

Zeolite

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Figure 1. Stilbite bowtie (6 cm long), Raigad, Maharashtra, India. Author's specimen and photo.

Ask a geologist and a chemist about zeolites and you are likely to get very different responses. Most mineral collectors think of the wonderful crystals of stilbite, natrolite, heulandite, and other silicates that are commonly found in the vesicles of basalts (a.k.a. trap rock) at locations such as Paterson, New Jersey; the Deccan Traps of India; or the other locations featured in this issue of *Rocks & Minerals*.

According to the classical definition, *zeolite* refers to a group of hydrous aluminosilicate minerals with porous atomic structures. They are framework (or tecto) silicates in which Si and Al are bonded to four O atoms in a tetrahedral arrangement, and all four O atoms are shared with other tetrahedra. In other words, the tetrahedra are fully cross-linked (Bish and Ming 2001; Mumpton 1977; Segeler and Bernhardt 1980). This can be seen in the structure diagram of stilbite (fig. 2). This is a partial polyhedral diagram. Instead of showing the positions of every Si and Al atom, and the four O atoms surrounding each of these, the SiO_4 and AlO_4 units are shown as blue polyhedra (specifically tetrahedra, or four-sided polyhedra) in which the corners represent the position of O atoms and the center of the tetrahedra is the position of the Si or Al. Note that every corner of each tetrahedra is connected to other tetrahedra,

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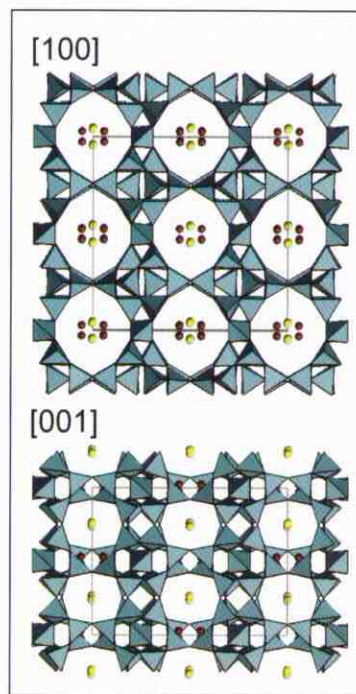


Figure 2. Schematic of the stilbite structure projected down the x-axis [100], top, and the z-axis [001], bottom. Blue tetrahedra are occupied by Si and Al. Ca is shown as yellow spheres and Na as brown spheres, with bonds omitted to highlight the channel structure of the tetrahedral framework. The unit cell is outlined in gray.

indicating shared oxygen atoms. The arrangement of tetrahedra in zeolites leads to large open spaces, or cages, typically 3–8 angstroms across, many of which are connected to form continuous channels that extend throughout the crystal. Because of the substitution of Al^{3+} for Si^{4+} in the tetrahedral framework of zeolites, there is a net negative charge that is balanced by positively

charged cations such as Na, K, Ca, and Ba that reside in the cages and channels of the framework (fig. 2). Water molecules may also reside in these channels and can be removed by heating without damage to the crystal structure. The origin of the term *zeolite*—which comes from the Greek *zeo*, to boil, and *lithos*, stone—is derived from this unusual property of these open-framework structures. The term was coined in 1756 by the Swedish mineralogist Axel Fredrick Cronstedt, who found that stilbite (fig. 1), the first zeolite recognized, would rapidly lose water and appear to boil when heated—thus the name *zeolite* (Mumpton 1977).

Unlike water molecules, removal of ions such as Na^{1+} or K^{1+} , which play the role of balancing the negative charge on the tetrahedral framework, does have a destabilizing effect on the structure. However, because channels allow the easy movement of the resident ions and molecules into and out of the structure, Na and K can be stably removed if other ions of the same charge are added in their place. This property is known as *cation exchange* and is one of many properties that is capitalized upon in the commercial use of zeolites. Indeed, one of the largest volume uses of zeolites is in detergent formulations, where they have replaced phosphates as water-softening agents. They do this by exchanging their sodium ions for the calcium and magnesium present in hard water. They are also used in water softening units for household and industrial water treatment. Cation exchange in zeolites is also used in industrial waste clean-up (to remove heavy metals and radioactive isotopes), sewage treatment, odor control, and soil conditioning, even to aid digestion and absorb toxins in livestock.

