger, 2001) and on land surfaces, commonly from weathering of volcanic rocks. Evaporation causes percolating rainwater to become acidic and this acid water alters the glasses and aluminosilicates in the soil. Common zeolites include: analcime, chabazite, clinoptilolite, natrolite and phillipsite. Examples include: Olduvai Gorge, Tanzania; and eastern San Joaquin Valley, California.
4. Hydrothermal alteration zones in geothermal areas (Utada, 2001b). Common zeolites include: analcime, clinoptilolite, heulandite, laumontite, mordenite, and wairakite. Examples include: Wairakei, New Zealand; Yellowstone Park, USA; and Onikobe, Japan.
5. Deep sea sediments: clinoptilolite and phillipsite are found in siliceous tephra and low-silica basaltic tephra respectively in cores from deep sea drilling in the Atlantic, Indian and Pacific Oceans.
6. Burial diagenesis and low grade metamorphism of

volcaniclastic rocks, including ignimbrites (Utada, 2001a). Common zeolites include: analcime, clinoptilolite, heulandite, laumontite and mordenite. Examples include: New Zealand (Southland Syncline), Japan, Ireland, Iceland, Mexico, Nevada and the Canary Islands.

Original rock composition, temperature, pressure, pH, and the presence of some ions (Mg, H) and paucity of other ions (Na, K, Ca), control the type of zeolite produced. Less hydrous zeolites (laumontite, analcime and wairakite) are stable at higher temperatures than more hydrous zeolites (clinoptilolite, chabazite and stilbite) (Sheppard and Hay, 2001). Early formed zeolites are commonly replaced by other zeolites, such as the time sequence of clinoptilolite replaced by analcime, which in turn is replaced by laumontite (Hay, 1978). Also, the number of common species of zeolite decreases with increasing age (e.g. greater than 30 species in Cenozoic age rocks, 7 in Mesozoic, 4 in Late Paleozoic, 2 in Early Paleozoic and 1 common in Late Pre-Cambrian rocks) (Iijima, 1980).

Experiments in the formation of natural zeolites have shown that the rate of formation is dependent on time, temperature, glass composition and the chemistry and flow rate of the pore water. Analcime, chabazite and phillipsite appear in five days from basalt glass maintained at 200° C, and mordenite and analcime from rhyolite glass in 40-60 days at above 50° C (Sheppard and Hay, 2001).

## Mining and processing

Standard open-pit mining techniques and earth moving equipment are used to break out and transport most Cenozoic age zeolite material to the processing plant. Quality control requires face sampling and drill coring to provide samples for laboratory analysis and to guide selective mining.

Processing consists of crushing and screening for products used as soil conditioners or pet litter. Further processing is required for some industrial applications and may include grinding and air separation to -60 to -325 mesh, micronising to 5 to 10 µm, or even micronising to 1 µm. Washing with acid to increase the H<sup>+</sup> content, or with sodium chloride to increase the Na<sup>+</sup> content can enhance the performance of some zeolites.

## Synthetic zeolite manufacture

Synthetic zeolites are normally synthesised from alkaline solutions of silica and alumina. Usually only sodium and potassium can be used as the counter ion. The most widely synthesised zeolite, zeolite A, is manufactured by two main commercial methods, either

1. Solutions of Na aluminate and Na silicate are heated to 70°-110° C and allowed to crystallise for 1 to 8 hours to produce zeolite NaA, or
2. Kaolin is heated to 500°-600° C to produce reactive metakaolin, which is then dissolved in a solution of NaOH to form amorphous Na aluminosilicate. After several hours cooling at 90°-110° C, zeolite NaA crystallises.

Zeolites X and Y, and mordenite are made by similar methods.

Over the last 20 years or so a new series of high silica zeolites have been synthesized using organic bases as structure directing species. The best known of these is the Mobil zeolite ZSM-5. Many of these can be prepared in pure silica forms and are hydrophobic, preferentially adsorbing organic molecules, even from dilute aqueous systems.

## World production

Total world production of natural zeolites is between 3 Mt and 4 Mt per year. Estimates for individual countries are China, 2.5 Mt; Cuba, 500,000 to 600,000 t; Japan, 140,000 to 160,000 t; USA, 42,000 t; Hungary, 10,000 to 20,000 t; Slovakia, 12,000 t; Georgia, 6,000 t; New Zealand, 5,000 t; Greece, 4,750 t; Australia, Canada, Italy, and other republics of the former Soviet Union, 4,000 t each; Bulgaria, 2,000 t; and South Africa 1,000 to 2,000 t (Virta, 2000). Small quantities of natural zeolites are also produced in Argentina, Germany and Indonesia. The main natural zeolite minerals produced are analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite.

