

A comparative Study for basic Characterization of three Clinoptilolite Specimens

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Physicochemical and mineralogical characteristics of the clinoptilolite tuffs of Chinese, Slovakian and American origin were investigated using various techniques, i.e. X - ray powder diffraction, water vapour desorption, ion exchange and chemical analysis.

Key Words: clinoptilolite, ion exchange, mineral composition, water vapour desorption

Introduction

Zeolites are crystalline, hydrated aluminosilicates of alkali and earth alkaline cations that consist of infinitely extending three-dimensional networks of AlO_4^{5-} and SiO_4^{4-} tetrahedra, linked by the sharing of all oxygen atoms. The intracrystalline voids make up 20 to 50% of the total crystal volume of most zeolites. The internal structure of these frameworks is decidedly hydrophilic. Owing to a large internal surface and considerable lower costs than the synthetic counterparts, clinoptilolite, mordenite, erionite, phillipsite and chabazite specimens in particular have attracted great interest among a broad scientific community all over the world.¹⁻⁴

Most zeolites in sedimentary rocks are formed from volcanic ash or other pyroclastics, by reaction of the amorphous aluminosilicate glass with pervading pore water. Others originate by the alteration of pre-existing feldspars, feldspathoids, biogenic silica or poorly crystalline clay minerals. The factors controlling whether a zeolite or a clay mineral will form are still insufficiently understood; however temperature, pressure, reaction time, alkalinity and dissolved salts in pore solutions seem to be important.⁵⁻⁸

At present, over 1000 occurrences of zeolite minerals have been reported, predominantly from sedimentary rocks of volcanic origin, in more than 40 countries. The improving knowledge of natural zeolite properties together with growing needs for selective, stable ion exchangers in pollution abatement, water treatment, energy production, aquaculture, horticulture, animal nutrition, metal processing, biomedical applications and other areas promises an exciting practical development of these unique materials.⁹⁻¹³

Experimental

Slovakian clinoptilolite from the industrial deposit Nižný Hrabovec (NH), Chinese clinoptilolite from the south-eastern Hubei Province and American clinoptilolite from the famous Hector ore (CA) were studied. Clinoptilolite of Slovakian origin was supplied by Zeocem, Share Holding Company, Bystré; Chinese clinoptilolite samples were received by means of Agrotec - Wasser und Bodenschutz, San Augustin, Germany and Tsinghua University, Department of Chemical Engineering, Beijing; and American clinoptilolite was obtained from Rheox Inc's Hectorite Mining and Processing Operations at the Plant in Newberry Springs, sampled directly from Hector deposit near Barstow, California.

About 60% clinoptilolite bearing volcanic rock was determined in Slovakian, 50% in Chinese and about 90% in active component enriched rock in American samples by standardized techniques, e.g. X-ray powder diffraction, water vapour desorption and ion exchange.

The chemical composition of clinoptilolite tuffs was analysed by ICP AES using a Kontron Spectrometer, Model Plasmakon S 35 (Germany) and Baird ICP 2070 Spectrometer (USA), and mineralogical specification was estimated by X-ray diffraction using a Philips Diffractometer (CoK α radiation, voltage 30 kV, intensity 15 mA, Fe - filter, diaphragm 1,1,05).

Scanning Electron Micrographs (SEM) were taken by Electron Probe Microanalyser Jeol-JXA 840A, Japan, using freshly broken (if possible) fragments coated with a gold alloy. For all other experiments, 0.2 - 0.7 mm grain-sized samples were used.

An ion exchange method was used for maximum capacity evaluation based on the saturation of natural zeolites with 5 M ammonium chloride solutions in a reflux apparatus under boiling conditions for a half hour, followed by decantation of ammonium exchanged zeolites with distilled water to remove physically adsorbed stock solution. The amount of exchanged ammonium in clinoptilolites was thus analysed only from the solid phase, i.e. zeolitic tuffs, by modified Kjeldahl method.

