

# GEOLOGICAL, MINERALOGICAL, GEOCHEMICAL PROPERTIES, AND CHARACTERIZATION OF MARINE ZEOLITE

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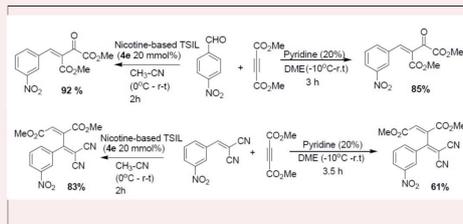
JOURNAL OF ONGOING CHEMICAL  
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Encouraging Young Chemists

A tidy laboratory  
means a lazy chemist.  
-- Jöns Jacob Berzelius (Swedish  
chemist, 1779-1848)



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## Geological, Mineralogical, Geochemical Properties, and Characterization of Marine Zeolite

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### Abstract

The study investigates marine Hekimhan (Malatya) zeolites. The unit was sandstone interlayered, green, hard, fine-thick-layered (5-500 cm), and fine-laminated. Its type section has a thickness of 37 m and has a consistency of 24 km in the lateral direction. Mineralogical and structural analyses such as X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR), Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA), and Brunauer-Emmett-Teller (*BET*) analysis were performed to carry out the physical, chemical, and mineralogical characterization of the examined zeolite. Moreover, grain size distribution, consistency limits, specific weight, and pH values were determined. The results of the XRD analysis showed that the main mineral was clinoptilolite-type zeolite. In addition, the calcite mineral was detected. The SEM images of the zeolite samples revealed a layered microstructure and the BET results revealed that the units had a mesoporous structure.

**Keywords:** Clinoptilolite, Clay, Mesopore, Marine Zeolite, Fourier Transform Infrared Spectroscopy

## INTRODUCTION

Zeolites are alkaline or aluminum silicates with high cation exchange capacity. While clay minerals contain silica structures with tetrahedron geometry and alumina structures with octahedron geometry, the silica and alumina structures in zeolites are tetrahedron-shaped [1]. The different tetrahedral links of zeolites lead to the formation of different zeolite types [2].

Zeolites contain channels and cavities (Figure 1) and losing the water kept in the channels at high temperatures without disrupting their structure is among their most important properties. They contain silicon, aluminum, and oxygen in their skeleton structure and water molecules and alkaline and soil alkaline cations that allow ion exchange in their pores [3]. One of the most important factors that determine the physical and chemical properties of zeolites and their use is their aluminum content, in other words, their Si/Al ratio. Zeolites can be divided into three groups as low-silica ( $\text{Si/Al} < 4$ ), intermediate-silica ( $4 < \text{Si/Al} < 20$ ), and high-silica ( $20 < \text{Si/Al} < 200$ ) zeolites based on their Si/Al ratios. The thermal, hydrothermal, and chemical stability of zeolites increases with increasing Si/Al ratio [4]. Silica-poor zeolites have a hydrophilic structure that is resistant at temperatures up to 700 °C while zeolites with a high silica content are resistant at temperatures up to 1300 °C and have a hydrophobic structure. They have a wide use in the industry due to their properties [5].

Commercially available natural zeolite formations are limited to certain special zeolite types. Clinoptilolite (CLP) is among the most abundant natural zeolite types [6]. Zeolites are colorless crystals and the sizes of their crystals, which are obtained by traditional synthesis from the gel phase, are usually between 1  $\mu\text{m}$  and 10  $\mu\text{m}$  and have densities in the range of 1.9-2.1  $\text{g/cm}^3$  [7].

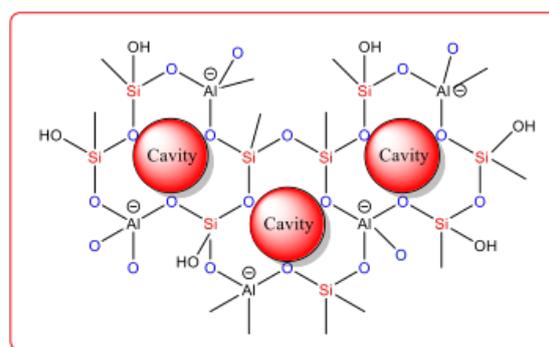


Figure 1. Chemical structure and cavities of zeolite

Recent studies have shown that natural zeolites could be used in the trapping and separation of non-iron metal ions. The commercial use of zeolites in the industry is based on three important properties, which are adsorption, ion exchange, and catalytic properties [8]. Zeolites can be used as adsorbents in purification and separation applications. The removal of volatile organic chemicals from gas flows and drying of reactive gases are examples of purification applications. The separation of normal paraffin from

branched paraffin is an example of bulk separation applications [9].

