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Clinoptilolite from zeolitized tuffs of Azerbaidzhan

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SUMMARY. A study has been made of a large clinoptilolite deposit in the Lesser Caucasus (Azerbaidzhan SSR). The geological conditions have been examined and a number of samples investigated by optical, electron-microscopic, chemical, X-ray, thermal, and infra-red methods. Based on these investigations and on comparison with previous literature, mineralogical, chemical, and geochemical conclusions are drawn and conditions for clinoptilolite genesis are considered.

CLINOPTILOLITE is apparently widely spread in the zeolite associations, particularly among altered glassy and feldspathic rocks of volcanic origin. A great interest in zeolites, particularly in the last decades, has been shown in connection with their utilization in the oil-working and oil-chemical industry, mainly as catalyst in oil-cracking, gas cleaning, and water purification (Deffeyes, 1966; Mikhailov and Krinari, 1970). Yet, clinoptilolite is described quite briefly in the Soviet Union, and only in some articles (Shamrai, 1952; Shashkina, 1958; Butuzova, 1964; Senderov and Khitarov, 1970; Mikhailov and Krinari, 1970; Gvakhariya *et al.*, 1973). So, till nowadays, a confusion remains in determining clinoptilolite, and it is often confused with mordenite, ptilolite, and heulandite. Taking into consideration the scientific and practical importance of clinoptilolite, the authors investigated a series of zeolite deposits of the Azerbaidzhan SSR (Kashkai, 1947, 1965), including, in detail, the one from Aydag in the Tauz region.[1] The present article deals with the results of complex studies of clinoptilolite.

Among zeolite deposits, the clinoptilolite ones (having formed like the heulandite, mordenite, and others by way of zeolitization of glassy volcanic tuffs) are of great importance.

Within the Somkhit–Agdam zone on the north-eastern slope of the Lesser Caucasus, the Tauz region, with the deposit studied by us, is characterized by anticlines and synclines of the second order formed by the Upper Cretaceous deposits (fig. 1). At one of the monoclines there is the Aydag deposit. Field studies showed that zeolitization occurred according to the anti-Caucasian direction of structures superimposed over All-Caucasian ones. Moreover, there appeared a joint network, which is seen more intensively at the knots of intersection of both joint directions. Such jointing created the conditions for penetration of thermal springs, which caused metasomatism, and particularly zeolitization of ash tuffs.

The limestones play an essential role in the geological structure of the deposit; they

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[1] Up to now in the Soviet Union there was not known such a large deposit as that from Aydag in the Azerbaidzhan SSR, and for practical purposes only artificially made zeolites were applied.

seem to have a great significance as a favourite environment in the process of tuff zeolitization.

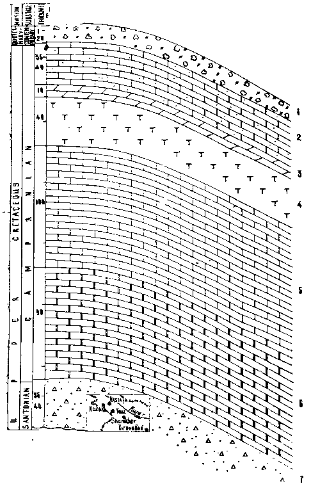

FIG. 1. Geological section (monocline) of the Aydag zeolite deposit in the Tauz region, Azerbaidzhan SSR: 1—deluvial deposits; 2—arenaceous limestones; 3—red pelitomorphic limestones with intercalations of marls; 4—zeolitized ash tuffs; 5—limestones; 6—marly limestones; 7—tuff sandstones, tuff breccias.

The lately zeolitized ash tuffs that are of interest to us were deposited on a shallow sea bottom together with the limestones (up to 400 m). The ratio of mineral components in them varies within wide limits. In some tuffs the amount of volcanic glass reaches 80 to 90 %, and that of carbonates 9 to 16 %; the content of quartz, biotite, and feldspars is insignificant. The mineral grains in the tuffs are angular, with dimensions up to 0·20 mm. The zeolitized calcareous ash tuff is whitish. Under the microscope it is composed of micrograined aggregates of fibrous, acicular, and scaly zeolites, among which there are found small but often more zeolitized varieties of ash tuffs that may be of practical interest. Besides zeolites, there are grains of calcite and dolomite (and pelitomorphic carbonate). Volcanic glass and altered feldspars are present in small amounts.