Chemicals for preparation of stock solutions were of analytical grade.

Results and Discussion

In Figure 1 are shown the X-ray diffraction patterns of all three clinoptilolite specimens. Diffractometer traces are typical for well-crystallized clinoptilolite corresponding with d- spacings, however differing in peak intensities. The peaks of Hector clinoptilolite are consistently much stronger and somewhat broader than those of the other locality samples.

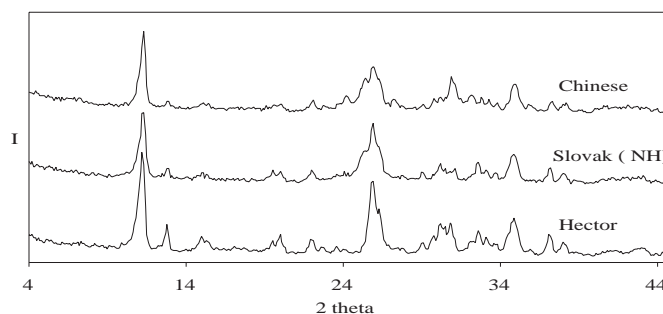


Figure 1. X-ray diffraction patterns of American, Slovakian and Chinese clinoptilolites

While mostly the reflection (004) at about $25.9^\circ 2\theta$ in X-ray diffraction patterns is high in intensity for all samples examined, the Hector clinoptilolite exhibits more intense (020) reflection at $11.3^\circ 2\theta$.

Chemical data of clinoptilolites studied are reported in Table 1. The chemical composition of Hector indicates that this mineral contains predominantly monovalent over divalent cations. Although not as conclusive as the differences in silica contents, the Hector clinoptilolite may also be differentiated from Chinese and Slovakian clinoptilolites by its water content.

Table 1. Chemical and mineralogical compositions of the various deposit's clinoptilolite in (% w/w).

Component	U.S. Hector	Hubei China	East Slovak NH
SiO ₂	66.21	73.57	70.51
Al ₂ O ₃	12.91	11.84	12.59
Fe ₂ O ₃	0.84	1.25	1.65
TiO ₂	0.10	0.08	0.23
CaO	1.33	2.44	3.56
MgO	0.39	0.63	0.64
Na ₂ O	5.82	0.57	0.66
K ₂ O	1.04	4.34	2.78
Loss-on-ignition	11.10	5.23	6.95
Sum	99.74	99.95	99.57
Clinoptilolite	90	50	60
Volcanic glass			13
Cristobalite	2	22	6
Quartz	7	16	4
Feldspar	1	12	10
Plagioclase			6
Biotite			1

According to mineralogical analysis and electron microscopy, the Hector clinoptilolite appears quite pure, containing only about 10% impurities (mostly quartz), whereas Chinese and Slovakian samples reveal the presence of more trace amounts of a foreign phase, predominantly cristobalite, feldspar and quartz. The electron micrographs (SEM) demonstrate well-formed plate or lath crystals in all samples examined (Figure 2).

Furthermore, the material available for investigation was subjected to calorimetric study, according to which the percent content of active mineral in rocks was calculated. The calorimetry method is based on the principle that the enthalpy of sample hydration and thus heat expansion or temperature increase of an insulated system is proportional to clinoptilolite content in the rock.

The method is standardized by numerous serial trials altering the experimental conditions and utilizing various clinoptilolite specimens of extensive scientific examination.¹⁴⁻¹⁷ By the above tests the correction coefficient K (26) for percentage content estimation in the tuffs studied was employed.

Table 2 presents the computed (%) data on the basis of temperature gradient by standardized rehydration of 10 g by 400°C calcinated sample in a 100 mL distilled water system at an ambient temperature of 20°C . The recorded data are in excellent conformity with X-ray mineralogical evaluation.

