*American Mineralogist, Volume 58, pages 287-290, 1973*

# First Reported Occurrence of Zeolites in Sedimentary Rocks of Mexico

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**Abstract**

X-ray diffraction of a massive, green tuff from late Miocene pyroclastic sediments in the Atoyac Valley, near Etla, northwest of Oaxaca, Mexico, has indicated the presence of abundant mordenite and clinoptilolite. This is the first identification of zeolites in sedimentary rocks of Mexico. The tuff contains about 10 percent quartz, feldspar, mica, and hematite in millimeter-size grains, surrounded by a matrix of micron-size zeolite minerals, formed by the alteration of pre-existing glass shards. Scanning electron micrographs show the euhedral nature of mordenite needles and clinoptilolite laths down to less than 0.1 micron-size particles.

The Etla tuff is similar in physical appearance and zeolite content to other massive marine tuffs of Japan, Yugoslavia, and Bulgaria and to several ash-flow tuffs of Nevada and California. It has been used as a facing and dimension stone since Mayan times and is currently being quarried at several locations in the area. From literature descriptions it is likely that numerous new occurrences of zeolitic sedimentary rocks will be recognized in southern Mexico in the next few years.

## Introduction

Since their discovery in saline-lake deposits of Tertiary age in the western United States in the late 1950's, more than a thousand occurrences of zeolites have been identified in sedimentary rocks of volcanic origin throughout the world. Long known as well-formed accessory minerals in the vugs and cavities of basalts and other basic igneous rocks, zeolites are recognized today as major constituents of many bedded pyroclastic deposits and are thought to be among the most widespread and abundant authigenic silicate minerals in sedimentary rocks. The flat-lying and near monominerallic nature of the deposits has aroused considerable commercial interest in sedimentary zeolites; currently more than 100,000 tons are mined each year in this country and abroad for use as fillers in the paper industry, as soil conditioners, as dietary supplements in animal husbandry, as ion exchangers in pollution abatement, in pozzolanic cements and concretes, and as acid-resistant adsorbants in gas drying (see Mumpton and Sheppard, 1972).

During the early stages of zeolite exploration in this country (1958–1962), the geological similarity of the volcanic and pyroclastic regions of northern Mexico and those of southern Arizona and Caliornia suggested that bedded zeolite deposits should also exist south of the border; however, no sustained effort was made to search out this possibility, and to this date zeolite minerals have not been reported from sedimentary rocks of Mexico. During the summer of 1972 the author examined a series of pyroclastic sediments in the Atoyac River Valley, about 15 km northwest of Oaxaca, southern Mexico. Although time limitations prevented an extensive survey of the area, several samples were collected from a prominent green tuff, about 100 m east of Highway 190, 3 km north of the town of Etla. Subsequent X-ray diffraction examination of these samples indicated that the tuff consists almost completely of the zeolites, mordenite and clinoptilolite. This identification confirms what is believed to be the first discovery of zeolite minerals in sedimentary rocks of Mexico.

## Description and Composition

The green tuff in question is about 10 m thick and outcrops along a northeast-striking hogback and dips steeply to the northwest. The massive tuff is currently quarried at this and other localities in the area and is in demand as an attractive facing and dimension stone. Tuffs of this kind have been used in the Oaxaca region in buildings, walls, foundations, and other structures since Mayan times, and are prominent in the archeologically famous edifices at Mitla and Monte Alban. It was the presence of such material in the walls of the central cathedral in Oaxaca that first attracted the author's attention and prompted the subsequent field examination.

The massive, fine grained tuff contains about 10 to 15 percent quartz, feldspar, biotite, and specular hematite grains, about 1 to 2 mm in diameter, in a very fine grained, green matrix. Elongate, greenish-white zones, about 1 to 20 mm in length, make up about 10 percent of the rock and have the megascopic appearance of collapsed pumice lapilli. Vugs and cavities about 0.1 to 0.5 mm in size are abundant in the tuff and are usually lined with white, micron-size crystals. Microscopically, the larger grains of quartz, plagioclase, hematite, and biotite are surrounded by a matrix of collapsed glass shards, which have been altered to platy and needle-like zeolite crystals. The needle-like grains are up to about 6 or 8 $\mu$m in length and about 1 to 2 $\mu$m in diameter. The lath-like grains are about 10 to 20$\mu$m in size and are easily visible in open spaces in the rock. Smaller laths are also abundant in the matrix of altered shards. Although the grain sizes are too small for reliable optical identification, the particle habits and the X-ray diffraction data (Table 1) suggest that the laths are clinoptilolite and that the needle-like grains are mordenite. Mordenite needles are abundant within the shadowy outline of the shard and are plainly visible at the edges of shards where they form rims of needles growing outwards from the shard boundaries into voids. The cores of the relict shards are yellowish green in color; the mordenite rims are colorless or white. Both the needles and the laths are nearly isotropic, although some show weak birefringence. With the exception of the larger mineral grains, the rock appears to have been transformed almost completely into zeolite minerals. Fresh glass has not been found. No evidence of welding or flow structures has been observed.