The dimensions of the irregular angular quartz fragments are 0·02–0·04 mm, feldspar plates up to 0·04 mm, biotite 0·1–0·015 mm. Small, finely distributed chlorite scales form isolated agglomerations. The glassy mesostasis is often recrystallized and zeolitized. Hydrous ferric oxides (from 0·05–0·1 to 0·2–0·3 mm) and agglomerations of microcryptocrystalline carbonates are found in small amounts; the latter form thin intergrowths with zeolite in some places. The zeolitized tuffs were divided into four size grades: $>$ 0·25 mm—from 4·7 to 18·6 %; 0·25–0·1 mm—from 5 to 12·1 %; 0·1–0·01 mm—from 46·8 to 54·2 %; and $<$ 0·01 mm—from 21·2 to 31·9 %.

The zeolite amounts in the light fraction of the 0·1–0·01 mm grade of these samples were precisely determined by mechanical analysis: from 75 to 95 %. The rest is composed of partially altered feldspars and carbonates. The heavy fraction only forms a small part, and is composed mainly of biotite, chlorite, hornblende, celestine, zircon, ilmenite, magnetite, and single grains of tourmaline, sphene, augite, garnet, and pyrite.

In the Aydag deposit the clinoptilolite is found in association with heulandite, nontronite, stilbite, analcime *et al.*, as acicular and fibrous agglomerations. Often it is colourless; however, there are observed clouded pelitomorphic formations, and also brown and reddish iron-stained crusted accumulations. Small (0·01–0·03 mm) microcrystals of clinoptilolite form pseudomorphs, mainly after feldspars. In the rock cement they are often placed perpendicularly to the relics of the primary minerals and fragments.

The refractive indices of clinoptilolite from the Aydag deposit (Azerbaidzhan SSR) are: α 1·480–1·483; γ 1·478–1·481; γ—α 0·002. For the associated heulandite they are rather higher: γ 1·501±0·002; α 1·497±0·002; γ—α 0·004. The increase in refraction index within the clinoptilolite and heulandite varieties is explained by an elevated Ca-content, reduced Na+K amount, and high Si : Al value. It was noted also by Ross and Shannon (1924), Mason and Sand (1960), Shepard (1961), Hay (1966). The specific gravity of clinoptilolite from the Aydag deposit is 2·11, and that of the mother tuff from 2·03 to 2·11.

Clinoptilolite microcrystals of tabular and acicular form and of quite different dimensions are clearly observed under the electron microscope (× 15 000); laminar cleavages by (010), (101), and (110) are characteristic for them. The difference in morphology of the relict crystalline individuals of clinoptilolite corresponds to that of the primary feldspars and other minerals. The main mass is a zeolitized glassy mass of the ash tuffs. Such a substitution of the tuff glassy mesostasis and feldspars by clinoptilolite and opal is described by Robinson (1966) and Moiola (1970) for the Esmeralda formation, Nevada.

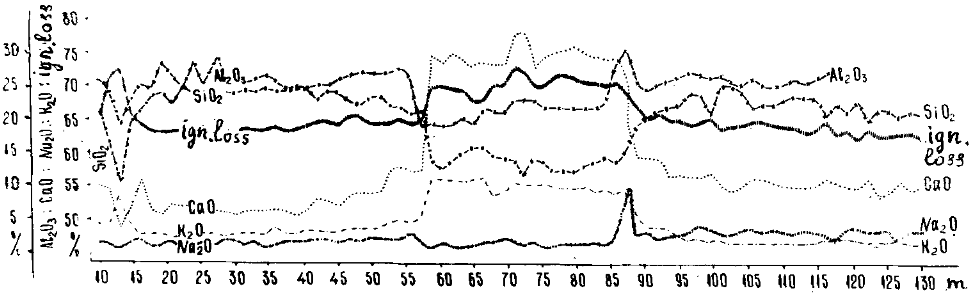

FIG. 2. Range in composition of oxides in white zeolitized (clinoptilolitized) tuffs from Aydag deposit (Tauz region, Azerbaidzhan SSR). Data in % according to the dried up to 110 °C substance.

