

Mineralogical study of mordenite from the Sierra Madre del Sur, southwestern Mexico

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ABSTRACT

As a result of mineralogical investigations, large accumulations of hydrothermal zeolite have been found in pyroclastic and volcanic flows sequences of Cretaceous age from the geologic province Sierra Madre del Sur (Tumbiscatío, Michoacán, southwestern Mexico). X-ray diffraction, optical and scanning electron microscopy, Raman and infrared spectrometry confirm the discovery of mordenite zeolite of hydrothermal origin in extrusive rocks of southwestern Mexico. The absence of previous records of zeolite deposits in this region of Mexico encourages to continue the mineralogical research in order to evaluate the practical importance of this discovery of mordenite in Michoacán.

Keywords: mordenite, volcanic sequences, Tumbiscatío, Michoacán, southwestern Mexico.

RESUMEN

Como el resultado de investigaciones mineralógicas se encontraron importantes acumulaciones de zeolitas hidrotermales en la provincia geológica Sierra Madre del Sur (Tumbiscatío, Michoacán, suroeste de México). Los minerales zeolíticos se observaron en las secuencias volcánicas del Cretácico. Las técnicas analíticas utilizadas (difracción de rayos X, microscopía óptica y electrónica, espectrometría infrarroja y Raman) confirman el descubrimiento de mordenita de origen hidrotermal en la rocas extrusivas de la región suroeste de México. La completa ausencia de reportes de depósitos zeolíticos en el área estudiada anima a continuar las investigaciones mineralógicas en esta área con el fin de evaluar la importancia práctica del descubrimiento de la mordenita michoacana.

Palabras clave: mordenita, secuencias volcánicas, Tumbiscatío, Michoacán, suroeste de México.

INTRODUCTION

At present, about 40 natural zeolite minerals (overcoat mordenite, clinoptilolite, chabazite, and erionite) have been found in sufficient amounts and considerably high purity. Successively, they have been developed into key materials in oil processing and in the petrochemical industries, as ion exchangers, sorbents and

catalysts (Sand and Mumpton, 1978; Marfunin, 1994; Bish and Ming, 2001). The advent of zeolite marketing as an industrial material helps to solve three major problems in the new millennium: the development of effective industrial technologies, the improvement of agricultural productivity, and the reduction of environmental pollution created by industrial and municipal effluents. For example, the natural mordenites are used

at the present in drying and purification of acidic gases, in view of its particular resistance to thermal cycles in acidic environments (Giannetto *et al.*, 1985).

Mordenite is a common zeolite widely found in silica-rich rocks (rhyolite, andesite, and tholeiitic basalt), altered volcanic ash beds, and rarely, in dense olivine basalts and pegmatites (Tschernich, 1992). Mordenite has never been found in deep sea sediments. The most common types of occurrence for mordenite are sedimentary or hydrothermal. Fine crystals that fills veins, fissures, geodes or amygdaloids of various types of igneous rocks are considered of probable hydrothermal genesis, whereas the massive transformation of the glassy components of volcanic rocks is considered of sedimentary origin (Gottardi and Galli, 1985).

The main economic deposits of mordenite are located in altered late Cretaceous tuffs in Japan and in Pliocene mafic volcanic rocks in Nevada, USA (Tschernich, 1992). In Mexico, the first description of sedimentary mordenite was made by Mumpton (1973) in zeolitic tuffs from the Atoyac Valley (State of Oaxaca) that represent the upper unit of the Miocene Suchilquitongo Formation (Wilson and Clabaugh, 1970). Sedimentary zeolites occur also southeast of the geologic province of the Sierra Madre Occidental (in the southern State of Guanajuato) in the Oligocene volcanic-rhyolitic sequence of the Chichíndaro Formation (Pablo-Galán and Chávez-García, 1996). These deposits are close to the boundary with the Trans-Mexican Volcanic Belt (TMVB) and are characterized by clinoptilolite, heulandite and mordenite formed from pyroclastic material of rhyolitic composition deposited in a subaerial lacustrine environment. Hydrothermal mordenite has not been reported in the volcanic sequences of Mexico.