The most important advantages of zeolites include chemical and physical properties such as non-swelling, ion exchange and their catalytic activity, function as a molecular sieve, high absorption, chemical stability, drying abilities, regeneration, and thermostability [10]. These properties of zeolites have emerged as important factors in industrial development due to allowing the treatment of petroleum, natural gases, and wastes. Natural zeolites are also used to improve the physical properties of concrete due to their hollow and porous structure. Zeolites are also used in water treatment to remove cationic pollutants such as ammonium [11].

Natural zeolites are found in many regions in the world. In the last five years, the natural zeolite production worldwide was around 1100 kton/year and their leading producers were China, Korea, the USA, New Zealand, Turkey, and Cuba [10]. Zeolites are formed by the closed-system alteration of volcanic ash in alkaline lake deposits, burial diagenesis of volcanic ash and/or vertical sedimentation from open-system alteration, hydrothermal alteration of volcanic or sedimentary rocks, and deep-sea sedimentation [12].

Zeolites around Turkey (Malatya-Hekimhan) are of marine origin and distributed around an area of about 90 km<sup>2</sup>. The upper cretaceous-old unit is divided into two units comprising a bottom zeolite unit and an upper zeolite unit. The bottom zeolite unit comprises levels that contain mafic mineral-containing zeolite and solid zeolite. The maximum thickness of the unit is 15 m and the unit has a consistency of 5 km in the lateral direction. The upper zeolite unit consists of zeolite minerals with a sandstone interlayer. The maximum thickness of this unit is 38 m and the unit has a consistency of 24 km in the lateral direction. The total geological reserve of the bottom and upper zeolite levels is 190 million tons [13].

The study carries out the mineralogical, chemical, and physical characterization of the natural marine zeolites in Hekimhan region of Malatya, Turkey.

## RESULTS AND DISCUSSION

### Physical Analysis

Physical properties analysis experiments of zeolite were performed at our geotechnics laboratory. We used standard test method of The American Society for

Testing and Materials [14-16]. Physical analysis results of marine zeolite was presented in Table 1.

**Table 1.** Physical properties of the zeolite

Properties	Value	
Grain size distribution (%)	Gravel	0,59
	Sand	38,16
	Fine	61,25
Atterberg limits (%)	Liquid Limit (LL)	72
	Plastic Limit (PL)	38
	Plastisity Index (PI)	34
Specific Weigth (Gs)	2,19	

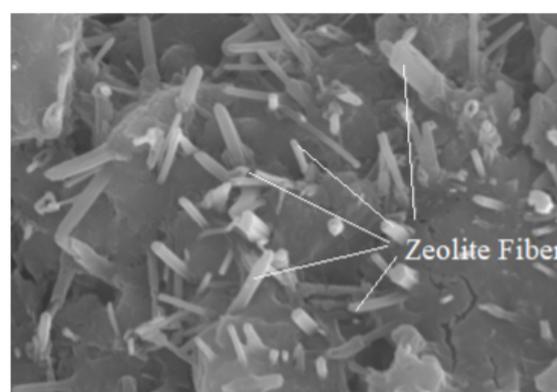
Chemical analysis of the zeolites has been discussed in the following lines:

### pH measurement

The pH value of the zeolite sample was measured using a total of 20 g zeolite sample after stirring the sample for 30 min in 50 mL pure water. The pH value of the sample was 9.56 [14]. Hence, the zeolite sample was determined to be alkaline.

### SEM Analysis

The SEM images were obtained to determine the mineral structure and micro-particle properties of the natural zeolite. Figure 2 shows the SEM images of the zeolite sample. The morphology of the clinoptilolite-type natural zeolite showed that crystals of different shapes and sizes formed the distributed particles by diffusing into the amorphous structure.



**Figure 2.** Tetragonal solid-core/tubular single-crystalline fibers of the zeolite

The surface of the natural zeolite sample revealed a rather heterogeneous structure. Single-fiber crystals and amorphous structures co-existed in the zeolite.

Crystal structures of varying sizes and shapes were observed together with amorphous masses. The size of the fiber crystals in the SEM images ranged from 0.1  $\mu\text{m}$  to 2  $\mu\text{m}$ . The SEM images of the zeolite samples revealed that the zeolite samples had a tetragonal single-fiber crystal structure.