Typical chemical analyses of the zeolitized tuffs of Aydag are included in Table I, and in fig. 2 the variation of their composition with depth, from 10 to 130 m, is plotted from 80 analyses. The Ca and K contents are small down to 55 m depth, then increase sharply from 55 to 90 m, with a concomitant fall in Al_2O_3; from 90 to 130 m depth the composition approximates to that in the first interval.

The literature data and our investigations lead us to consider clinoptilolite an independent mineral of the heulandite group (see above). The frequent finds of clinoptilolite in association with heulandite, mordenite, *et al.* with analogous structure allow us to consider this group a heulandite–clinoptilolite one. Clinoptilolite usually contains more silica than heulandite does, which was considered to be the main diagnostic feature (Schaller, 1923; Hey and Bannister, 1934; *et al.*). Later and more thorough investigations showed, besides SiO_2, another series of more important clinoptilolite diagnostic features. According to our chemical analyses and those taken from the literature, the SiO_2-content in the composition of clinoptilolite varies mainly within 64–67 %, and in heulandite from 54 to 57 %. Alumina is mainly from 11 to 13 % in

TABLE I. *Chemical analyses of clinoptilolite-containing tuffs (1, 2), clinoptilolite from the Aydag deposit (3–6), and heulandite from the Dashkesan iron ore area (7), Azerbaidzhan SSR.*

	Clinoptilolite-containing tuffs North-eastern flank of the Aydag deposit, well No. 13		Monomineralic clinoptilolite, obtained from light fraction (0·1–0·01 mm). Output is 96–98 %.				Heulandite Dashkesan north-western iron ore area
	Depth 9 m	Depth 23 m					
	1	2	3	4	5	6	7
SiO_2	64·31	68·73	65·95	64·66	65·05	67·08	53·95
TiO_2	0·06	0·05	0·09	0·10	0·08	0·10	0·06
Al_2O_3	10·90	9·37	12·13	11·75	12·02	12·68	16·11
Fe_2O_3	1·65	0·82	1·22	1·26	0·80	0·69	0·85
FeO	—	—	0·07	0·05	0·02	0·32	no
MgO	0·35	0·30	0·99	1·09	0·62	—	—
MnO	—	—	0·02	0·01	0·01	—	—
CaO	3·85	3·35	3·63	3·70	2·90	1·80	8·06
Na_2O	2·32	2·56	1·37	2·23	1·03	0·49	1·09
K_2O	1·38	1·36	1·95	2·15	5·30	3·40	no
SO_3	no	no	0·06	0·03	0·42	no	—
H_2O^-	5·09	5·04	3·38	4·26	2·75	4·43	19·93
H_2O^+	10·03	8·62	8·26	8·74	8·40	8·95	—
Total	99·94	100·20	99·12	100·03	99·40	99·94	100·05
Ionic ratios to 72 oxygen:		Si	29·14	27·93	29·13	29·75	26·43
		Ti	0·03	0·03	0·03	0·03	—
		Al	6·32	7·70	6·35	6·66	9·30
		Fe^{3+}	0·42	0·42	0·27	0·11	0·29
		Mg	0·66	0·71	0·40	—	—
		Na	1·22	1·87	0·86	0·43	1·00
		Ca	1·73	1·71	1·40	0·85	4·24
$Z = (Si+Ti+Al+Fe^{3+})$		K	1·06	1·14	3·01	1·92	—
$R_a = (Mg+Na+Ca+K)$		$\left.\begin{matrix}H_2O^+\\H_2O^-\end{matrix}\right\}$	16·42	18·74	16·64	19·82	32·53
		Z	35·91	36·08	35·78	36·55	36·02
		R_a	4·67	5·43	5·67	3·20	5·24

clinoptilolite, less than in heulandite, and that also must be taken as a distinctive feature. In general, Al in clinoptilolite can substitute a small part of Si or as an amphoteric element it can probably enter in the base composition in small amount.