In southwest Mexico, we did not find any previous study of zeolite minerals (Ostroumov *et al.*, 1999). In particular, the State of Michoacán appears as an important region with potential for zeolite deposits because it is situated in the heart of the Trans-Mexican Volcanic Belt (TMVB) with more than 1,000 cinder cones (Hasenaka and Carmichael, 1985). Moreover, this young magmatic belt is superimposed on older Eocene pyroclastic rocks and, in addition to this, the transitional-marine Cretaceous volcanic sequences of the Guerrero terrane (Centeno-García *et al.*, 1993; Corona-Chávez, 1999) are exposed in the southern region of Michoacán.

The aim of this paper is to characterize the petrography, mineralogy, chemistry and spectrometry of mordenite of probable hydrothermal origin in the southwestern region of Mexico.

GEOLOGY AND PETROGRAPHY

The study area is located in the Sierra Madre del Sur near the town Tumbiscatío and the village Apo El Viejo (Figure 1). In this region a Mesozoic volcanic-sedimentary sequence known as Playitas Formation (PF)

was described (Centeno-García, 1994). The PF is characterized by andesitic-dacitic volcanic rocks interbedded with typical conglomerate and sandstone red beds, pyroclastic deposits, and horizons of shelf facies limestones with abundant invertebrate fossils. Mollusks such as *Pterotrigonia plicatocostata*, *Toucasia* sp., *Acateolnella* sp. and microfossils such as *Orbitolina* sp. (Gutiérrez, 1975) indicate an Early Cretaceous age for this sequence. Consequently we can suggest this biostratigraphic age for the zeolite specie of this study.

The zeolite and its mineral assemblage is closely related to porphyric dacitic flows and pyroclastic rocks with dacitic-rhyolitic composition from the PF. The structure of the zeolitic volcanic rocks is massive for the lava flows and interbedded for the rhyolitic-dacitic rocks. Nevertheless, the typical feature of zeolite-bearing rocks is the disseminated texture and the presence of white geodes from a few millimeters to 2–3 centimeters. In fact, we observed a high concentration of such zeolitic geodes which are characterized by the typical radial structure of zeolite minerals associated with minor calcite, quartz and rarely chlorite. This mode of occurrence is typical for almost all hydrothermal mordenite (Pe-Piper, 2000).

Petrographically, the andesitic-dacitic lava flows show a porphyric texture with phenocrysts of plagioclase and a fine matrix composed by plagioclase-hornblende \pm quartz \pm oxides. Generally, the zeolitic pyroclastic rocks are crystalline tuffs with a predominating red-brown glass matrix and sporadic lithics. Microscopically, the mordenite can be observed as excellent very slender prismatic crystals elongated and striated along the c-axis and thin fibers 10–20 μ m to 100–500 μ m long and 0.5 to 3.0 μ m wide (Figure 2).

SAMPLING AND ANALYTICAL METHODS

Ten samples were collected from the zeolitic-volcanic sequences for analytical studies. Thin sections were studied with an optical microscope by oil-immersion methods to identify the minerals and their paragenesis. The minerals were identified by X-ray diffraction (XRD) with a Siemens D5000 diffractometer equipped with filtered CuK α radiation, scanning at 0.6° 2 θ /min over the range 3 to 70° 2 θ . The chemical composition of the selected mordenite crystals was determined by X-ray fluorescence (XRF) on pressed powders. Morphology and composition of the mineral were determined by scanning electron microscopy (SEM) coupled with a Kevex energy dispersive spectrometer (EDX) calibrated with glass and feldspar. The composition obtained by this technique is considered semi-quantitative, but useful in establishing SiO₂/Al₂O₃ and other ratios.