TABLE 1. X-ray Diffraction Data for a Zeolitic Tuff from Etla, Oaxaca, Mexico

| 25-21-10 Etla Tuff "d" | I/I$_o$ | Mineral Identification | ASTM 6-0239 Mordenite "d" | I/I$_o$ | ASTM 13-304 Clinoptilolite "d" | I/I$_o$ |
|---|---|---|---|---|---|---|
| 13.7 | 19 | M | 13.7 | 50 | - | - |
| 10.05 | 28 | Mica | - | - | - | - |
| 9.05 | 100 | M,Cp | 9.10 | 90 | 9.00 | 100 |
| 7.97 | 13 | Cp | - | - | 7.94 | 40 |
| 6.81 | 9 | Cp | - | - | 6.77 | 30 |
| 6.61 | 32 | M,Cp | 6.61 | 90 | 6.64 | 20 |
| 6.46 | 19 | M | 6.38 | 40 | - | - |
| 6.07 | 8 | M | 6.10 | 50 | - | - |
| - | - | | - | - | 5.91 | 10 |
| 5.79 | 13 | M | 5.79 | 50 | - | - |
| 5.25 | 6 | Cp | - | - | 5.24 | 30 |
| 5.12 | 8 | Cp | - | - | 5.11 | 10 |
| - | - | | 5.03 | 10 | - | - |
| - | - | | 4.87 | 20 | - | - |
| 4.65 | 12 | Cp | - | - | 4.69 | 20 |
| 4.53 | 30 | M | 4.53 | 80 | 4.48 | 20 |
| - | - | | - | - | 4.34 | 20 |
| 4.27 | 13 | Quartz | - | - | - | - |
| 4.15 | 8 | M | 4.14 | 30 | - | - |
| 3.99 | 69 | Cp,M | 4.00 | 90 | 3.96 | 100 |
| 3.92 | 27 | Cp | - | - | 3.90 | 80 |
| 3.88 | 14 | M,Cp | 3.84 | 60 | 3.83 | 10 |
| 3.77 | 16 | Cp,M | 3.76 | 20 | 3.73 | 10 |
| 3.63 | 7 | M | 3.62 | 10 | - | - |
| 3.55 | 12 | M,Cp | 3.56 | 10 | 3.55 | 20 |
| 3.47 | 73 | M,Cp | 3.48 | 100 | 3.46 | 20 |
| 3.39 | 46 | M,Cp | 3.39 | 90 | 3.42 | 60 |
| 3.35 | 56 | Qtz,Mica | - | - | - | - |
| 3.33 | 26 | M | 3.31 | 10 | - | - |
| 3.30 | 17 | | - | - | - | - |
| 3.22 | 53 | M | 3.22 | 100 | - | - |
| 3.19 | 25 | Feldspar | - | - | - | - |
| 3.11 | 9 | M,Cp | 3.10 | 20 | 3.12 | 30 |
| 3.08 | 9 | Cp | - | - | 3.07 | 20 |
| - | - | | - | - | 3.04 | 20 |
| 2.98 | 24 | Cp | - | - | 2.97 | 50 |
| - | - | | 2.946 | 20 | - | - |
| 2.89 | 21 | M | 2.896 | 60 | 2.87 | 10 |
| - | - | | - | - | 2.82 | 30 |
| 2.80 | 7 | Cp | - | - | 2.80 | 10 |
| 2.79 | 9 | M | - | - | - | - |
| 2.73 | 7 | Cp,M | 2.743 | 10 | 2.73 | 10 |
| - | - | | 2.700 | 30 | 2.72 | 10 |
| 2.59 | 13 | M | 2.639 | 10 | - | - |
| 2.57 | 13 | Mica,M | 2.560 | 40 | - | - |
| 2.52 | 9 | M,Cp | 2.522 | 50 | - | - |
| 2.46 | 7 | M | 2.465 | 20 | - | - |
| 2.44 | 5 | Cp | 2.437 | 20 | 2.44 | 10 |
| - | - | | 2.343 | 20 | 2.42 | 10 |
| - | - | | - | - | 2.38 | 10 |
| 2.29 | 5 | Cp,M | 2.299 | 10 | 2.29 | 10 |
| - | - | | 2.275 | 10 | - | - |
| - | - | | 2.228 | 20 | - | - |

M = *mordenite;* Cp = *clinoptilolite;* Qtz = *quartz.*

## Study Methods

The samples were examined by standard X-ray diffraction techniques using a Siemens diffractometer and Ni-filtered, Cu K$\alpha$ radiation. The high degree of crystallinity of the sample is illustrated by the X-ray tracing shown in Figure 1. The diffraction data (Table 1) clearly indicate the abundance of mordenite and clinoptilolite in the tuff in a ratio of about 60/40. A differential thermal analysis of the sample shows no endothermic peaks other than the normal zeolitic-water-loss peaks at low temperatures, thus confirming the identification of clinoptilolite rather than heulandite (Mumpton, 1960). After heating to 500°C, the mineral content of the sample is essentially unchanged.

