Relationship Between New Structural Data on Clinoptilolite and Its Behaviour in Ion-Exchange and Heating

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Low degrees of removal of K in ion-exchange as well as alterations of relative intensities of $(0k0)$ X-ray reflections under heating have been found for clinoptilolite. These observations are in good accord with the newly provided structural data of clinoptilolite.

Clinoptilolite is one of the most abundant natural zeolites, and interest in it has rapidly grown in the last years [1, 2, 3, 4, 5]. Information on the exact structure of clinoptilolite is badly needed. The structure of heulendite [6] has been suggested, but there are significant differences [7, 8] between the two zeolites.

In 1975 Alberti proved [9] the heulendite framework to be true for clinoptilolite. He announced new cation positions but stated that there was no definite evidence of a strong enrichment of any cation at any one site. In 1977 Koyama and Takéuchi confirmed [10] the heulendite framework for clinoptilolite and determined the positions of the different cations.

A structure proposed for a particular zeolite must fit to its physico-chemical properties. The latter could prove or disprove the former. In the present work some data on ion-exchange and heating of clinoptilolite are compared with Koyama and Takéuchi's structure.

The original clinoptilolite used for ion-exchange was from North-East Rhodopes, Bulgaria. The particle size was below 1 mm. Ion-exchange was carried out at 25 °C and atmospheric pressure by stirring during 6 hrs in 2 n solutions of the chlorides of Na, K, Ca, Sr, Cr and Fe, to obtain the respective forms. The cationic compositions of the different forms are presented as equivalent percentages *a* in Table 1. These data give information on the ability of ion-exchange for different cations in the clinoptilolite structure. These abilities, as expressed by degrees of removal *b* of each cation during ion-exchange, are also given in Table 1. The degrees of removal of K are below 3% for all ion-exchanged forms considered. The other cations have much higher degrees of removal: for Ca the values are above 30% (reaching 60% for the Na-form) and for Na above 40%, being as high as 88% for the K-form. Magnesium is not of interest as its quantity is very low. Torii [5] also found it difficult to exchange K. The degrees of removal computed from the chemical analyses of his samples do not exceed 3% as well. However, ion-exchange performed under elevated temperatures and pressures [11], leads to removal of K.

From the above data it becomes clear that the cations mostly involved in the ion-exchange process are Na and Ca. Potassium hardly takes part in the process. This behaviour of K points to a low mobility of K in the clinoptilolite structure, as compared to the other cations. According to

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Table 1. Data on Ion-exchange of Clinoptilolite.

Cation (M)	Sample (N)												
	Na-form		K-form		Ca-form		Sr-form		Cr-form		Fe-form		Original form
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*
Ca	23	60	23	54	71	7	42	32	41	38	45	34	57
Na	56	7	2	88	6	44	7	52	9	44	11	46	14
K	20	3	74	—	22	2	29	−2*	31	−1	32	−1	27
Mg	1	60	1	60	1	60	1	50	1	50	1	50	2
Sr (Cr, Fe)	—	—	—	—	—	—	21	—	17	—	11	—	—

* The Sr-, Cr- and Fe-forms were obtained at pH $\leqq 4$; as hydrogen cations are not considered in the sum of cation equivalents, *b* can become negative in cases. a = equivalent percentage of cation M in sample N,

$$b = 100\left(1 - \frac{\text{equiv. of cation M in sample N}}{\text{equiv. of cation M in original sample}}\right).$$

