

Structural comparison of clinoptilolite and heulandite

C.R. González², R. Roque Malherbe¹, R. Drake²

¹Centro Nacional de Investigaciones Científicas, Havana, Cuba

²Centro de Investigaciones Geológicas, Havana, Cuba

ABSTRACT

With the aid of X-ray diffraction cell parameters were determined, and diffractograms of 12 natural zeolites of the heulandite-clinoptilolite group were identified. It was concluded that the classification of the minerals of this group in heulandite and clinoptilolite is artificial, so that they are crystallographically the same, notwithstanding the changes of their physical properties. The variations of cell parameters with the acid treatment were also studied.

RESUMEN

A través de la difracción de Rayos X se determinaron los parámetros de la celda que permiten, mediante difractogramas de 12 zeolitas naturales la identificación del grupo heulandite-clinoptilolite. Se concluyó que la identificación de los minerales de este grupo en heulandite y clinoptilolite es artificial, ya que ellos son cristalográficamente los mismos, independientemente de los cambios de sus propiedades físicas. Se estudió igualmente las variaciones de los parámetros de la celda con tratamiento en ácido.

INTRODUCTION

Owing to crystallochemical differences in the cationic composition and distribution in the frame-work or the Si/Al rate, the natural zeolites may change their catalytic, thermal, diffusive, sorbitic properties, etc. It provokes that these materials, in natural state, between the limits of one deposit, or from one to another, show very variable properties. Hence the necessity of accurately determine their crystallochemical parameters.

Heulandite like a new mineral was first introduced by Brooke (ref. 1) and polymorphism described by Rinne (ref. 2). Later, by rigorous and extensive works, Alietti and Breger (ref. 3,4) found three polymorphic forms. Parallely, Shaller (ref. 5) introduced clinoptilolite like a new mineral of the heulandite group and similar to mordenite. Hey and Bannister (ref. 6) defined it like a Si-rich heulandite, Mumpton (ref. 7) distinguished each from the other by the non-distribution of the structure of clinoptilolite from an all-night heating at 450 °C, and imputed its high thermal stability to Na and K ions in clinoptilolite (ref. 8) as contrasted with divalent Ca in heulandite. Consequently with this, Alietti (ref. 9) demonstrated that the behaviour of heulandites becomes clinoptilolite-like in K-rich forms. It is in agree with the results of Sheppard and Starkey (ref. 10). Nevertheless, Ca-rich clinoptilolites were founded (ref. 11) and several authors reported Si-rich heulandites. The rigorous X-ray diffraction studies of the structure of these zeolites (ref. 12-15) showed that they are crystallographically isomorphic. The structure of heulandite-clinoptilolite is monoclinic with cell parameters about $a = 15,82 \text{ \AA}$, $b = 17,94 \text{ \AA}$, $c = 7,41 \text{ \AA}$, $\beta = 91,6^\circ$.

The purpose of this work is to report the crystallochemical characteristics of the cuban natural zeolites and to discuss the isostructurality of heulandite and clinoptilolite, as soon as to study the stability of the cristalline network after the acid treatment of these zeolites.

METHODS

Samples of clinoptilolite-modernite from Villa Clara, and heulandites from Villa Clara and Havana were taked for investigation. These samples were studied in natural state, as soon as treated with HCl 0.1, 2.5, 5.0, 7.5 and 10 normal, using 25 cm³ per gram of zeolite. The list of the investigated samples and their mineralogical contents determinated by the method developed by the authors (ref. 16-18) are given in Table 1. The results of chemical analysis are given in Table 2.

In addition to the cuban zeolitic samples given in the Table 1, clinoptilolite from Kherkodzula (USSR) and macrocrystalline heulandite from Nicaragua were studied to compare the results. Also Ca-clinoptilolite elaborated by cationic exchange (ref. 19) included.

At last, X-ray data reported in the literature for clinoptilolite from Agoura (USA) (ref. 13) and from Kuruma Pass (Japan) (ref. 14) were used.

Diffractograms were obtained by a DRON 2.0 equipment, with Co or Cu anticathode, goniometer GUR-5, scintillation detector with fotomultiplier FEU-85, scanning rate of $1/2^\circ$ per minute, in duplicate, calibrating with quartz to correct systematic errors. Computer programs for indexing (ref. 20) were developed starting from the reported ones by Durruthy et al (ref. 21), taking into account the criteria of Frank-Kamenetsky (ref. 22) for selection of diffraction maxima.

High temperature X-ray diffraction was performed in a Co-anticathode Phillips A.P.D. 10 equipment.

Thermic stability by DTA Table 3, high temperature X-ray diffraction Table 4 and maximum adsorption of nitrogen and ammonia (Table 5) were taken like starting criteria for classification in heulandite and clinoptilolite.