Infrared and Raman spectrometry were applied especially for the determination of vibrations of water molecules, hydroxyl groups, ionic substitutions and local

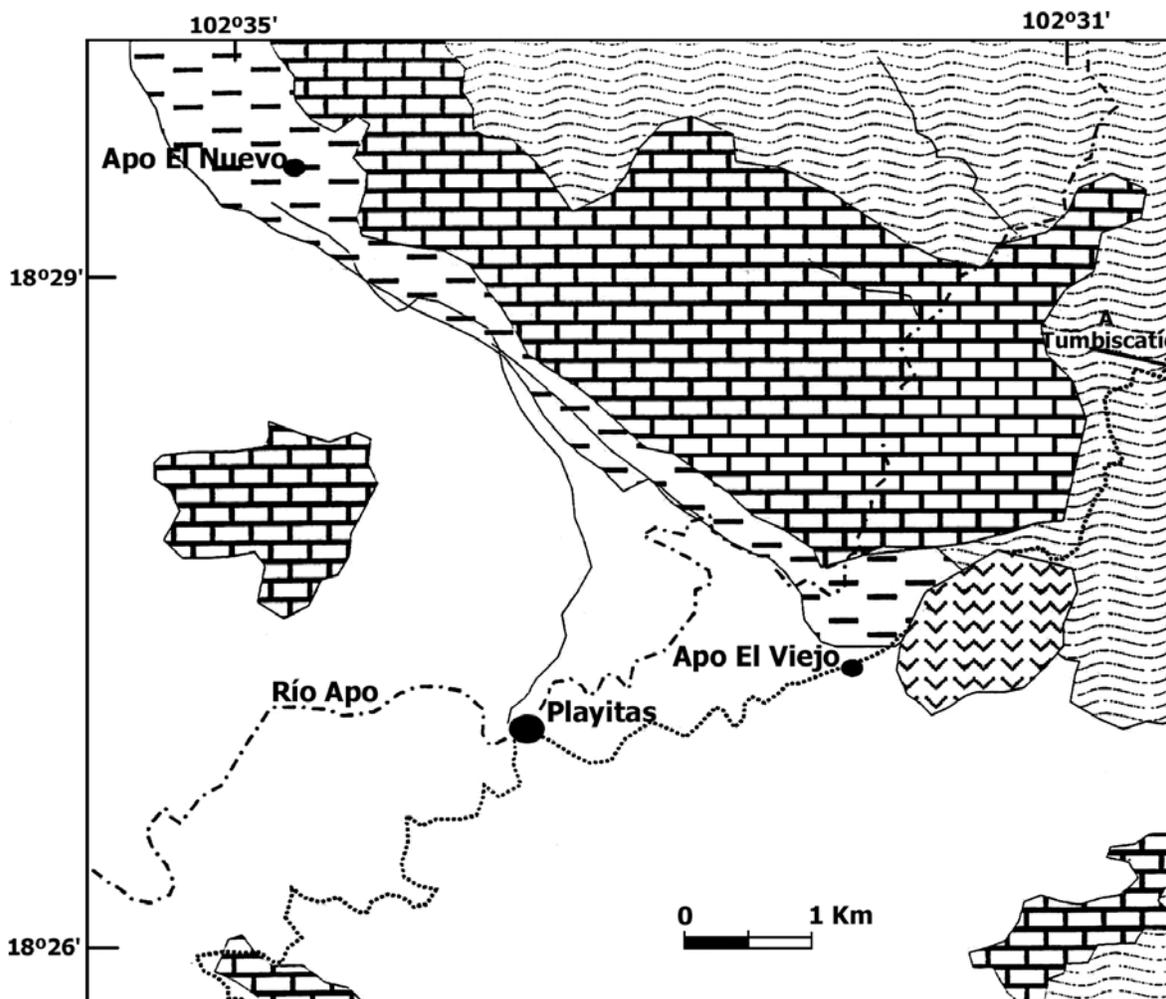


Figure 1. Geological map and location of mordenite occurrence in Michoacán, in southwest Mexico.

bonds in the structure of zeolite minerals. The infrared absorption spectra of natural mordenite were measured with a FTIR (Fourier transform infrared) Nicolet 20 SXC spectrometer for a scanning from 4,000 to 400 cm^{-1} wavenumber on material dried at 50°C and pressed into KBr discs. Fourier-transform Raman spectra were

obtained with a Bruker instrument (RFS100) at the 1,064 nm excitation line of a Nd:YAG laser, both in microscopic and macroscopic modes, for a scanning from 4,000 to 100 cm^{-1} with an actual spectral resolution of $\pm 2 \text{ cm}^{-1}$. In both cases, the beam power was kept between 200 and 250 mW.