We therefore consider the ratio Si : Al is important for the distinction of clinoptilolite and heulandite, and appears to range from 4·12 to 5·60 and 2·67 to 3·41 respectively. Thus, one can assign the zeolites under consideration to clinoptilolite when the ratio Si : Al is equal to or greater than 4, and to heulandite when less than 4.

Chemical analyses of clinoptilolite from the Azerbaidzhan SSR showed Fe_2O_3-contents greater than 1 % (Table I, nos. 3–4): this is due to the presence of hydrous ferric oxides and ferrierite, which also accompany the clinoptilolite in Agur, California (Wise, Nokleberg, and Kokinos, 1969). The presence of magnesium deserves attention; it varies from 0·18 to 1·35 %. There is little manganese up to 0·02 %; only in one sample from Azerbaidzhan there was noted 3·63 %, which is explained by the characteristic accumulation of this element, which possesses a high migration capacity.

K, Na, and Ca, being variable in their percentage, mainly determine the type or variant of clinoptilolite.

The potassium amount sharply increases with the increase of Al-content to two and more per cent. Potassium is almost absent in heulandite; and sodium is about 1 %. In their places there is more calcium, as, e.g., in the Dashkesan heulandite—8·06 %. Note should be made that Kirov (1967), Alietti (1967, 1972), and Minato and Utada (1971) found clinoptilolite with a high calcium content.

According to the data cited above, clinoptilolites have a variable chemical composition; depending on the prevailing amount of the three elements, one has to distinguish the following isomorphous series; K-Na clinoptilolites, Na-K clinoptilolites, and K-Na-Ca clinoptilolites. The structural, thermal, and other peculiarities of these isomorphous series must be taken into account. Note should be made that the extreme terms of clinoptilolite isomorphous series have not been met with in nature. Such a method of approach corresponds to the specificity of the zeolite tetrahedral framework, i.e. $Ca \rightleftarrows 2Na_2$; $(Ca, Na) \rightleftarrows 2K$; $NaAl \rightleftarrows Si$; $CaAl \rightleftarrows NaSi$.

The last two are due to the substitution of one Si-atom by Al in the silicon-oxygen tetrahedra. Thus, $Ca \rightleftarrows 2(Na, K)$ and $CaAl \rightleftarrows (Na, K)Si$ must be considered as particular cases. The proximity of ionic radii $Na_{Ri} = 0{\cdot}98$ Å, and $Ca_{Ri} = 1{\cdot}06$ Å does not appear to inhibit substitution by K ($Ri = 1{\cdot}33$ Å).

Recalculations of chemical analyses from the Table I show that the water in clinoptilolite ranges from 16·42 to 19·82 %; for heulandite it reaches 32 %. Judging by these comparative data one can come to the conclusion about a direct connection between the H_2O-content and Ca ions, which was noted by Hey and Bannister (1934), Merkle and Slaughter (1968), Pécsi-Donáth (1968), Breger *et al.* (1970), and Boles (1972). It seems that H_2O has a comparatively weak bond with Na and K-ions. In 1970 Senderov and Khitarov noted a much lower water content in the elemental cell of clinoptilolite in comparison with the heulandite cell.

Hence, the sequence of the H_2O-content increase in zeolites, particularly in the clinoptilolite–heulandite group, can be written: $(K \rightarrow Na) \rightarrow Ca$, which is possibly characteristic for other zeolites, Therefore, such H_2O-dependence of the divalent cations content is correct for $Mg+Ba+Sr+Fe$.

In the analyses of the clinoptilolite from Aydag, the ratio $H_2O : Al_2O_3 = 4{\cdot}83$–$7{\cdot}08$. According to Mumpton (1958, 1960) this ratio for Patagonia clinoptilolite is 6 to 7, and for heulandite is 5 to 6, which does not agree with our data based on more analyses.