By thermic analysis is noticed that samples HPA and HC exhibit in the water desorption zone other peaks (250°C and 340°C) corresponding to transition to heulandite B, as long as HT and CMT-C have not peaks in this zone.

Nevertheless, high-temperature X-ray diffraction of sample HT shows a shortening in the interplanar spacing d_{020} by a factor 0.946, indicating the formation of heulandite B. It happened not with the sample CMT-C (Table 4).

On the other hand, nitrogen is not adsorbed by samples HPA, HT and HC, but ammonia do it. This is the typical behaviour of heulandites. The sample CMT adsorpts both gases.

Scanning electron microscopy shows the tendency of clinoptilolite to be microcrystalline, as contrasted with the larger dimensions of the studied heulandites (ref. 23).

RESULTS AND DISCUSSION

The cell parameters of heulandite-clinoptilolite in the different natural state samples are reported in Table 6. These minerals possess a centred monoclinic (pseudorhombic) cell.

According to general accepted criteria for the classification in heulandite and clinoptilolite (ref. 3, /-9), the arrange done in Tables 3, 4 and 5 is correct. Nevertheless, the results of indexing process done by computer machines starting from very accurate X-ray diffraction data; and complementary calculation of cell parameters (ref. 20) show that the different clinoptilolite-like and heulandite-like specimens possess the same crystalline network (Table 6 and 7) also according with Alberti (ref. 13) and Koyama (ref. 14) for other samples.

All these facts make us to think that heulandite and clinoptilolite are the same mineral with different properties, in accord to very variable cationic contents in the network, easily occurring by exchange processes.

Nevertheless, literature may generate some confusion owing to the habit of report 12/m space group for clinoptilolite (ref. 24) and C2/m for heulandite, when really they are crystallographically equivalents. In addition, starting from any one of these space groups, is possible to successfully obtain identical indexes with the same extinction rules for all samples, merely noticing several unimportant non-systematic differences in cell parameters, not allowing to establish groups.

Thus, it may conclude that in spite of diversity of the heulandite-clinoptilolite group, it notice not the reflex of this variability on the crystalline cell parameters. On the other hand, the observed variation in the X-ray patterns allow not a clear classification into two mineral species. Thus, in our opinion it is more vigorous establish that these zeolites constitute only one mineral with a long range of isomorphic substitutions altering their properties, that is, heulandite and clinoptilolite are isostructural terms of an isomorphic series whose properties are determined by the cationic contents, the Si/Al rate and the minuteness of crystals.

These facts also manifest from the study of the acid-treated and exchanged zeolites. By HCl treatment, the minerals sensity lost crystallinity, however, the fraction retaining crystallinity mantained cell parameters unchanged (Table 8).

Ion exchange was done with a mixture of samples CMT-29, CMT-30, CMT-64 and CMT-66 obtaining the average contents: 69 % heulandite-clinoptilolite, 11 % mordenite y 20 % other non-zeolite minerals. This composite was exchanged with Na^+ , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ chlorides, replacing liquor 20 times to reach a 80-90 % homoionicity (ref. 25). After a 450 °C heating, the Na^+ , K^+ and NH_4^+ forms were stable, but the Mg^{2+} and Ca^{2+} ones, do not. The same heating of the MH_4^+ -exchanged form of the sample HC showed that this treatment stabilized heulandite thermically (25).

TABLE 1

Quantitative phase analysis of the studied samples

Sample	heulandite-clinoptilolite (%)	mordenite	others (%)
CMT	40	40	20
HT	80	-	20
HPA	85	-	15

HC	80	5	15
CMT - 29	56	10	34
CMT - 30	67	10	23
CMT - 64	77	11	12
CMT - 66	77	14	9

others: volcanic glass, quartz, calcite, feldspar,
montmorillonite

TABLE 2
Chemical analysis of the studied samples

	CMT	HT	HPA	HC
SiO ₂	66.6	64.1	65.9	66.4
Al ₂ O ₃	12.5	13.8	11.5	-
Fe ₂ O ₃	1.9	1.85	1.1	1.6
CaO	2.7	4.3	3.2	4.5
MgO	0.7	1.1	1.4	-
K ₂ O	0.8	1.5	0.3	1.89
Na ₂ O	2.9	0.7	1.0	0.0
PPI(H ₂ O)	11.0	12.3	10.0	11.0
Others	0.9	0.2	0.4	-

Others: Mn, Ti, Ba, Sr

TABLE 3
Results of the differential thermal analysis of the studied samples

Sample	Temperature of the endothermic peak (°C)	Temperature of the exothermic peak (°C)	Remarks
CMT-29			
CMT-30	50-400	no	Only one minimum in the endothermic peak
CMT-64			
CMT-66			