RESULTS AND DISCUSSION

Chemical composition

The chemical composition was determined by X-ray fluorescence and, successively, the structural formulae was calculated on the basis of 96 oxygen (Breck, 1974) to $(\text{SiO}_2)_{40} (\text{Al}_{0.91}\text{Fe}_{0.008}\text{O}_2)_8 (\text{Na}_{0.37}\text{Ca}_{0.27}\text{K}_{0.029}\text{Mg}_{0.04})_8 \text{H}_2\text{O}$. The obtained Si/Al ratio (5.47) is higher than those corresponding to sedimentary mordenites (Table 1) from the Miocene Suchilquitongo Formation and from the Oligocene Chichindaro Formation (Pablo-Galán and Chávez-García, 1996). The same ratio was determined by scanning electron microscopy (SEM) coupled with energy dispersive spectrometer (EDX).

The chemistry of mordenite was reviewed by Passaglia (1975), who showed that there are no large variations in the chemical composition of this zeolite mineral with probably sedimentary and hydrothermal origin. Hydrothermal mordenite have higher silica and water contents, and their lattice constants are a little larger than those of sedimentary mordenite (Godovikov, 1985). Thus, the observed chemical composition indicates a hydrothermal origin for the mordenite from Michoacán (Senderov and Petrova, 1990; Pe-Piper, 2000).

X-ray diffraction analyses

The X-ray diffraction data of the studied samples indicate a high degree of crystallinity for the mordenite, and almost correspond to the analogous diffractogram of the standard from Aros, Scotland (JCPDF 06-0239), with the formula $(\text{CaNa}_2\text{K}_2)\text{Al}_2\text{Si}_{10}\text{O}_{24} \cdot 7\text{H}_2\text{O}$. The principal reflections of the studied mordenite are listed in Table 2.

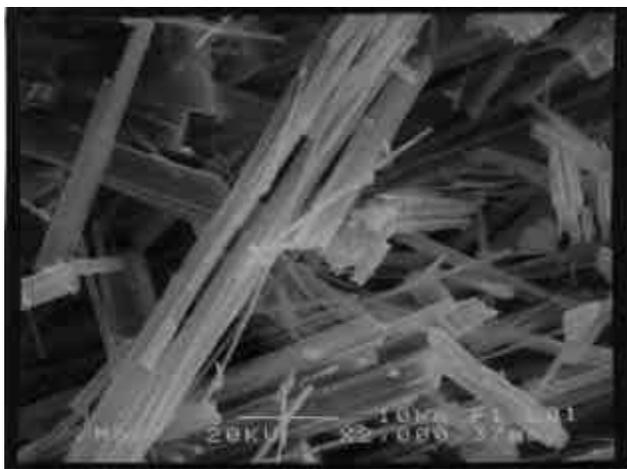


Figure 2. Scanning electron micrograph of mordenite fibers from Tumbiscatío, Michoacán.

The lattice constants in are a: 18.142 Å, b: 20.501 Å, c: 7.521 Å. According to Gottardi and Galli (1985), sedimentary mordenites are characterized by a little smaller lattice constants than those determined in most of the hydrothermal mordenites.

Spectrometry

In the Raman spectral region up to 500 cm^{-1} , a deformation ($\nu \sigma$) O–Si (Al)–O of the frame and Me–O vibrations were observed (Figure 3a). At higher frequencies of $500\text{--}1,200 \text{ cm}^{-1}$, symmetrical vibrations of valence (ν_s) and antisymmetrical (ν_{as}) of the same structural frame were observed.