A series of rare and minor elements was determined by means of chemical and spectral analyses. In particular, in the clinoptilolites from the Aydag deposit, Sr is from 0·21 to 0·47 % and Ba up to 0·02 %, which isomorphously substitute calcium;

Ti, up to 0·04 % goes together with Si; up to 0·008 % Ge and about 0·001 % Ni content is conditioned by presence of Fe; Zn and Pb, up to 0·02, Zn, up to 0·004, and Sn, up to 0·008 isomorphously substitute the main mineral-forming elements, or they are arranged in the characteristic structural clinoptilolite cavities.

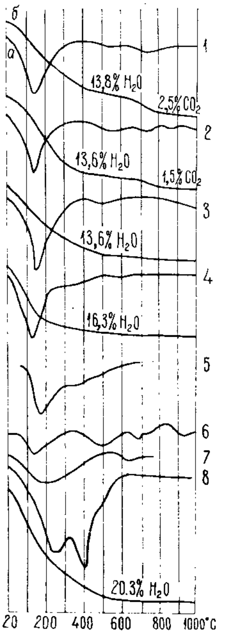

FIG. 3. DTA (*a*), and TG (*b*) curves of clinoptilolites and zeolitized tuffs: I—clinoptilolite-containing tuffs from the Aydag deposit: 1—from the quarry (from the surface); 2—from the well No. 13, depth 19 m. II—clinoptilolites: 3—particles 0·1–0·01 mm from zeolite-containing tuffs (sample No. 2, well No. 13), Aydag deposit; 4—light fraction of particles 0·1–0·01 from the sample No. 3; 5—from Zucanti, Italy; 6—from Hector deposit, USA (Mason and Sand, 1960); 7—from Argentine Patagonia (Mumpton, 1958); 8—heulandite from the Dashkesan iron ore deposit (Dashkesan, Azerbaidzhan SSR).

In the clinoptilolites rich in calcium there is a heightened (about 1% or more) strontium content, due to which, possibly, Hawkins (1967) synthesized strontium and calcium clinoptilolite; but they were not thoroughly described by this author. Clinoptilolite was also synthesized by Ames (1963). Černý and Povondra (1969) noted the strontium content in minerals of this group.

The present investigations allowed us to approach the deciphering of the physico-chemical peculiarities of clinoptilolite and at the same time to determine its distinction from heulandite and other analogous zeolites.

DTA and TG data of clinoptilolites and their tuffs, obtained by us, showed their exclusive uniformity (fig. 3). They are characterized by a great endothermic effect with a temperature maximum in most cases within 140–170 °C (possibly up to 200 °C) and by the absence of any exothermal effect; with this endothermal effect there takes place a complete evaporation of water, up to 16·3 %.

In thermograms nos. 1 and 2 (fig. 3) of clinoptilolite tuffs there is one more endo-effect at 750–830 °C due to emanation of carbon dioxide; the CO_2-content in these zeolitized ash tuffs varies from 2·5 % to 3·7 %.

In comparison with these data, the DTA curves of clinoptilolite cited in the literature (fig. 3), i.e. no. 6 (Mason and Sand, 1960), and no. 7 (by Mumpton, 1958, 1960), cannot be considered as characteristic, because, judging by the form of differential curves, the samples under investigation were probably not pure. Analogous thermal data are given in an article by Goto, Sato, and Matsuda (1968). Therefore, our thermal curves can be considered as standards for clinoptilolite.

X-ray investigation of natural and heated clinoptilolite confirm the conservation of the clinoptilolite crystalline structure when heated up to 750 °C (Table II). Further investigations showed (Table II) that after a complete evaporation of zeolite and crystallization water within the above mentioned range of temperature and when the heating is going on, clinoptilolite does not change its crystalline structure. The structure destruction begins just above 750 °C, and at 1000 °C we see already completely new data for newly formed substances.

Hence, the above cited data confirm the absence of polymorphism in clinoptilolite. Koizumi and Kiriyama (1953), Mumpton (1958, 1960), Shepard and Starkey (1964), Alietti (1967, 1972), Breger *et al.* (1970), and Kostov (1971) state that polymorphous phase transformations are characteristic for heulandite. In particular, Alietti (1972) studied this process in detail and determined two types of polymorphous phase transformations in heulandite at different temperatures. He stated by way of experiment that the 1st type when heated up to 400 °C transforms into phase B, and its framework is destroyed at temperatures below 550 °C; the 2nd type, phase A and B (or 1), is destroyed at above 550 °C. Mumpton (1960) considered this limit at 450 °C. Alietti (1972) connects the polymorphism of heulandite with the reduced Si : Al ratio in it and increased amount of bivalent elements. These correlations are reversed in clinoptilolite.