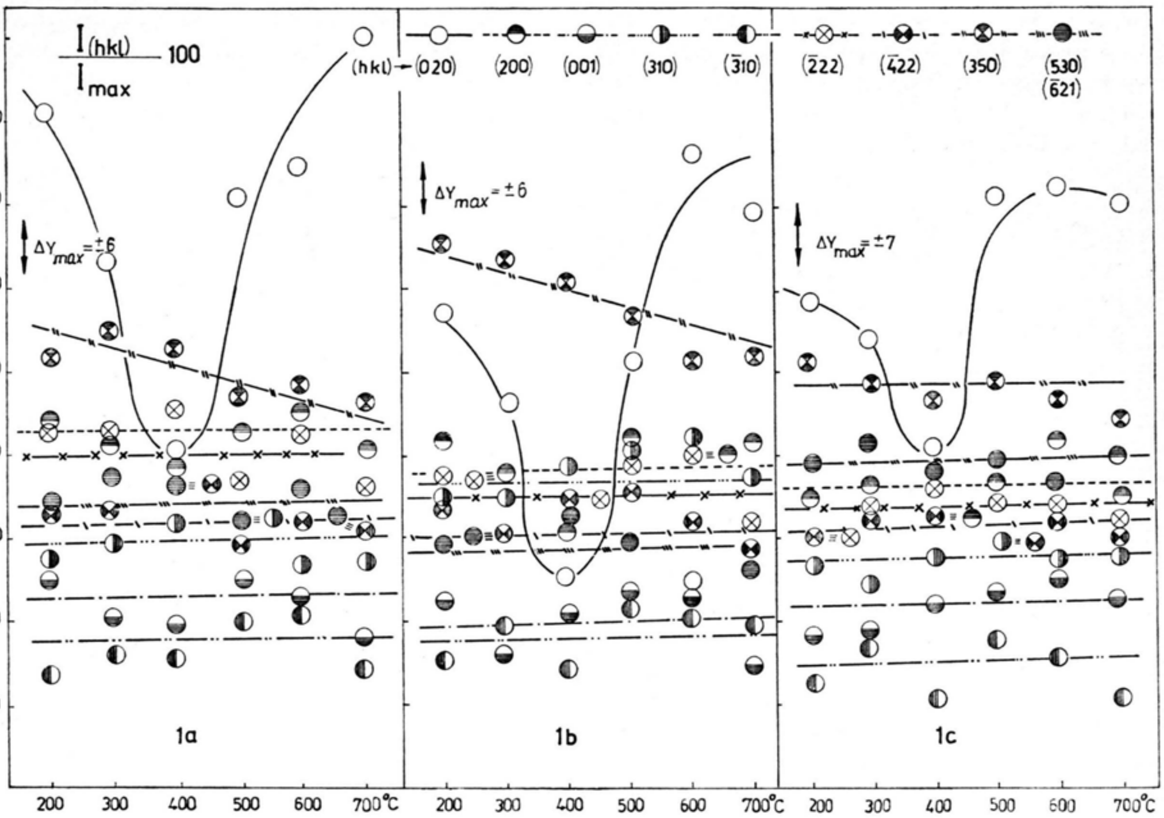

Fig. 1. Relative intensities of X-ray reflections vs. temperature. a) Na-form; b) Sr-form; c) Fe-form.

Koyama and Takéuchi's structure, K is indeed located in the specific site M(3), which is situated in an 8-membered ring and has the highest coordination among all the cation sites in the unit cell, the site being coordinated with 6 framework oxygens and 3 water molecules. In contrast to M(3), the M(1) site, which is occupied by Na and Ca, is coordinated by two framework oxygen atoms and five water molecules, M(2), also occupied by Ca and Na, by three framework oxygen atoms and five water molecules, and M(4), occupied by Mg, by only six water molecules. The strong bonding of K at the M(3) site would be the reason for the poor ion-exchange ability of K.

All cation positions allocated by Koyama and Takéuchi [10] can be considered lying in the planes parallel to (010). If that is so, a migration of cations during heating should affect the intensities of $(0k0)$ X-ray reflections. To justify such an effect, the samples described above were thermally treated and examined by X-rays. The thermal treatment includes heating for 4 hrs at given temperatures (200, 300, 400, 500, 600, and 700 °C). After heating, the samples were cooled immediately to room temperature in a dessicator maintaining constant humidity and then X-rayed. The powder diffractometer was M61 with horizontal goniometer HZG-3. Radiation CuK_α was used. To avoid systematic errors in the observed intensities, relative intensities $I_{hkl}/I_{\max}$ were evaluated. Figure 1 presents the dependence of the relative intensities on temperature. X-ray reflections with relative intensities above 10 are plotted only. Data on the Na-, Ca- and Fe-forms are shown as examples. As the absolute and relative errors essentially vary with the absolute values of I_{hkl} and $I_{\max}$, a diagram was prepared to estimate the possible error in intensity of each reflection; the maximum standard deviations were then estimated and given in Figs. 1a, 1b and 1c. Among all reflections plotted, only (020) exhibits an essential change with temperature. On the other hand, of all $(0k0)$ reflections, (020) is the only one observed [6]. Thus the change in the intensity of (020) is in good accord with the expected intensity alteration of $(0k0)$ caused by migration of cations locating in the planes parallel to (010).

In conclusion, the data on ion-exchange and heating of clinoptilolite presented and discussed here fit well to Koyama and Takéuchi's structure, thus supporting the cation distributions elucidated by these authors.

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