HT	60-250	450	"	"	"
HPA	60-300	no	Two effects in the range 60-300 °C, indicating other transition		
HC	60-380	no	Two effects in the range 60-380 °C		

TABLE 4

Shortening factor* for the interplanar spacing in the high-temperature X-ray diffraction for samples HT and CMT-C

hkl	R_{hkl} (HT)	R_{hkl} (CMT-C)
020	0.946	0.990
002	0.982	0.992
110	0.984	0.993
111	0.953	-
112	0.990	-
112	0.996	-
130	0.965	0.999
033	0.944	0.998
200	0.989	0.997

$$*R_{hkl} = \frac{d_{hkl} (400 \text{ } ^\circ\text{C})}{d_{hkl} (25 \text{ } ^\circ\text{C})}$$

TABLE 5

Maximum adsorption of nitrogen and ammonia for the studied samples

sample	nitrogen (m mole/g)	ammonia (m mole/g)
CMT	2.16	5.87
HT	no	6.38
HPA	no	7.02
HC	no	7.00

TABLE 6

Cell parameters of the studied samples in comparison with the data of typical samples taken from literature

Sample	a (Å)	b (Å)	c (Å)	B
HT	7.39 ± 0.01	17.931 ± 0.001	15.85 ± 0.08	91.3 ± 0.2
HPA	7.39 ± 0.01	17.931 ± 0.001	15.85 ± 0.08	90.8 ± 0.2
HC	7.3 ± 0.1	18.0 ± 0.1	16.0 ± 0.1	90.3 ± 0.8
HVP	7.41 ± 0.01	17.89 ± 0.01	15.85 ± 0.01	91.5 ± 0.2
CMT-C	7.34 ± 0.06	17.92 ± 0.08	15.76 ± 0.05	91.3 ± 0.5
CK*	7.41 ± 0.05	17.90 ± 0.002	15.71 ± 0.06	91.4 ± 0.5
CMT-29	7.40 ± 0.01	17.885 ± 0.0006	15.81 ± 0.01	92.1 ± 0.2
CMT-30	7.389 ± 0.007	17.879 ± 0.0004	15.81 ± 0.01	92.1 ± 0.2
CMT-64	7.40 ± 0.02	17.884 ± 0.001	15.82 ± 0.03	92.1 ± 0.2

TABLE 6

Cell parameters of the studied samples in comparison with the data of typical samples taken from literature

Sample	a (Å)	b (Å)	c (Å)	B
CMT-66	7.39 ± 0.001	17.887 ± 0.0001	15.798 ± 0.005	91.8 ± 0.2
CA**	7.407	17.911	15.826	91.62
CJ***	7.400	17.963	15.186	91.71
CC****	7.42	17.856	15.84	91.7

* clinoptilolite from kher-kodzula (USSR)

** clinoptilolite from Agoura (USA), data from (13)

*** clinoptilolite from kumura Pass (Japan), data from (14)

**** Ca-clinoptilolite, data from (11) indexes by us

TABLE 7a

Interplanar spacing and Miller indexes of the different natural zeolites of the heulandite-clinoptilolite group (Interplanar spacing in Å)

hkl	HT	HPA	CMT-29	CMT-30	CMT-64	CMT-66
020	8.98	8.98	9.00	8.98	8.96	8.98
002	7.97	7.96	7.91	7.91	7.89	7.91
110, 101	6.80	6.78	6.76	6.78	6.74	6.77
101	6.72	6.70	6.60	6.58	6.61	6.60
022	-	-	-	-	-	-
031	-	-	-	-	-	-
121	-	-	-	5.34	-	-
112	5.24	5.22	5.23	5.23	5.23	5.22
112	5.17	-	5.09	5.10	5.10	5.09
130	4.663	4.663	4.645	4.645	4.637	4.645
040	-	-	-	-	-	-
103	-	-	4.344	4.348	4.338	4.320

132	-	-	-	-	-	-
132	3.962	3.962	-	-	-	-
042	3.929	3.924	-	-	-	-
123	-	-	-	-	-	-
141	3.697	3.697	3.695	3.700	3.697	3.699
211	-	-	-	-	-	-
051	-	-	-	-	-	-
114	-	-	-	-	-	-
220	3.445	3.445	3.416	3.414	3.414	3.415
222	3.171	3.176	3.168	3.170	3.166	3.168
015,143	3.135	-	3.118	3.115	3.123	3.120
231,143	2.083	3.083	3.072	3.069	3.068	3.072
213	-	-	-	-	-	-
060,152	2.997	2.993	2.968	2.964	2.967	2.964
105	-	-	-	-	-	-
240	-	-	-	-	-	-
036,125	-	-	2.792	2.795	2.792	2.790
161,233	2.737	-	-	-	-	-

