The Zeolite Deposit of Hekimhan in the Malatya Basin

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Abstract. Zeolite deposits in the Malatya Basin which is formed of the Yüksekova Group were investigated in the present study. The zeolites were occurred in the two layers: the lower zeolite layer and the upper zeolite layer of the Sarıkız Formation of Campanian-Maastrichtian age within the flysch like sediments at Hekimhan in the northern part of the Malatya Basin. Characterization studies of the zeolite samples were done by XRF, XRD and SEM images and the results showed that the main structures of the zeolites were clinoptilolite-(Cs), heulandite and calcite and the geological occurrences of zeolite is in marine environments.

1. Introduction
Nearly 50 different type of natural minerals are called zeolite [1] and zeolite depositions generally occur from volcanic materials in closed saline-alkaline lakes, alkaline soils, open fresh—water lakes or groundwater, low-grade metamorphosed sediments, altered deposit and diagenetic systems [2]. Zeolite has a three dimensional crystalline alumina-silicate framework structure and is one of the important industrial minerals which is used in many application area, like adsorbents and catalysts [3]. Therefore, the finding new zeolite deposits and their characterization are important for the developments of the region and economy.

Economically important zeolite deposits are commonly formed by the alteration of vitric volcanic materials in sedimentary environments, especially at relatively low temperatures in deep-sea sediments [4]. Turkey has several zeolite deposits of mostly sedimentary origin and they are located at Beypazarı, Yozgat, Nevşehir, Kula, Emet, Şile, Bigadiç, Gördes and Keşan [5] and Alaçatı (Çeşme) [6]. The common zeolites reported in Turkish deposits are clinoptilolite, heulandite and analcime [7].

The objective of the current contribution is to present an overview of the stratigraphic, mineralogical and geochemical characterizations of marine zeolites of Upper Cretaceous in the northern part of the Malatya Basin, Eastern Anatolia, Turkey.

2. Materials and methods
Zeolite samples were to investigate the mineralogical and geochemical characterizations of marine zeolites which occurred in the two layers: the lower zeolite layer and the upper zeolite layer of the Sarıkız Formation of Campanian-Maastrichtian age within the flysch like sediments at Hekimhan in the northern part of the Malatya Basin (figure 1).

The samples were crushed, ground and sieved to obtain the size of 60 meshes. All samples were characterized by X-ray fluorescence spectroscopy analysis (XRF- ACME laboratory in Canada), Rigaku Miniflex 600 with Cu Kα (40 kV, 15 mA, λ=1.54050 Å) XRD and Leo Evo-40x VP Electron Microscope.
3. Results and discussion

3.1. Geological and stratigraphic setting

The study area is located in the Malatya Basin which is formed of the Yüksekova Group which is the product of Late Cretaceous to Early Eocene island-arc volcanism on an ophiolitic basement (Hocalikova Melange) [8]. The samples were collected from Sarıkız Formation that consists of flysch like sediments with the Campanian-Maastrichtian Hasançelebi Volcanic rocks, which are represented by trachyandesite, alkalitrachyte, dacite and tuff [9, 10]. The zeolite deposition in the study area was divided into two layers: the lower zeolite layer and the upper zeolite layer within the Sarıkız formation (figure 2 and figure 3). The lower zeolite layer is a massif zeolite that is greenish in colour, has consolidated, locally thinly laminated structure. The type section of the lower zeolite layer is located about 1.5 km southeast of Kandil village and deposited in mainly deep-sea environment of the Sarıkız Formation. The thickness of zeolite layers was in the range of 2 m to 12 m and the estimated geological reserve was nearly 14 million tons. The upper zeolite layer consists of sandstone interbedded zeolite which is greenish in colour, consolidated, thin to thick-bedded (5-500 cm) and thinly laminated. The type section of the layer is located on the road of Malatya-Hekimhan. At the type section, the layer is of 37 m thick and is a laterally continuous for about 24 km. The layer is located with the volcano-clastic and trachyandesite of the Hasançelebi Volcanics and the upper parts deposited in deep-sea environment. The geological reserve of the upper zeolite layer was estimated to be 176 million tons.

