

# State Department of Geology and Mineral Industries

1069 State Office Building  
Portland 1, Oregon

## CLINOPTILOLITE, A ZEOLITE WITH ECONOMIC POSSIBILITIES

The General Electric Company at Hanford, Washington, has been working on selective removal of certain long-life radioactive wastes produced by the Hanford reactors. One of these is cesium 137, which is required to be locked up for about 200-300 years (7-10 half lives). It was found that certain zeolites had the proper space lattice relationship to selectively remove cesium from a liquid as it was pumped through a column of finely ground material. The best zeolite for this purpose was found to be clinoptilolite (pronounced clinoptylolite). This zeolite occurs as a hydrothermally altered volcanic ash in layers within or overlying deposits of bentonite and hectorite at Hector, California. One other deposit is known in Nevada. One thing which makes these samples stand out from the common altered volcanic ash is that they taste salty. This may not be a valid criterion, however.

This sample is for your reference for comparing possible Oregon material which could be competitive. It represents pit run material, about 80 percent pure and easily (they think) upgraded. The General Electric Company is looking for more deposits for several reasons: (1) they do not want to be restricted to a single producer for economic reasons, and (2) there may be closer material resulting in lower costs and assured availability. The present usage there would amount to several hundred tons per year at \$30 per ton, but use could be expected to be much greater when other plants would begin using it. At present it appears that clinoptilolite could be the method of concentrating cesium for sale to users of this metal.

Report by: H. G. Schlicker  
February 1, 1962



## NATURAL AND SYNTHETIC ZEOLITES FOR INDUSTRIAL USE

Leonard B. Sand

### SUMMARY

A description is given of the currently important natural and synthetic zeolites that have industrial use in adsorption and catalytic applications. The participation of Massachusetts industry in this new and growing chemical technology, utilizing applied geology and geochemistry, is outlined.

### INTRODUCTION

Until 1950 the industrial use for zeolites was minor and restricted to their use as ion exchangers in water-softening processes. Moreover, these materials are not true zeolites, although they possess zeolitic properties, but are of a group called permutites which are synthetic, amorphous, aluminosilicate precipitates or chemically degraded glauconites. Even in this industrial use, 90 percent of the market has been replaced by synthetic ion exchange organic resins.

Crystalline zeolites have been known, since the pioneering work of Weigel and Steinhoff<sup>1</sup> in Germany in the 1920's, to possess the property to selectively adsorb certain small molecules. Investigations were conducted by McBain<sup>9</sup> in England, by Sameshima and Hemmi<sup>2</sup> in Japan, and by Barrer<sup>3</sup> in England starting in the 1930's and continuing to the present. Prior to 1950 the studies had been confined on natural zeolites occurring in small quantities, or from deposits which are not commercially feasible to mine, or on synthetic zeolites prepared by laboratory techniques which are not conducive to scale-up for commercial manufacture.

Then a sequence of events rapidly changed the industrial outlook. First was the recognition that these crystalline zeolites could be synthesized under economic conditions of manufacture; second, the recognition that one of these synthetics contained pores capable of adsorbing larger molecules than previously thought possible; and third, the discovery in the western United States of large, mineable deposits of zeolites. An indication of the current industrial interest in the use of zeolites is the patent literature which shows more patents issued on these materials than on any other single chemical area.

The current industrial uses for zeolites are primarily as catalysts<sup>4,5,6</sup> and as adsorbents, particularly for desiccation and hydrocarbon separations. Several hundred tons of zeolites are consumed each month.

### MOLECULAR SIEVE ZEOLITES

Zeolites are defined as crystalline, hydrated, alkali and/or alkaline earth aluminosilicates with a network crystal structure in which the alkali or alkaline cations can be partially or completely and reversibly ion exchanged and the water can

be partially or completely and reversibly removed. A network structure consists of a linkage of (Si, Al) O<sub>4</sub> tetrahedra in which all four oxygens of a tetrahedron are shared by other tetrahedra. The water and exchangeable cations are located in the cavities of the skeletal silica-alumina network. Recent classifications of zeolites based on crystallography are given by Fischer and Meier<sup>7</sup> and by Smith.<sup>8</sup>

In 1932 McBain<sup>9</sup> coined the phrase "molecular sieves" for those zeolites discovered to be capable of selectively adsorbing certain molecules and excluding others. Although zeolites are at present still the most important group of molecular sieves, the phrase also applies to other materials, such as porous glasses, metals, and organic polymers with selective adsorption properties. The industrially important zeolites thus are referred to as molecular sieve zeolites. These crystalline zeolites are not to be confused with those colloidal, non-crystalline, hydrated aluminosilicates, referred to more properly as permutites, which do, however, exhibit zeolitic properties of ion exchange and reversible dehydration. Although the permutites can be regarded as precursors of crystalline zeolites, they lack the uniform intracrystalline pore structure which imparts such unusual properties to the molecular sieve zeolites.