TABLE 7b

Interplanar spacing and Miller indexes of the different natural zeolites of the heulandite-clinoptilolite group (Interplanar spacing in A)

Ck	CAG**	CCa*	Cli*	CNa*	HVP***
8.92	8.92	8.97	8.97	8.97	9.00
7.86	7.97	7.89	7.95	7.95	7.94
6.75	6.78	6.75	6.75	6.75	6.81
6.63	-	-	-	-	6.65
5.88	-	-	-	-	5.93
-	5.61	-	-	-	5.62
-	-	-	-	-	5.35
5.18	-	5.22	5.23	5.23	5.27
5.10	5.15	-	5.12	5.11	5.14
4.651	4.65	4.64	4.65	4.66	4.671
-	-	-	-	-	4.493
4.333	4.35	4.34	4.36	4.34	4.404
-	-	-	-	-	4.062
3.965	3.96	3.96	3.96	3.96	3.986
-	3.90	3.92	3.92	3.92	3.907
-	-	-	-	-	3.847
-	3.74	3.71	-	3.71	3.748
3.539	3.55	3.55	3.55	3.55	3.553
-	-	-	-	-	3.509
-	-	-	-	-	3.466
-	-	3.42	3.42	3.41	3.427
-	3.17	3.18	3.17	3.17	3.186
-	3.12	-	3.13	-	3.132
-	3.07	3.08	3.08	3.07	3.079
-	-	-	-	-	3.030
2.971	2.974	2.98	2.98	2.97	2.982
-	-	-	-	-	2.885
-	-	-	-	-	2.861
2.793	2.793	2.80	2.79	2.80	2.807
-	2.728	2.71	2.74	2.74	2.735

TABLE 8

Cell parameters of the acid-treated samples

Sample	normality of the acid treatment	a (Å)	b (Å)	c (Å)	B
CMT-C	2.5	7.35	17.92	15.75	91.4
CMT-C	5.0	7.33	17.93	15.76	91.5
CMT-C	7.5	7.35	17.93	15.77	91.3
HPA	0.5	7.38	17.94	15.86	91.3
HPA	10	7.39	17.93	15.85	91.5
HPA	2.0	7.38	17.93	15.86	91.4

REFERENCES

1. Brooke, E.
Edinburg Phil.J. 6 (1922) 112.
2. Rinne, E.
Z. Krist., 59.(1923) 230.
3. Alietti, A.
Amer. Miner., 57 (1972) 1448.
4. Breger, I.A.
Amer. Miner., 55 (1970) 825.
5. Schaller, W.J.
Amer. Miner. 8 (1923) 93.
6. Hey, M., F.A. Bannister
Miner. Mag. 23 (1934) 556.
7. Mumpton, F.A.
Amer. Miner. 45 (1960) 351.
8. Mason, B., L.B. Sand
Amer. Miner. 45 (1960) 341.
9. Alietti, A.
Mineral Petrog. Acta, 13 (1967) 119.
10. Sheppard, A.O., H.C. Starkey
U.S. Geol. Surv., Prof. Paper, 475-D, p. D-89. (1964).
11. Kirov, G.N.
Gödishnik na SU, Geol.-Geogr. Fakultet, kninga 1, Geologiya,
Tom 60, 193 (1967).
12. Merkle, A.B., M. Slaughter M.
Amer. Miner., 53 (1968) 1120.

13. Alberti, A.
Tshermarks Miner., Petr. Mitt. 18 (1972) 129 and 22, 25 (1975).
14. Koyama, K., Y. Takeuchi
Z. Krist 145 (1977) 216.
15. Breciani-Pahor, N. et al
J. Chem. Soc. Dalton (9) (1980) 1511.
16. González, C.
Rev. Cubana de Física, 1 (1981) 61
17. —————, R. Roque
KINAM, 5 (1983) 67.
18. Roque-Malherbe et al
Rev. Cubana de Física, 3 (1983) 105.
19. Chelichev, N.F. et al
Izv. Akad. Nauk SSSR, Neorg. Mater, 11 (1975) 704.
20. Roque, R. et al
Aplicaciones del método de los mínimos cuadrados. Algoritmos y programas.
CNIC (1984).
21. Durruthy, O., F. Fajardo
Rev. Cubana de Física, 1 (1981) 95.
22. Frank-Kamenetskii, V.A. (ed.)
Rukovodstvo po rentgenovskomu issledovaniya mineralov, Leningrad, Nedra
(1975)
23. Lariot, C.
IV Conferencia Científica de la Universidad de La Habana, January 1984.
Abstracts.
24. Breck, D.W.
Zeolite molecular Sieves, Wiley-Interscience, N.Y. (1974), tables 2.23
and 2.29.
25. Rodríguez, G., J.A. Sosa, R. Roque
In preparation.