This type of spectra with predominant low-intensity frequencies is common in other Raman spectra measured from natural zeolites (Angell 1973; Pechar and Rykl 1983). Nevertheless, all bands of Michoacán mordenite feature a lower intensity than characteristic bands of typical low frequencies. Generally, the zeolites are characterized by Raman spectra with an intense band at about $510\text{--}480 \text{ cm}^{-1}$. In fact, our mordenite Raman spectra show bands at frequencies lower than 400 cm^{-1} . This fact can be explained by a very high Si/Al ratio ($>5\text{--}10$) that is typical for the zeolites of the mordenite group.

The band of the antisymmetrical and symmetrical vibration of hydroxyl groups lies in the region of

Table 1. Average chemical composition (wt%) of mordenite from 1: tuffs of the Suchilquitongo Formation; 2: Chichindaro Formation; and 3: Playitas Formation, Tumbiscatío.

Oxides	1	2	3
SiO ₂	70.00	78.57	69.86
Al ₂ O ₃	11.80	13.67	10.72
TiO ₂	na	0.07	0.02
Fe ₂ O ₃	0.46	0.87	0.13
MnO	na	0.07	0.01
MgO	na	1.52	0.41
CaO	2.14	2.71	3.43
K ₂ O	2.53	1.76	0.31
Na ₂ O	1.33	0.76	2.65
H ₂ O	11.74	-	12.82
Unit-cell contents			
Si	40.00	39.85	40.00
Al	8.00	8.16	7.31
Ti	na	0.02	0.01
Fe	0.20	0.33	0.06
Mg	na	1.15	0.35
Ca	1.31	1.47	2.13
K	1.87	1.14	0.23
Na	1.41	0.75	2.97
H ₂ O	22.56	-	28.64
O	96	96	96
Si/Al	4.64	4.88	5.47

Table 2. Powder X-ray reflections of mordenite from Tumbiscatío, Michoacán. Operating conditions: Siemens diffractometer Kristalloflex K4 (30 kv, 22 mA, Cu Ka radiation). FULLPROF program: I obs and d obs through profile matching mode; d calc according to the single crystal structure study ($a = 18.142\text{Å}$; $b = 20.501\text{Å}$; $c = 7.521\text{Å}$).

d (Å)		I (%)	hkl
d obs	d calc		
13.65	13.700	17	110
9.10	9.105	65	200
6.51	6.520	27	111
6.41	6.405	20	130
6.10	6.105	10	021
5.81	5.802	24	310
4.53	4.525	57	330
4.15	4.145	15	420
4.00	4.005	89	150
3.85	3.843	19	241
3.77	3.767	10	002
3.48	3.483	100	202
3.40	3.395	87	350
3.22	3.223	96	511
3.10	3.102	6	441
2.89	2.893	33	332
2.70	2.705	13	171
2.56	2.563	13	461
2.52	2.525	23	442
2.46	2.463	13	641
2.11	2.115	6	712
2.049	2.050	13	391
2.016	2.017	10	353
1.955	1.953	17	680
1.882	1.883	17	004
1.812	1.814	19	4101
1.795	1.793	11	1111
1.701	1.700	17	880
1.665	1.667	10	483
1.546	1.545	12	6102
1.526	1.527	16	644
1.444	1.445	13	194
1.412	1.411	9	1171
1.386	1.385	12	0104
1.376	1.375	14	914

$3,300\text{--}3,600\text{ cm}^{-1}$. They have a strong intensity in the infrared spectrum and a low intensity in the Raman spectrum (Figure 3 a).

The H–O–H bending frequency of the H_2O molecule lies at a wavenumber of $1,629\text{--}1,646\text{ cm}^{-1}$, with a medium intensity in the infrared absorption spectrum (Figure 3b) and a low intensity in the Raman scattering spectrum. For the OH–stretch region, the H–bonded stretch occurs with high intensity at $3,614$ and $3,460\text{ cm}^{-1}$ in the infrared spectrum and at $3,377$ and $3,285\text{ cm}^{-1}$ in the Raman spectrum. The infrared and Raman spectra contain bands of the antisymmetrical stretching vibration of the tetrahedral T–O bonds ($T = \text{Al, Si}$), with a wavenumber range of 880 to $1,046\text{ cm}^{-1}$.