The channels in many zeolites are big enough to allow relatively large molecules, such as ammonia and hydrocarbons, to enter them. Thus, cation exchange can occur between resident ions such as Na^{1+} and larger molecules. Of course, such exchange is dependent on the size and shape of a given molecule and the size of the channels in a given zeolite. Because of this, zeolites can be used to selectively absorb molecules of one size and exclude molecules of other sizes. In essence, they can act as “molecular sieves” by capturing relatively small molecules and allowing larger ones to flow by unhindered. Zeolite molecular sieves can also segregate molecules of the same size but different electrical characteristics. This is another very important property that is utilized in many applications, including drying of refrigerants, removing atmospheric pollutants such as sulfur dioxide, separating and recovering hydrocarbons, recovering radioactive ions from waste solutions, and curing of plastics and rubber.

Once molecular species have been absorbed into a zeolite structure, chemical reactions can take place that change the chemistry and structure of the molecule. Absorption and chemical change can occur repeatedly; thus, the zeolite acts as a catalyst of the reaction. This type of reaction is extensively utilized in one of the most economically important applications of zeolites, the catalysis of hydrocarbon reactions used to refine crude oil into gasoline and other products. In fact, zeolites are the main catalysts in petrochemical

refineries today. One of the important reactions in oil refinement is hydrocarbon cracking. This occurs when large hydrocarbon molecules called “gas oil” are absorbed into specially treated zeolites. Hydrogen ions found within the channels attach themselves to the gas oil molecules and cause them to break, or crack, into smaller hydrocarbon molecules, including gasoline. This process can increase the yield of gasoline from crude oil by 10 to 20 percent!

There are more than eighty different natural zeolite minerals (Bish and Ming 2001) and many hundreds of synthetic zeolites with no naturally occurring equivalents. Natural zeolites have numerous applications in agriculture, water treatments, and so on (Mumpton 1999); however, most industrial uses involve synthetics, and their use is of immense significance to human welfare and world economics (Sherman 1999). In the fields of chemistry and materials science, the term *zeolite* has been expanded to include other crystalline materials that have tetrahedral framework structures with large open channels but that are based on elements other than Si and Al. Many of these have the same structures as their silicate equivalents. These include beryllium phosphates, beryllium arsenates, and aluminum phosphates, some of which occur naturally, such as the mineral pahasapaite, which has the structure of a synthetic aluminosilicate zeolite known as RHO (Parise et al. 1994; Rouse, Marino, and Peacor 1989).

Natural zeolites form in several different geologic environments, all of which involve the activity of water. These include weathering under high pH conditions, diagenesis of sediments, hydrothermal alteration, and contact and burial metamorphism. Large, well-formed zeolite crystals are common as vesicle fillings in basalts that have been altered by hydrothermal waters (fig. 1). Much smaller zeolite crystals, but volumetrically much larger and more concentrated, are those that form from the weathering and alteration of volcanic ash deposits in alkaline surface waters (fig. 3). Because zeolites form in hydrous environments, typically through alteration of igneous rocks, they may ultimately be found on Mars, if liquid water did once exist on that planet. Indeed,

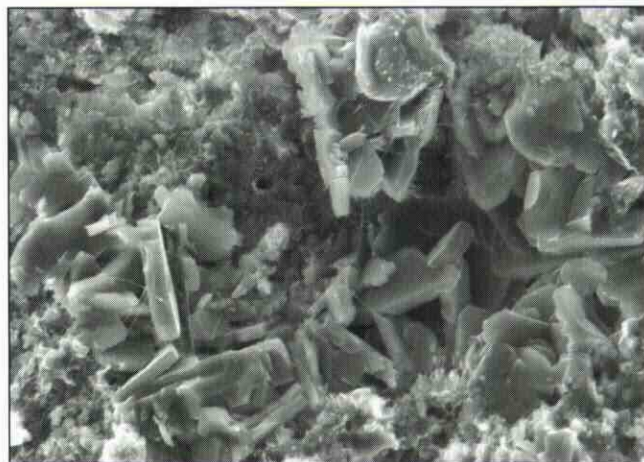


Figure 3. SEM photomicrograph of clinoptilolite-heulandite from a weathered volcanic ash deposit, Nankai Trough, offshore Japan; Seiko Nakagawa photo.

the presence of zeolites may be an important indicator of preexisting water.

Because of the importance of zeolites in numerous commercial processes, they are one of the most studied groups of minerals. In fact there are numerous professional societies and journals dedicated solely to the advancement of zeolite research. Zeolite crystal growth experiments have even been conducted on several space shuttle missions and on the international space station (<http://www1.msfc.nasa.gov/newsroom/background/facts/zeolites.html>). The literature on zeolites is voluminous, but two good references for review of many different aspects of zeolites are Bish and Ming (2001) and Mumpton (1977). Several extensive Web sites are also dedicated to zeolites, including those of the International Committee on Natural Zeolites (<http://icznz.lanl.gov/>), which includes a listserve, and the International Zeolite Association (<http://www.iza-online.org/>), which includes an extensive database of zeolite structures.

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