The wide range of applications of natural zeolites results in diverse markets. Japan has a particularly wide range of zeolite markets for agricultural, industrial, and consumer uses. North American sales are principally for agricultural and pet litter applications. A large proportion of Chinese zeolite production is used as a cement additive. Markets in Western Europe, the former Eastern block countries, and Cuba are primarily for agricultural products, with a growing industrial market sector.

Synthetic zeolites are manufactured in many industrialised countries in Europe, East Asia and North America. Their consumption is dominated by companies manufacturing detergents and catalysts. Restrictions on the use of phosphate detergents have increased the demand for synthetic zeolites.

Synthetic zeolites (molecular sieves) are the major alternate materials to natural zeolites. They can be tailored in physical and chemical characteristics to serve many applications more closely and they are more uniform in quality than their natural equivalents.

Natural zeolites are preferable to synthetic materials in some applications (e.g. cesium and strontium adsorption in radioactive waste cleanup). They are also generally much lower in cost than synthetic zeolite products so they are in the unusual position of being a challenger to their synthetic counterparts for low cost applications.

The main potential substitutes for zeolites in specific applications include: for animal feed - clays (e.g. bentonite, atapulgite) and dolomite; carrier - clays, diatomite and pumice; detergent builder - sodium polyphosphate; lightweight aggregate - pumice and perlite; molecular sieve - activated carbon, activated clay and silica gel; pet litter - diatomite and various clays (e.g. bentonite, atapulgite).

## Price

As mining costs are generally low, the price of zeolites is related more to the amount and cost of processing required by the market. The price of natural zeolite ranges from about NZ \$75/t to \$350/t. Synthetic zeolite A ranges from US \$500 to \$600/t for detergent grade, and up to US \$45/kg for catalyst-grade material.

## New Zealand occurrences

Zeolite resources of New Zealand have been reviewed previously by MacFarlan and Barry (1991) and Thompson et al. (1995). Deposits in the Northland-Auckland region have been described by Sameshima (1975), and in the Taupo Volcanic Zone by Roberts (1997), Mowatt (2000) and Brathwaite and Christie (2001). Those in Southland have been described by Coombs (1959) and Coombs et al. (1986). The main New Zealand occurrences (Fig. 1) are in:

- Hydrothermally altered silicic tephra in lake beds and ignimbrites of Quaternary age in the Taupo Volcanic Zone.
- Marine tuffs and volcanoclastic sandstones of Miocene age in Northland and Auckland.
- In vein and joint fillings in Mesozoic age greywacke.
- Weakly metamorphosed marine tuffs and tuffaceous sandstone of Triassic age in Southland.

New Zealand zeolite production is from altered silicic tephra in lake bed sediments of Quaternary age, although there is

also potential for production from Miocene and Triassic marine tuffs.

## Zeolites in silicic tephra in lake sediments and in ignimbrites of Quaternary age in the Taupo Volcanic Zone

Zeolite minerals are widespread in the Taupo Volcanic Zone. They occur as vein minerals and as hydrothermal alteration products of vitric-rich tephra and ignimbrites in some of the active and extinct geothermal fields (Steiner, 1953, 1955, 1977; Henneberger and Browne, 1988; Simmons et al., 1992; Roberts, 1997; Brathwaite and Christie, 2001). The most common minerals are mordenite, clinoptilolite, laumontite and wairakite. Mordenite also occurs as coatings on sand and gravel at Sulphur Point, Rotorua.

Zeolites are most abundant in lacustrine tuffites of the Ngakuru Formation, a 100-300 m thick sequence of finely stratified siltstone, tuffite, diatomite, sandstone, conglomerate and interbedded tuffs. The formation overlies Ohakuri Ignimbrite and is unconformably overlain by alluvial sediments, which are younger than 0.022 Ma.

Individual zeolite deposits contain 30-80% zeolite over a thickness of up to 45 m in thinly stratified tuffite beds (Figs 2 and 3). The tuffites are composed mainly of glass shards and pumice clasts, with minor volcanic plagioclase, quartz and biotite crystals. Glass shards in the tuffites are replaced by zeolite minerals, which from X-ray diffraction (XRD) analysis consist of the silica-rich zeolites mordenite and clinoptilolite. Amorphous silica (opal A), opal C-T, K-feldspar, smectite and illite are also present. Scanning electron microscope (SEM) micrographs show that mordenite occurs as a mesh of acicular crystals replacing glass shards (Fig. 4), and as thin fibres coating platy crystals of clinoptilolite (Fig. 5). Both the mordenite and clinoptilolite are very fine grained (1-10  $\mu\text{m}$ ).