### XRD Analysis

Powder XRD pattern of the of zeolite presented in Figure 3 gives information related to triple phases as quartz, calcite and clinoptilolite structure. In this prepared zeolite. The XRD peaks at 26.60, 27.66, 42.15, 50.41 and 62.24 reflection planes of the quartz. The peaks of 29.39, 39.48, 43.12, 47.55 and 48.50 reflection planes of calcite. Similarly peaks of 9.75, 10.47, 17.28, 18.95, 19.58, 22.63, 31.92 and 35.45 reflection planes of clinoptilolite. According to the results of the XRD analysis of the natural zeolite was observed main mineral in the structure of the zeolite is clinoptilolite. The results are consistent with the literature [17,18].

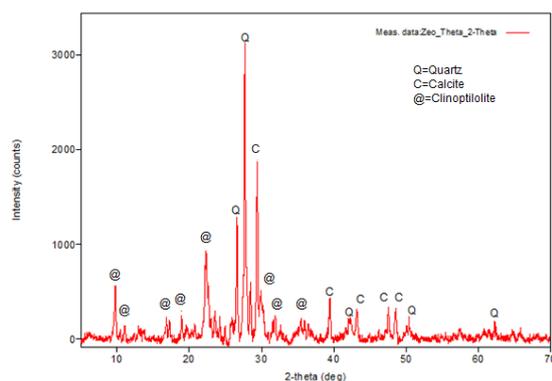


Figure 3. X-ray diffraction spectra of the zeolite

### XRF Analysis

The XRF analysis result of zeolite presented in Table 2 gives information related to mineralogical analysis data. Chemical analysis shows 46.0 wt.%  $\text{SiO}_2$ , 10.8 wt.%  $\text{Al}_2\text{O}_3$ , 16.1 wt.%  $\text{CaO}$  as major components, 5.11 wt.%  $\text{Fe}_2\text{O}_3$ , 3.27 wt.%  $\text{MgO}$ , 2.11 wt.%  $\text{K}_2\text{O}$  and 1.49 wt.%  $\text{Na}_2\text{O}$  as minor components and 1.32 wt.% trace-element. Si /Al ratio was observed as 8.12 and according to the Si /Al ratio, the sample is in the middle silica zeolite group. The results are consistent with the literature [18].

Table 2. Chemical compositions of the zeolite samples (weight %)

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{TiO}_2$	$\text{MnO}$	$\text{SrO}$	F	LOI
45.96	10.77	5.11	16.09	3.27	0.09	2.11	1.49	0.52	0.17	0.15	0.18	13.89

### FTIR Analysis

The FTIR spectra for zeolite, are shown in Figure 4. The peak at  $512\text{ cm}^{-1}$  belongs to vibration of Fe-O bonds. The absorption bands at 1004, 873, and  $422\text{ cm}^{-1}$  were attributed to Si-O-Si antisymmetric stretching vibrations, Si-O-Si symmetric stretching, and Si-O-Si or O-Si-O in zeolite, respectively. The peak at  $713\text{ cm}^{-1}$  belongs to vibration of Al-O bonds. In the region of  $422\text{ cm}^{-1}$  and below there are many differences in the number and frequency of the absorption, reflecting the variation in framework composition. These values of the zeolite studied are consistent with the literature [19,20].

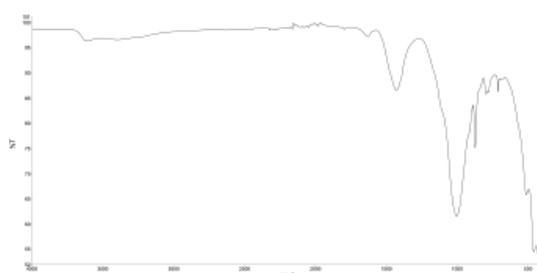


Figure 4. FTIR spectra of the zeolite

### DTA and TGA Analysis

The thermal stability of zeolite was evaluated by thermal gravimetric analysis-differential thermal analysis (DTA and TGA) and presented in Figure 5. DTA and TG analysis shows that there are three regions for both data which are related to endothermic activity in the samples. The first reaction up to  $100^\circ\text{C}$  should be due to the decomposition of the adsorbed water of zeolite which corresponds to the highest temperature for the stability of samples. The second reaction between  $600\text{--}800^\circ\text{C}$  are the transition should be the formation of a new phase with losing water from the structure.