Scanning electron micrographs of the Etla tuff are shown in Figures 2 and 3. Fibers of mordenite measuring about 0.1 × 3 $\mu$m in size are shown in Figure 2 enclosing laths of what appear to be clinoptilolite. The platy nature of this latter zeolite is readily apparent in Figure 3. In the upper-center

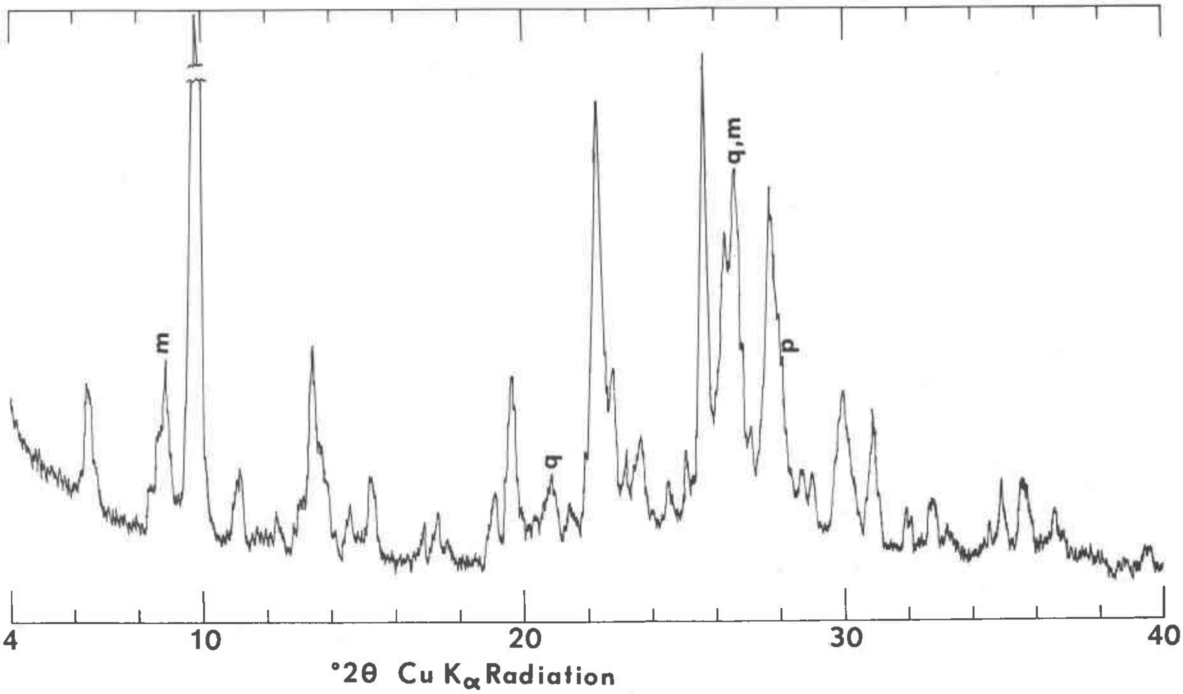


FIG. 1. X-ray diffraction tracing of zeolitic tuff from Etla, Oaxaca, Mexico. Unmarked peaks are those of mordenite and clinoptilolite. m = biotite mica; q = quartz; p = plagioclase.

portion of Figure 2, it appears as if mordenite needles are growing out of a flat plate; however, this may only be an illusion and the genetic relationship of the zeolite phases requires additional study.