These last bands have a high intensity in the infrared absorption spectrum and a low intensity in the Raman spectrum. All the spectra contain bands of symmetrical stretching vibration of Si (Al)–O bonds.

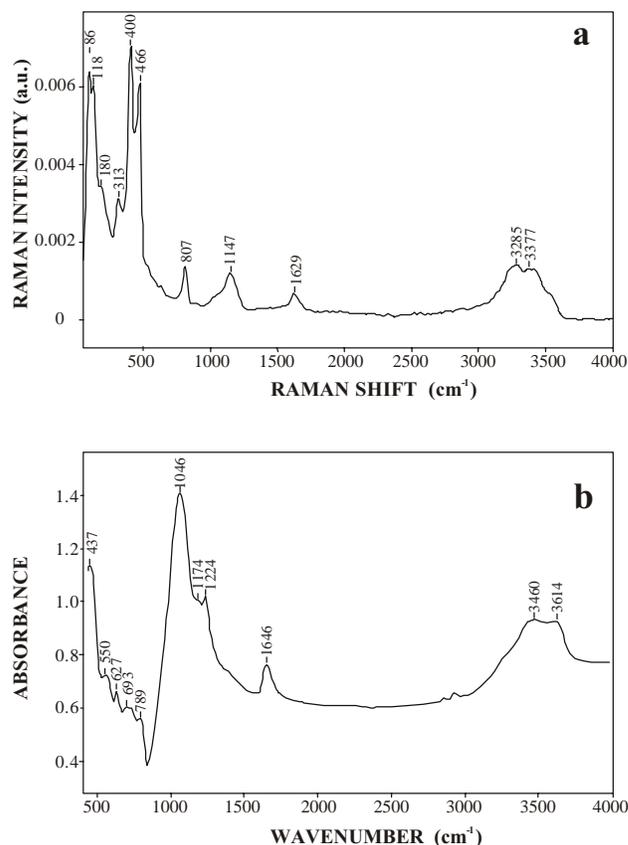


Figure 3. a) Raman and b) infrared spectra of mordenite from Tumbiscatío, Michoacán.

These bands can be found in the wavenumber region of 627 to 789 cm^{-1} . In Table 3, a complete interpretation of the Raman and infrared spectra is presented.

CONCLUSIONS

X–ray diffraction (lattice constants), chemical (Si/Al ratio, water content) and spectrometric (high intensity of the antisymmetrical and symmetrical vibration of hydroxyl groups and H_2O molecule) examinations confirm the discovery of hydrothermal mordenite in the Sierra Madre del Sur, southwestern Mexico. The lithologic association (pyroclastic and volcanic flows sequences of Cretaceous age) and the mode of occurrence (deposition in geodes and amygdales of porphyric dacitic flows and pyroclastic rocks with dacitic–rhyolitic composition) also indicate a hydrothermal origin for the mordenite.

The mordenite discovery could represent an interesting economic opportunity, particularly because of the complete absence of zeolite deposits southwest of the Mexican Volcanic Belt in the Sierra Madre del Sur. Even though the economic potential of Michoacán

Table 3. Evaluation of Raman and infrared spectra of Michoacán mordenite.

Type of vibration	Infrared absorption spectra, medium range	Raman spectra
OH-stretching	3614w	3377w
	3460w	3285w
H ₂ O bending	1646w	1629w
External TO ₄	1224m	1147w
Antisymmetrical stretching	1046s	
	880w	
Symmetrical stretching	789w	807w
	693w	
	627w	
Bending O-Si (Al)-O	437s	466s
		443w
		400s
Translational H ₂ O		313w
Translational Na,Ca-O Na,Ca,-H ₂ O		180w
		118s
		86s

Note. Intensity of the bands: s-strong, m-medium, w-weak.

mordenite has not been determined, it is indicated by the good exposition of the Mesozoic volcanic successions, and by the mineralogical, petrologic and geologic characteristics analogous to other important zeolite deposits in the world (Senderov and Petrova, 1990; Tschernich, 1992). Naturally, we believe that other specific geological and experimental studies should be carried out to understand the true potential applications of the mordenite from the Michoacán region in southwestern Mexico.

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