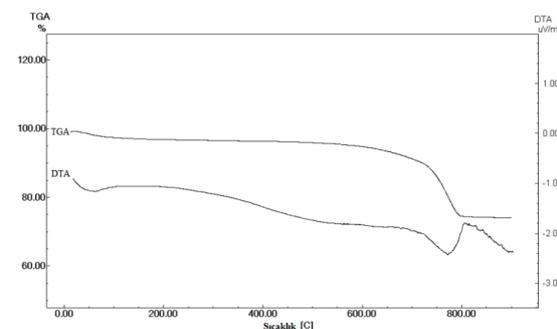


Figure 5. DTA and TGA spectra of the zeolite

The main endothermic peak is seen at about 750-800 °C. This peak of endothermic reaction is due to the removal of the structure water and is observed at around 750-800 °C in keeping with the TGA curves. The DTA and TGA of the zeolite revealed an intermediate-silica structure. These values of the zeolite studied are consistent with the literature [21].

### BET (Brunauer-Emmett-Teller) Analysis

The BET analysis is the most widely employed procedure to evaluate the surface area of porous and finely-divided materials despite its weak theoretical foundations. The *BET area* of nonporous, macroporous, or mesoporous solids can surely be viewed under specific controlled conditions. The International Union of Pure and Applied Chemistry (IUPAC) defines the pore size in nanoporous compounds as mesopores of sizes ranging from 2 to 50 nm [22]. BET analysis results of marine zeolite was presented in Figure 6 and Table 3, BET surface area results of the zeolite sample was observed that the surface area of the sample is 55.29 m<sup>2</sup>/gr and the pore diameter is 5.19 nm. When we compared with IUPAC data, it is observed that it has a mesoporous structure.

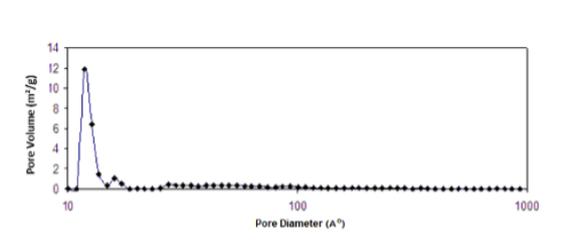


Figure 6. BET analysis of the zeolite

Table 3. BET analysis of zeolite

Sample	BET (m <sup>2</sup> /g)	V <sub>Total</sub> (cm <sup>3</sup> /g)	D <sub>BET</sub> (nm)
Zeolite	55,29	0,072	5,19

## EXPERIMENTAL

### Materials and Methods

The FTIR analysis was performed with a PerkinElmer Spectrum 100 GladiATR FT/IR spectrometer. The crystal structure analysis of the zeolite was performed by an X-ray diffractometer labeled Rigaku Rint 2000, which is powered by Cu K<sub>α</sub> radiation, was used for characterization. The Leo EVO-40 VPX scanning electron microscope (SEM) was used to examine the

microstructural properties and the surface morphology of the synthesized powders. Tristar 3000 Micromeritics was used in the Brunauer-Emmett-Teller (BET) analysis. The X-ray fluorescence (XRF) analysis was performed using the Rigaku ZSX Primus II. The thermogravimetric analysis (TGA) was made using the Shimadzu TGA-50 instrument in a temperature range from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under air atmosphere. Shimadzu DTA-50 was used to perform the differential thermal analysis (DTA) in the temperature range from room temperature to 800 °C at a heating rate of 10 °C per minute. Physical trials were performed in the Geotechnics Laboratory of the Malatya Turgut Özal University Hekimhan Mehmet Emin Sungur Vocation College.

## CONCLUSION

The results of the study led to the following conclusions:

1. According to the United Soil Classification System (USCS), the zeolite was in the MH group.
2. The pH measurements revealed that the zeolite was alkaline.
3. The SEM analyses showed that the zeolite sample was made up of a tetragonal single-fiber crystal structure and the structure was clinoptilolite.
4. The results of the XRD analysis showed that the main mineral in the zeolite structure was composed of clinoptilolite, calcite, and quartz.
5. The XRF results revealed that the main structure was formed by SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, and Fe<sub>3</sub>O<sub>4</sub>. The structure was in the intermediate-silica group due to its Si/Al ratio of 8.12.
6. The FTIR analyses showed the characteristic bond vibration frequencies of Si-O, Al-O, and Fe-O.
7. The DTA/TGA of the zeolite revealed an intermediate-silica structure.
8. The results of the BET analysis showed that the zeolite had a mesoporous structure with respect to its pore size.

The use of zeolite with established physical, chemical, and morphological structure will greatly contribute to the energy, agriculture, animal husbandry, mining, metallurgy, construction, and ceramic industries, and prevention of environmental pollution, which severely threatens human health. The results indicated that the studies in the said fields

should continue.

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