Three of the deposits near Ngakuru are being worked and current uses include: 1) adsorbents for oil/chemical spills and animal wastes, 2) water treatment and filters, and 3) conditioners for sports turf and slow release fertiliser (Mowatt, 2000). The zeolites produced have low density (650  $\text{kg/m}^3$ ), high liquid (60% of dry weight) and odour absorption properties, and high cation exchange capacity (40-110 meq/100 g).

Other deposits occur near Ohakuri dam, where glass within the Ohakuri Ignimbrite is hydrothermally altered to mordenite, clinoptilolite, opal and smectite (Henneberger and Browne, 1988).



Figure 1. Location of zeolite deposits in New Zealand

## Marine tuffs of Miocene age in Northland and Auckland

The zeolites analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite are present variously in the Miocene age Waitemata Group sediments in the wider Auckland area, and in its correlatives near North Cape, Whangarei, Kaipara Harbour, and on the Colville Peninsula at the northern end of the Coromandel Peninsula (Fig. 1). They were formed by the alteration of volcanic glass (Sameshima, 1975).

At Whareana Bay, near North Cape, Tom Bowling Bay Formation contains clinoptilolite, which was formed in a lacustrine, sedimentary environment. At Paradise Creek, southeast of Whangarei, a 5-m thick, hard, altered, siliceous tuff consists of mordenite and lesser amounts of quartz and chlorite. At Puketotara Peninsula, in the Kaipara Harbour, a 90m-thick tuff bed in the deep, marine Timber Bay Formation contains erionite and lesser amounts of chabazite and clinoptilolite. Analcime is also present in the sedimentary rocks in this area, in the matrix of andesitic grit in the Colville Formation at Fletcher Bay, Colville

Peninsula, and in the Albany Conglomerate in the Wainui and nearby Auckland metropolitan areas. The Parnell Grit contains chabazite at Takapuna Beach and at Karaka Bay, clinoptilolite in Auckland City, and phillipsite between Auckland and Leigh, to the north.

## Mesozoic age greywacke

Laumontite, together with calcite, prehnite and a small amount of quartz, fills veinlets, joints and shatter zones in the greywacke rocks that form the main mountain ranges from Auckland southwards to western and central Waikato (e.g. Marakopa), from East Cape to Wellington, from Marlborough to South Canterbury (e.g. Hurunui Gorge), and in Southland. In many places the presence of zeolite minerals makes the greywacke unsuitable for use as concrete aggregate (Christie et al., 2001).

## Weakly metamorphosed marine tuffs and tuffaceous sandstones of Triassic age in Southland

Bedded masses of laumontite and less pure deposits of analcime and other zeolites have been described in Triassic Murihiku Supergroup strata of the northern Taringatura Hills (Coombs et al., 1959). The main deposit, of up to 70% laumontite with fine quartz, feldspar, clay and chlorite minerals, forms a near vertical bed about 3 m thick and several kilometres long. Some of the smaller beds also contain clinoptilolite and analcime. Heulandite occurs in several places. One bed of low purity extends for about 14 km along the full length of the north edge of the Taringatura Hills, between Mossburn and Lumsden (Coombs, 1959).

Coombs et al. (1959) established a zonation of mineral assemblages characterised by an upward succession of prehnite-pumpellyite-albite, laumontite-albite and then clinoptilolite-heulandite-analcime.

## Production and resources

NZ Natural Zeolite Ltd produces about 9,000 tonnes of zeolite annually from three deposits near Ngakuru. Substantial tonnages of zeolite are present in these and nearby deposits, but there are no published resource estimates.

## Future

Natural and synthetic zeolites have a growing number of uses, particularly in environmental, agricultural, industrial and domestic applications. Natural zeolites are used mainly in the domestic market for odour and waste treatment and soil conditioning and selective



Figure 2. Zeolite quarry at Mangatete Road, Ngakuru. Photo: NZ Natural Zeolite.