The industrially important properties of molecular sieve zeolites are derived principally from the size and shape of the cavities within the crystals and secondarily by the modifications in properties resulting from chemical treatment such as ion exchange. The porous structure of molecular sieve zeolites results from the linkage of rings of 4-, 5-, or 6-membered (Si, Al) O<sub>4</sub> tetrahedra to form larger 8-, 10-, or 12-membered rings. It is these latter pores in the crystals, in some cases leading to larger cavities, which impart the molecular sieve characteristic to the zeolites. It is convenient to designate the zeolites with properties exhibited by 8-, 10-, or 12-membered rings in the structure as small port, intermediate port, and large port molecular sieve zeolites with pore diameters approximating 4Å, 7Å, and 10Å, respectively. Mordenite is unique in that it occurs naturally as a small port sieve but can be synthesized as either a small port or a large port sieve.

<u>Small Port</u>	<u>Intermediate Port</u>	<u>Large Port</u>
<u>Zeolite A</u> (Synthetic)	Ferrierite	Faujasite
Chabazite	Dachiardite	Mordenite
Erionite (offretite)		
Phillipsite		
<u>Mordenite</u>		
Clinoptilolite		

Figure 1. Molecular sieve zeolites of current industrial interest.



In Figure 1 are listed some of the molecular sieve zeolites of current industrial interest. In Figure 2 these are plotted according to anhydrous chemical composition on a mole percent basis. The general oxide formula for a molecular sieve zeolite is  $M_{2/n}O \cdot Al_2O_3 \cdot x SiO_2 \cdot yH_2O$  where  $n$  is the valence of the exchangeable cation  $M$ ,  $x$  varies between 2 and 11, and  $y$  varies between 4 and 10.