3.2. Analysis of samples

Major element analyses of the samples showed that the main composition of the zeolite consists of SiO$_2$ and Al$_2$O$_3$, as expected (in Table 1). The main difference between the lower and upper zeolite
layer is CaO content. The percentage of CaO content of the upper zeolite layer is higher than that of the lower zeolite layer. The most likely source of CaO is Kirankaya Formation. On the other hand, the trace elements analysis of the samples indicated that the values of Sr, Ba and Zr as major elements are much more than other elements (not given in the text), representing the formation of Ba-rich clinoptilolites in a sulfate-depleted environment in marine sediments [11].

![Image](image.png)

**Figure 2.** a) Lower zeolite layer (l), Hasançelebi Volcanics (Ch), Sarıkız Formation (Cs), b) Mud-crack in the lower zeolite layer, c) Massif zeolite horizon in the lower zeolite layer and d) Upper zeolite layer (u), Hasançelebi Volcanics (Ch), Sarıkız Formation (Cs).

**Table 1.** Major elemental composition of the samples collected from the lower and upper zeolite layer

| % Oxides | The lower zeolite layer | The upper zeolite layer |
|----------|-------------------------|-------------------------|
|          | L-1 | L-2 | L-3 | U-1 | U-2 | U-3 |
| SiO₂      | 61.74 | 63.86 | 64.37 | 51.19 | 48.82 | 53.72 |
| Al₂O₃     | 13.01 | 12.95 | 12.74 | 11.91 | 10.53 | 11.30 |
| Fe₂O₃     | 2.77  | 1.97  | 1.88  | 2.59  | 2.09  | 2.60  |
| MgO       | 2.53  | 1.91  | 1.92  | 2.38  | 1.90  | 2.06  |
| CaO       | 1.63  | 1.67  | 1.80  | 10.44 | 14.15 | 10.83 |
| Na₂O      | 1.29  | 2.36  | 2.17  | 0.54  | 0.70  | 1.15  |
| K₂O       | 0.83  | 0.99  | 0.96  | 0.91  | 1.00  | 1.81  |
| TiO₂      | 0.12  | 0.14  | 0.15  | 0.23  | 0.19  | 0.31  |
| LOI       | 15.9  | 13.8  | 13.8  | 19.1  | 20.1  | 15.6  |
| TOT/C     | 0.10  | 0.10  | 0.04  | 1.61  | 2.45  | 1.76  |
| TOT/S     | 0.01  | 0.04  | 0.01  | 0.01  | 0.01  | 0.01  |
| SUM. %    | 99.86 | 99.70 | 99.85 | 99.41 | 99.61 | 99.53 |
Figure 3. Generalized stratigraphic section of the study area
The crystal structures of the samples were determined by XRD and just one pattern is given in figure 4. a, as an example. The patterns indicated that main structure of the zeolite was clinoptilolite-(Cs) (ICDD-PDF2.DAT 00-044-1398), heulandite and calcite (ICDD-PDF2.DAT 01-072-1937) which was supported with the SEM image (figure 4b) Clinoptilolite and heulandite are widespread in deposits of salin-alkaline lakes in burial diagenetic environments and in deep-sea sediments and they are most often associated with acidic rocks [6]. In the study area, the most likely sources of zeolite occurrences are marine tuff and reworked tuff of the Campanian-Maastrichtian volcanic rocks (Hasançelebi Volcanics) interfingering with the flysch-like sediments (Sarıkız Formation) deposited in deep-sea conditions. Clinoptilolites in acidic vitric tuffs and vitric sediments interbedded with the deep-sea deposits in the rapid sedimentation areas adjacent to continents and island arcs seem to be caused by burial diagenesis [12].

![Figure 4. XRD pattern (a) and SEM image (b) of the zeolite sample](image)

4. Conclusions
The zeolite deposition in the study area was divided into two layers: the lower zeolite layer and the upper zeolite layer within the Sarıkız formation and the lower zeolite layer is massif zeolite and its estimated geological reserve is nearly 14 million tons. The upper zeolite layer consists of sandstone interbedded zeolite which is greenish in colour, consolidated and thin to thick-bedded (5-500 cm) its geological reserve of the upper zeolite layer is estimated to be 176 million tons. The characterization studies showed that the main structure of the zeolite was clinoptilolite-(Cs), heulandite and calcite and the most likely sources of zeolite deposits are marine tuff and reworked tuff of the Campanian-Maastrichtian volcanic rocks interfingering with the flysch-like sediments (Sarıkız Formation) deposited in deep-sea.

Acknowledgment(s)
This study was supported by Inonu University with the project number of 2007/32 and 2015/54. Authors also special thanks to Dr. Yunus Onal for helping with some experiments.

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