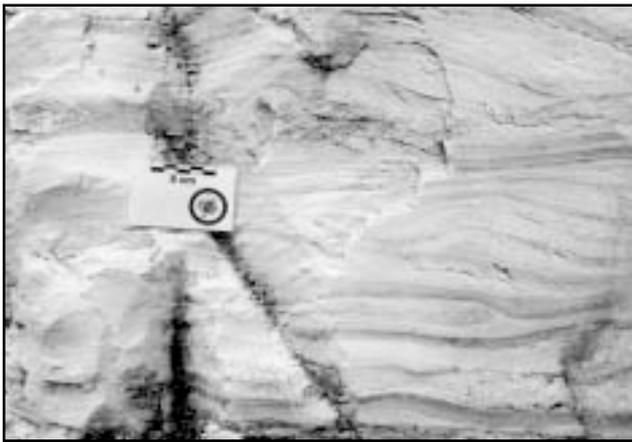


Figure 3. Zeolitised tuffite exposed in a quarry face at Mangatete Road, Ngakuru. Photo: Bob Brathwaite

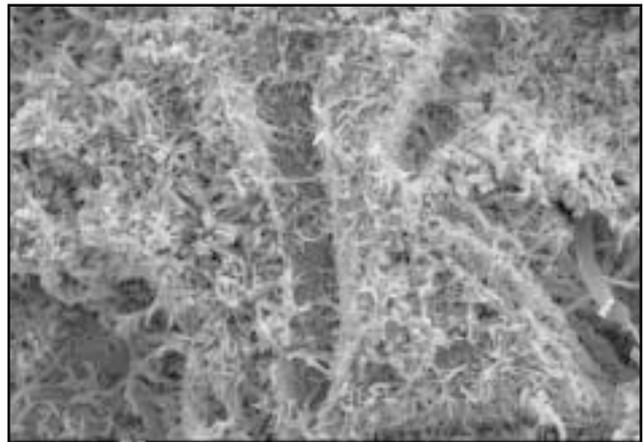


Figure 4. Scanning electron microscope (SEM) image showing acicular mordenite crystals replacing glass shards (curved) in tuffite from Ngakuru. SEM micrograph: Bob Brathwaite

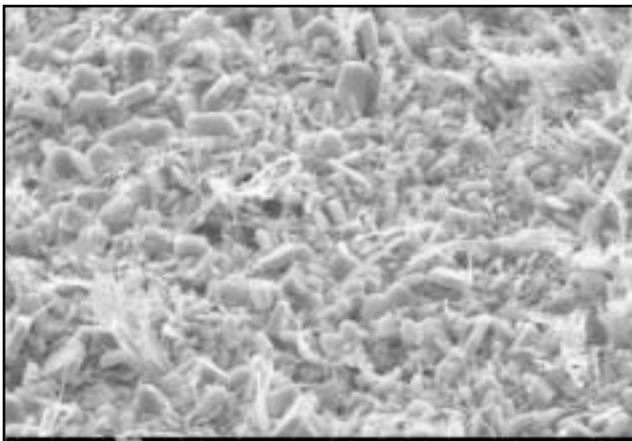


Figure 5. Scanning electron microscope (SEM) image showing plates of clinoptilolite with minor fibrous mordenite from Mangatete Road zeolite deposit. SEM micrograph: Bob Brathwaite

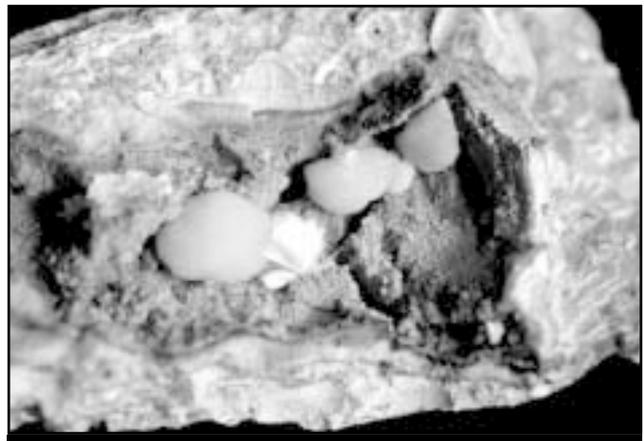


Figure 6. Zeolites from Tairua (30 mm x 15 mm). Photo: Eric Coppard

adsorption. These marketing areas can be expected to expand. Low-tonnage niche markets should offer opportunities for producers to introduce high-unit-value products, particularly for environmental applications (Virta, 2000). The zeolite property of being able to absorb gasses and then release them when the temperature is raised, is being investigated to reduce the risk of explosion in storing fuel hydrogen.

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