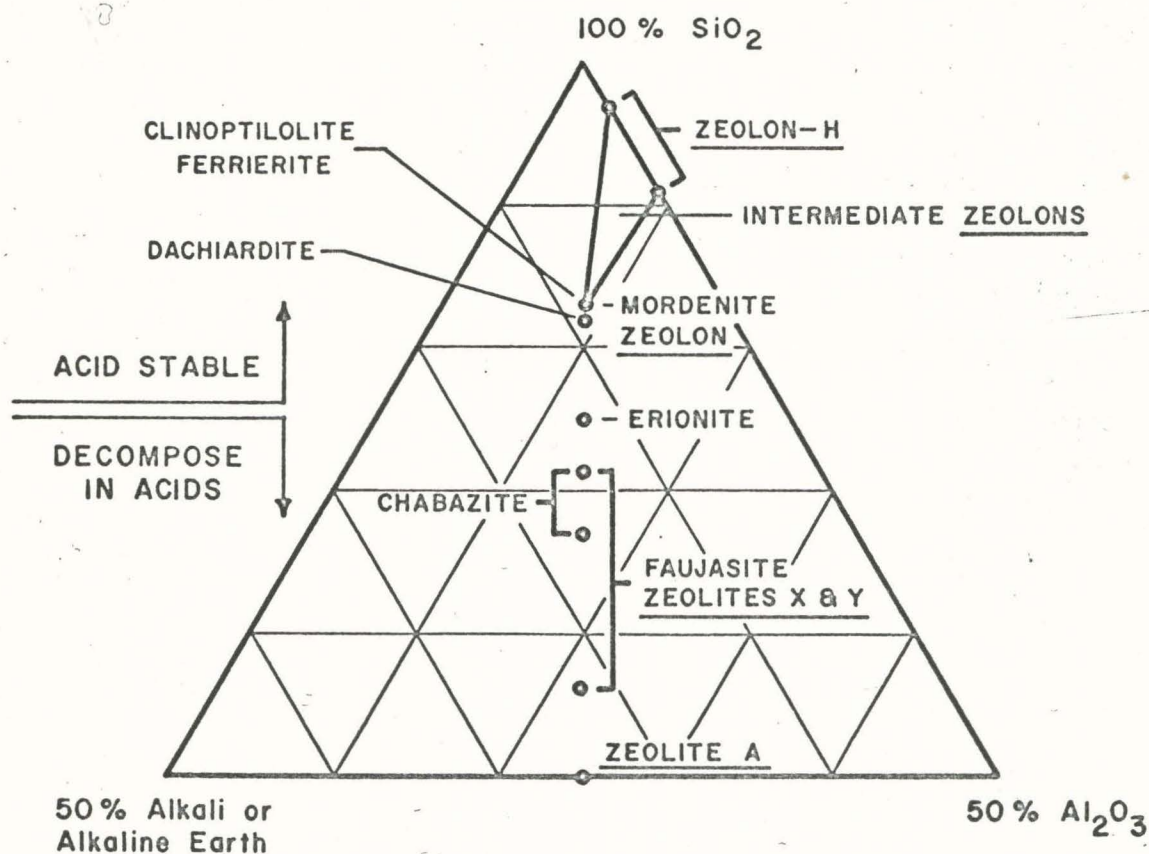


Figure 2. Molecular sieve compositional diagram, mole percent basis.

The large port zeolites are primarily of interest in catalytic applications; the small port zeolites are primarily of interest in adsorption applications.

#### SYNTHETIC MOLECULAR SIEVE ZEOLITES

From an industrial standpoint, the use of synthetic molecular sieve zeolites originated with the introduction in the early 1950's of a group of synthetic zeolites by Linde Air Products resulting from the work of Milton and his associates.<sup>10</sup> The low temperature hydrothermal synthesis of zeolites had been

accomplished in the last century, but the Linde group translated these techniques into modern technology and put on the market two synthetic zeolites, one a small port molecular sieve designated Zeolite A which has not been reported to occur as a mineral, and the other a large port molecular sieve which is a synthetic analogue of the natural zeolite faujasite and designated as Zeolite X or Zeolite Y depending on its silica content. In the early 1960's Norton Company introduced the second large port molecular sieve, synthetic mordenite, and designated their group of sieves Zeolons.

A considerable number of zeolites have been synthesized, and undoubtedly many of these also will be commercialized. At present, however, the commercially important synthetic molecular sieve zeolites are the small port Zeolite A and the large port faujasites and mordenites. These are synthesized hydrothermally in the sodium form and are offered in a variety of exchange forms for an increasing number of adsorption and catalytic applications.

Synthetic zeolites dominate the molecular sieve field and offer a number of advantages over the natural molecular sieve zeolites. The principal advantages are chemical purity, uniformity of crystallinity resulting in uniformity of derived properties, and more favorable kinetics of ion exchange leading to the various modified forms.

#### NATURAL MOLECULAR SIEVE ZEOLITES

Zeolites, particularly analcime and clinoptilolite, had been reported by early workers<sup>11, 12</sup> as alteration products of pyroclastics in the intermountain west. Probably the first recognition of the existence of very large tonnages in relatively pure deposits was by the author and his associates in the early 1950's.<sup>13</sup> Deffeyes,<sup>14</sup> as a result of graduate thesis work in Nevada, precipitated commercial activity on these deposits by his discovery of the first known extensive quantities of erionite. Since these initial discoveries, industrial exploration programs have uncovered large reserves of chabazite, erionite, small port mordenite, phillipsite, clinoptilolite, and a mordenite which can be converted easily by chemical treatment to a large port molecular sieve. These have all been found to occur in sufficient purity to be of commercial interest although several will require beneficiation for some applications. All the deposits are Tertiary in age and occur in volcanic provinces. Most of the zeolites are the product of the alteration of water-laid siliceous pyroclastics but some result from the alteration of siliceous flows. Figure 3 lists the geological setting and gangue minerals of some of these deposits. Figure 4 shows the bedded nature of one deposit in which a uniform two-to three-inch bed of phillipsite, overlain by a four-foot bed of erionite and underlain by a ten-foot bed of mordenite, covers an area of ten square miles. Figure 5 is a representation of a toluene molecule approaching a port (12-membered ring of oxygens) of mordenite.