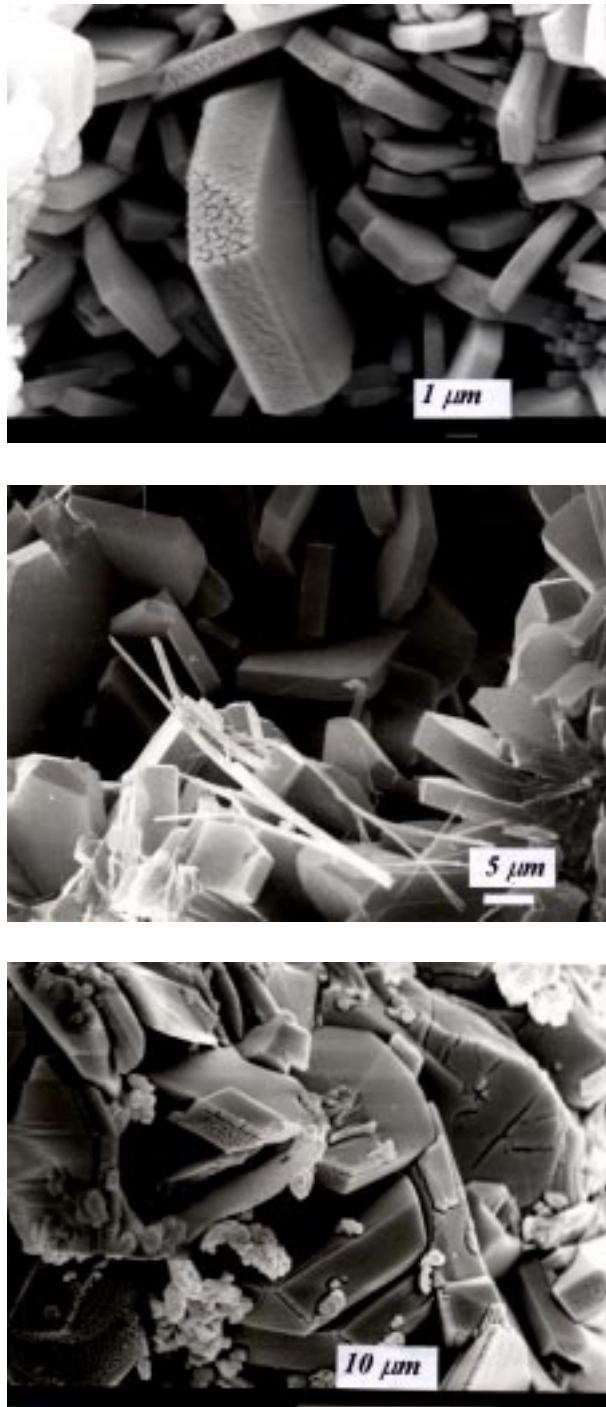


Figure 2. Scanning Electron Micrographs (SEM) of clinoptililite tuffs from a) Hector (USA), b) Nižný Hrabovec (Slovakia), c) Hubei Province (China)

Table 2. Selected physico-mineralogical properties of zeolites studied

Clinoptilolite specimens	Temperature gradient by rehydration (400 ° C)	Clinoptilolite content in rock using calorimetry (%)	Maximum ion exchange capacity of clinoptilolites towards NH ₄ ⁺ (mol/kg)
U.S. Hector	3.28	90	2.2
Hubei China	1.80	47	1.1
East Slovak NH	2.40	63	1.4

Finally, the maximum ion exchange capacity of three clinoptilolite specimens towards ammonium ions was accomplished to prove the above mineral's quality. As shown in Table 2, the values determined correlate quite well with each other when compared to previous studies.^{18–21}

Conclusion

In this study, three deposit's clinoptilolites, i.e. U.S. Hector, Slovak (NH) and Hubei-China, were compared with respect to their mineral quality. However, although the methods used for quality determination may have been considered as only "estimation techniques", the presented results are in good agreement with each other and the applied techniques satisfactorily confirm the samples' differences.

Acknowledgements

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