TABLE II. *Results of X-ray analyses of clinoptilolites and their heating products, Aydag deposit, Tauz region, Azerbaidzhan SSR.* (*M.-A. Kashkai and I. A. Babaev*)

Clinoptilolites				After heating of the clinoptilolite sample No. 3						Heulandite, Dashkesan north-western iron ore area	
Sample No. 3		Sample No. 4		Up to 700 °		Up to 800 °		Up to 1000 °			
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*
6	8·9 Å	6	8·9 Å	4	8·8 Å	2	3·68 Å	2	4·71 Å	10	9·3 Å
5	7·4	1	7·9	7	7·1	10	3·35	2	4·28	1	7·6
2	6·7	1	6·7	4	6·3	2	3·17	3	3·69	1	6·4
1	6·0	1	6·0	7	5·2	2	3·08	10	3·35	1	5·9
2	4·61	2	5·10	8	3·95	3	2·52	2	3·00	1	5·3
4	4·40	5	4·36	6	3·32	2	2·249	1	2·896	1	4·45
10	3·96	2	4·26	3	3·14	2	1·672	2	2·500	6	4·08
6	3·35	10	3·96	8	2·96	1	1·614	1	2·283	1	3·37
7	2·98	4	3·33	4	2·78	2	1·444	1	2·111	4	3·08
2	2·430	2	3·18	1	2·73			1	1·798		
1	1·947	5	2·96	1	2·265			1	1·664		
1	1·831	1	2·83	2	2·132						
2	1·729	4	2·78	3	1·814						
1	1·690	3	2·58	3	1·768						
3	1·599	2	2·46								
		1	2·335								
		2	2·127								
		4	1·978								
		7	1·818								
		1	1·693								
		6	1·545								

In the DTA curve of the Dashkesan heulandite (fig. 3, No. 8) there is noted a deep endothermal effect with maximum at 240 °C (evaporation of zeolite water; see chem. analysis in Table I, and transformation of one modification of heulandite into another). Beginning at a temperature above 530 °C there is destruction of the crystalline framework of heulandite; clinoptilolite from Aydag conserves its structure up to 700 to 750 °C.

Results of X-ray analyses of natural clinoptilolites and products of their heating (up to 700, 800, and 1000 °C) are given in Table II. The most typical values of interplanar spaces for clinoptilolite from Aydag (Tauz region, Azerbaidzhan SSR) are: 8·9, 3·96, 2·96–2·98, 2·430–2·464.

According to Alietti (1972), in the natural phases of heulandite and in clinoptilolite d_{020} for phase A is 8·95 Å, phase B 8·25 Å, and phase 1 8·70 Å. As one can see from the above data, our Aydag clinoptilolite with d_{020} 8·9–9·0 stays closer to the phase A. Alietti gives unit cell dimensions for the heulandite–clinoptilolite group of minerals:

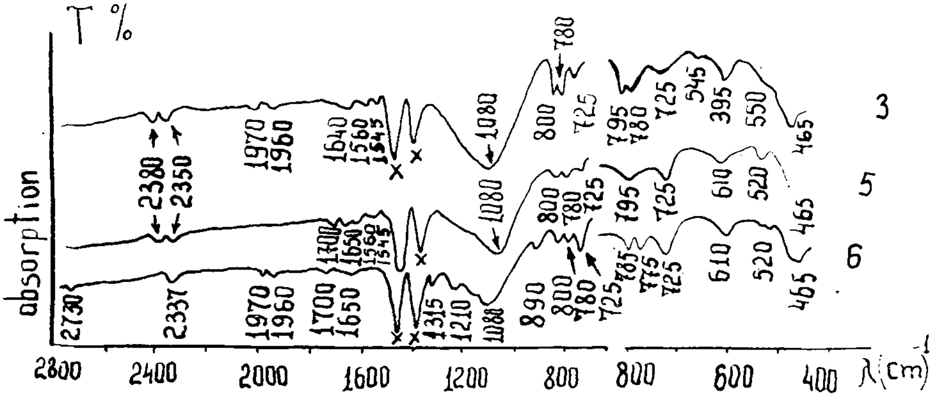

FIG. 4. Infra-red absorption spectra of clinoptilolite from the Aydag deposit.