<u>Zeolite</u>	<u>Geological Setting</u>	<u>Associated Minerals</u>
Chabazite Chabazite-erionite	Altered Tertiary lake bed pyroclastics bordered by mountain-building extrusives	Clinoptilolite, analcime, thenardite, halite, calcite, feldspar, quartz
Erionite Phillipsite Mordenite	Altered Tertiary lake bed pyroclastics overlain by basalt flow	Clinoptilolite, quartz feldspar, gypsum, glauuberite
Clinoptilolite	Hydrothermally altered Tertiary pyroclastics	Cristobalite, tridymite, opal, heulandite
Mordenite, small port	Hydrothermally altered Tertiary rhyolite flow	Clinoptilolite, opal, quartz, cristobalite, tridymite, montmorillonite

Figure 3. Several natural zeolite deposits of commercial interest.

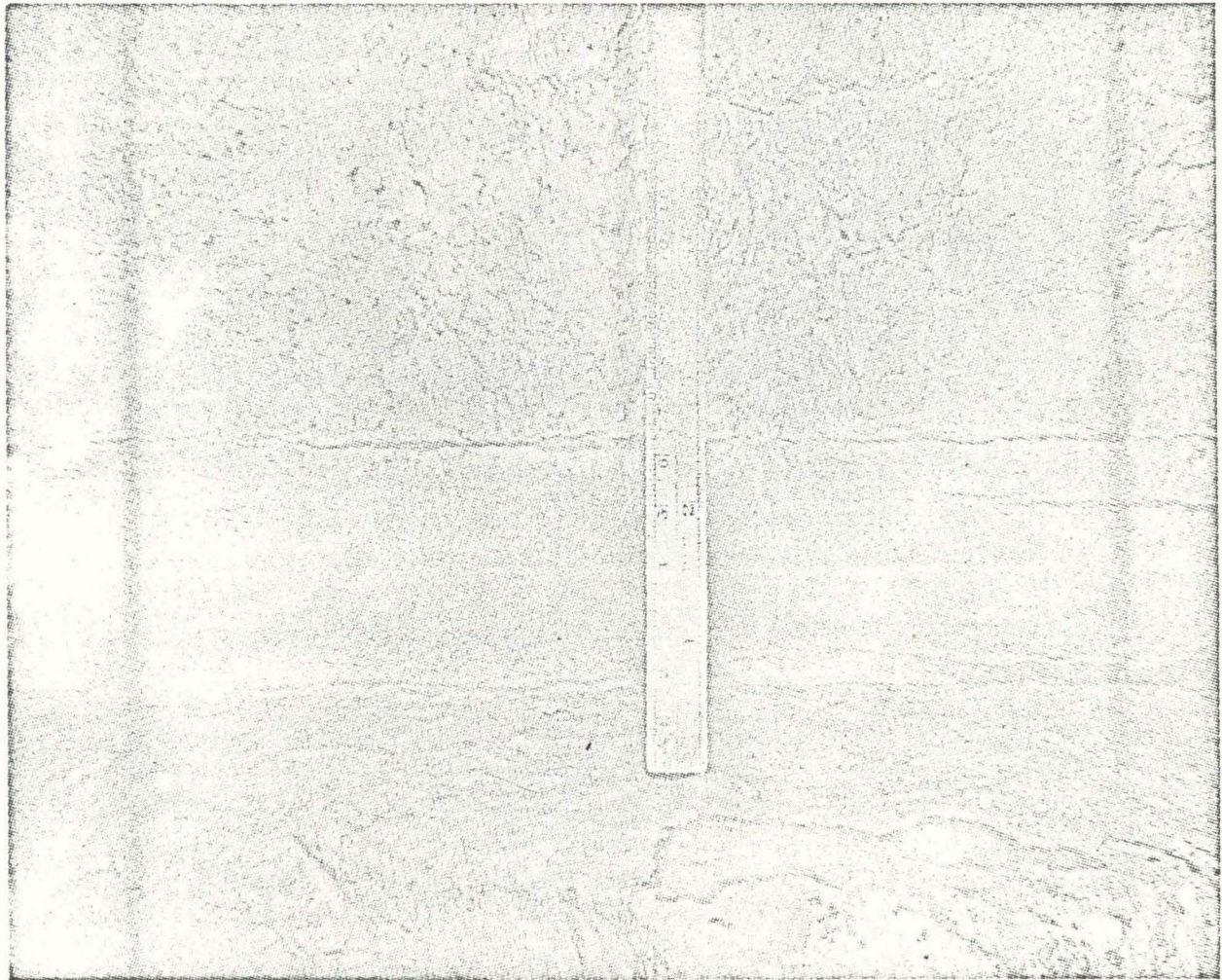
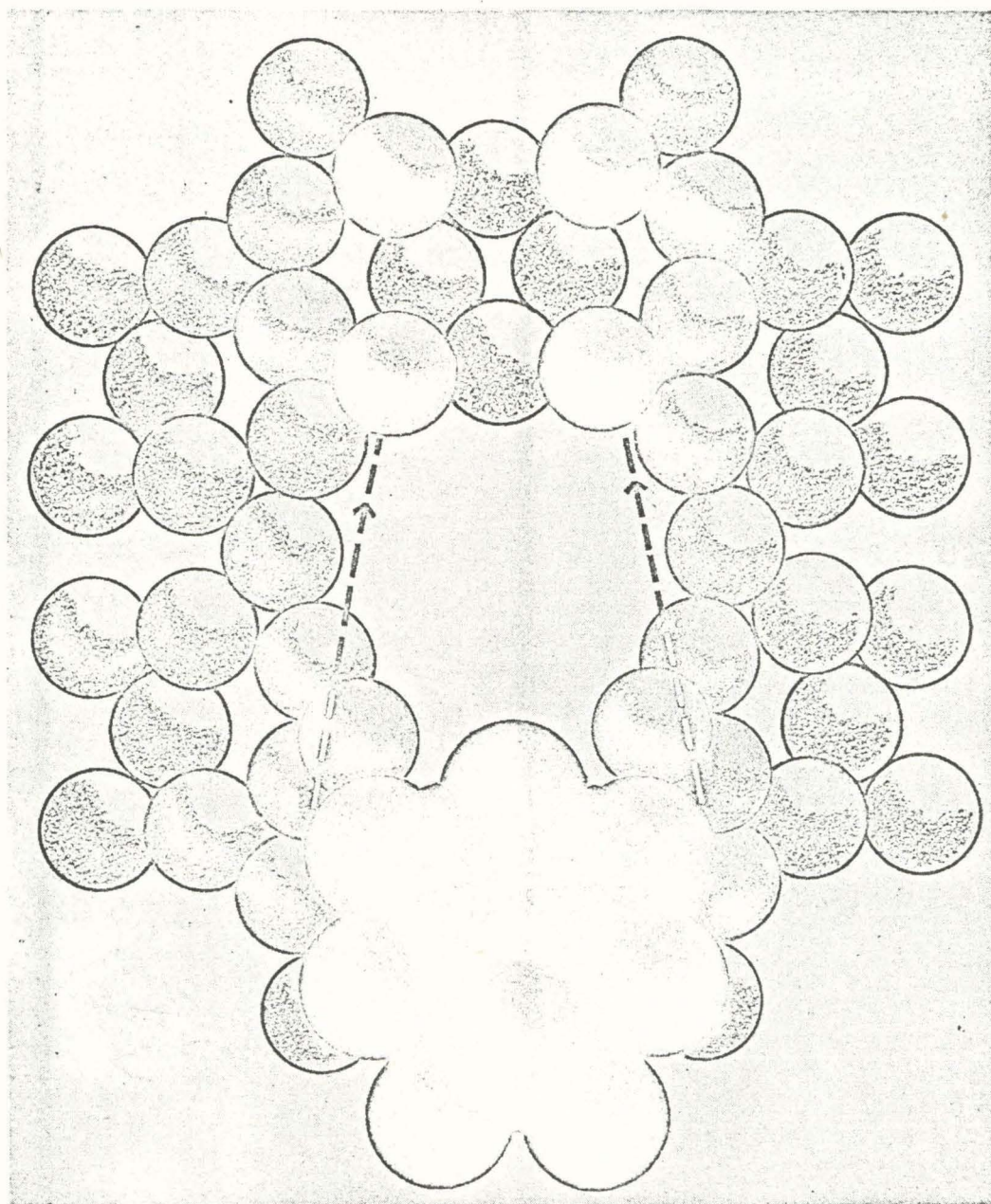


Figure 4. A two-inch bed of phillipsite overlain by an erionite bed and underlain by a mordenite bed. Altered Tertiary lake bed pyroclastics in southeastern Oregon.