## Comparison with Other Occurrences

The continental sedimentary rocks in the northern part of the Atoyac River valley were mapped by Wilson and Clabaugh (1970) and dated by vertebrate fossils as Late Miocene in age. As described by

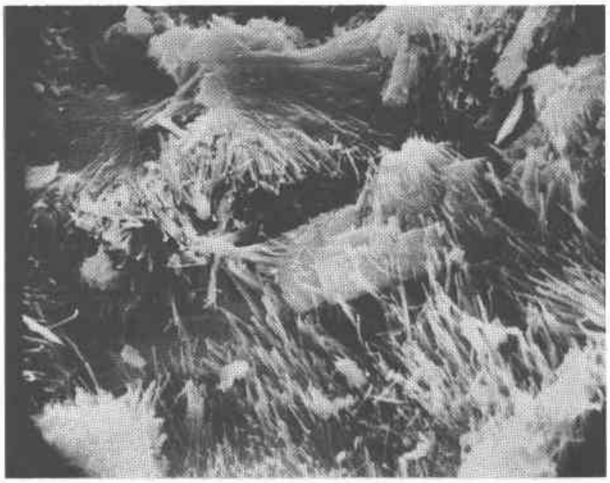

FIG. 2. Scanning electron micrograph of the Etla tuff showing mordenite needles approximately 0.1 × 3 microns in size, enclosing what appears to be laths of clinoptilolite. Magnification = 650 X.

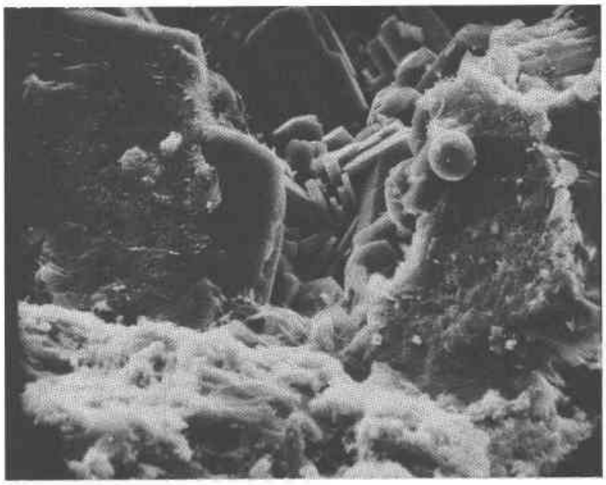

FIG. 3. Scanning electron micrograph of the Etla tuff showing laths of clinoptilolite with lesser amounts of mordenite needles and fibers. The small sphere in the micrograph is a glass-bead impurity. Magnification = 350 X.

these authors the Suchilquitongo Formation consists of about 300 m of interbedded tuffs, tuffaceous siltstones, tuffaceous limestones, and bentonites, capped by what they termed an "Etla ignimbrite member." According to Wilson and Clabaugh (1970), the latter rock is a 5 to 10 m thick, massive, green tuff consisting almost completely of glass shards with thin, bleached margins in a matrix of birefringent "dust." The green tuff examined in the present study was collected from this member. It is indeed unfortunate that the examination of Wilson and Clabaugh was limited to the petrographic microscope, as the abundance of mordenite and clinoptilolite is unmistakable from X-ray diffraction tracings. Professor Wilson generously supplied small samples of several beds described in his type section and of the Etla "ignimbrite." X-ray diffraction data obtained on these samples confirm the zeolitic nature of this tuff and indicate that several other units of the section also contain small amounts of clinoptilolite (5 to 10 percent), demonstrating an abundance of pyroclastic material in the depositional environment.

Micropaleontological evidence indicates that the Suchilquitongo sediments were deposited in a shallow, playa lake (Wilson and Clabaugh, 1970). The absence of evaporites (*loc. cit.*) and the recent studies of Sheppard and Gude (1968, 1969) and Parker and Surdam (1971, 1972) suggest that the water of this lake was fresh, because zeolitized tuffs deposited in saline lakes are generally characterized by phillipsite, erionite, and chabazite, rather than by clinoptilolite and mordenite alone.

The Etla tuff closely resembles in both physical appearance and mineralogy the thick marine tuffs at Oya, Tochigi Prefecture, Japan; at Kurdzali, Bulgaria; and at several locations in southern Yugoslavia, all of which are rich in clinoptilolite and/or mordenite. It also resembles a number of ash-flow tuffs of the United States, most notably those in the Fish Creek Mountains, Nevada (Deffeyes, 1958), in the Obispo Formation near Pismo Beach, California, and in the Oak Springs formation south of Beatty, Nevada. The field and petrographic descriptions of similar rhyolitic and andesitic tuffs by Gonzales-Reyna (1962), Barrera (1946), and Pesquera-Velazquez and Bermudez (1956) argue strongly for the existence of additional deposits of zeolites in similar sedimentary/volcanic environments north and south of the city of Oaxaca and in other parts of southern Mexico. There is little doubt that X-ray diffraction examination of such rocks will confirm these predictions.

## Acknowledgments

The author wishes to thank Ing. Salvadore Ulloa, Penoles Mining Co., S.A., for his assistance in the field and for his aid in surveying the literature. He is also grateful to Professor J. A. Wilson of the University of Texas for supplying several samples for X-ray examination.

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*Manuscript received, November 6, 1972; accepted for publication, December 8, 1972.*