*Sec 29  
Norton Claims*



Figure 5.



Representation of a toluene molecule approaching a port (12-membered ring of oxygens) of mordenite.

The natural molecular sieve zeolites are of commercial interest because of their lower cost to market as compared with the synthetics. They occur on the surface and are mined easily by strip operations. Several have found their way into the market place in desiccation applications and in the atomic energy waste disposal program.<sup>15</sup> The deposit of mordenite, which can be converted to a large pore sieve, is the only natural zeolite occurrence which has significant potential for use as a catalyst.

#### ECONOMIC SIGNIFICANCE TO MASSACHUSETTS

There are no commercial deposits of zeolites in Massachusetts. Zeolites are found in the state only as amygdaloidal fillings in the Triassic basalts. Actually, there is no industry involved in marketing molecular sieve zeolites that is based in any of the states with commercial zeolite deposits. The principal companies currently in the field are located in New York, Alabama, New Jersey, Maryland, and Massachusetts. Norton Company was the third United States company to enter the market as a supplier and is the sole supplier of synthetic mordenite, one of the two large pore molecular sieves. Norton Company also has discovered and holds ore reserves of all of the natural molecular sieve zeolites. It has the dominant position on the natural mordenite deposit to be exploited as a catalyst. It is Norton Company's participation in this new and growing technology which will contribute to the economy of the state. This involves the factory production and fabrication of the synthetic zeolites, as well as the fabrication and modification into useable shapes and varieties of the natural zeolites shipped in from the western United States.

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### ZEOLITE LOCALITIES

1. Coffin Butte - about 9 miles north of Corvallis on U.S. 99 W. Minerals found - calcite, heulandite, apophyllite, chabazite.
2. Wren quarry - on State Highway 223, 1 mile north of Wren, Oregon, which is about 8 miles west of Corvallis. Minerals found - calcite, apophyllite, natrolite.
3. Kings Valley quarry - 10 miles north of Wren on Highway 223. Excellent locality for major zeolite types.
4. Enegren Slough - 3 miles east of Waldport, Oregon. Mineral found - analcite.
5. Goble, Oregon - major source of zeolites.
6. Clackamas River area - excellent stilbite and heulandite area.



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ZEOLITES IN SEDIMENTARY DEPOSITS OF THE NORTHWESTERN UNITED STATES --  
POTENTIAL INDUSTRIAL MINERALS

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Zeolites have been reported from sedimentary deposits since 1891, but their utilization as industrial minerals is in its infancy. Zeolites occur in rocks that are diverse in age, lithology, and depositional environment, but they are most common in sedimentary rocks that originally contained abundant vitric material. Most zeolites in sedimentary deposits formed during diagenesis mainly by the reaction of vitric material with interstitial water. Of the more than 30 naturally occurring zeolites, only eight commonly occur in bedded deposits of the Northwest. These are analcime, chabazite, clinoptilolite, erionite, heulandite, laumontite, mordenite, and phillipsite. Most zeolitic sedimentary rocks consist of two or more zeolites as well as authigenic clay minerals, silica minerals, or feldspars, and relict glass and crystal and rock fragments. Extensive and relatively pure beds of zeolite, however, occur in Cenozoic deposits of the Northwest.

The ion exchange, adsorption, molecular sieve, and reversible dehydration properties of zeolites, coupled with their seemingly low cost of mining, suggest a variety of industrial applications. Uses or potential uses include hydrocarbon separations, purification and drying of gases, removal of cesium and strontium from radioactive wastes, removal of ammonia from sewage and agricultural effluents, and production of high-purity oxygen from air. Zeolites are also used as soil conditioners, carriers of pesticides and fungicides, and dietary supplements for poultry and swine. Certain properties of zeolitic tuffs, such as their light color, light weight, and low abrasiveness, permit uses for pozzolan in cement, building stone, lightweight aggregate, and filler in paper.

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              4 Mordenites                            2 Analcimes  
  2 Potassium Feldspars

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