a 17·691±0·001 b 17·973±0·002 c 7·407±0·001 Å β 116°37′±1′ V 2105·486 Å^3
17·658±0·002 17·957±0·001 7·388±0·001 116°23′±1′ 2102·116

Infra-red spectra of three Aydag clinoptilolites are given in fig. 4. Here are marked absorption bands of OH deformation vibrations in H_2O molecules (1545–1700 cm^{-1}), framework vibrations (400–800 cm^{-1}) and (Al, Si)–O vibrations (890–1080 cm^{-1}). The last is shown intensely.

In conclusion the question of the hydrothermal alteration of the original ash tuffs of Aydag deposit into white zeolitized ash tuffs, including the alteration into clinoptilolite must be considered (Table III).

According to these chemical analyses, taking the molecular value of characteristic oxides of original tuffs for a unit, we calculate values for the hydrothermal derivative (Table III).

According to these calculations, the sequence of hydrothermal phase alteration of the primary rock appears to be: primary rock (tuff) → zeolitized rock → clinoptilolite. The SiO_2-content varies insignificantly, and the Al_2O_3-content remains constant. At the same time, as was to be expected, during the clinoptilolitization process a considerable part of the calcium and sodium was consequently washed out, and the mineral was enriched by potassium oxide more than twice as much. According to the chemical analyses, one can judge in an analogous way about the accessory components—Mg, Fe, *et al.* The experiments of Ames and Mercer (1961) who determined the succession of isolation of elements from solutions: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and $Ba^{2+} > Ca^{2+} > Mg^{2+}$, should be noted. A certain role in the process of tuff clinoptilolitization is played by the increased SiO_2-content ($SiO_2 : Al_2O_3 \approx$ 8–9) and pH of the environment.

TABLE III. *Average chemical analysis and comparative molecular ratios of samples of Aydag deposit*

	1	2	3		1′	2′	3′	2″	3″
SiO_2	66·61	65·88	65·68	SiO_2	1108	1096	1093	0·989	0·986
TiO_2	0·13	0·08	0·09	Al_2O_3	119	118	119	0·991	1·000
Al_2O_3	12·14	12·12	12·14	CaO	80	77	53	0·962	0·662
Fe_2O_3	0·95	1·03	0·99	Na_2O	34	33	20	0·970	0·588
FeO	0·32	0·18	0·11	K_2O	15	17	34	1·133	2·267
MnO	0·05	0·03	0·01	H_2O	645	643	681	0·997	1·056
MgO	0·26	0·57	0·90						
CaO	4·49	4·32	3·00						
Na_2O	2·09	2·03	1·28						
K_2O	1·41	1·67	3·20						
H_2O^-	3·46	3·07	3·70						
Ignition loss	8·17	8·52	8·58						
SO_3	0·15	0·15	0·17						
Total	100·23	99·65	99·85						

1. Mean of 7 analyses of primary ash tuffs (greenish).
2. Mean of 5 analyses of zeolitized ash tuffs (white).
3. Mean of 4 analyses of clinoptilolite.

1′, 2′, 3′. Molecular ratios of analyses 1, 2, and 3.

2″, 3″. Comparative molecular ratios, taking the ratios of 1′ as unity.

That is why the Aydag zeolitized tuffs also contain quartz or opal. This phenomenon for other regions was noted by d'Anglejan (1967), Estéoule *et al.* (1971), Sassis and Jacob (1972), and Hunahashi, Watanabe, and Kim (1972). Depending on geological conditions and petrochemical peculiarites, altered rocks and different zeolites in the Aydag deposit are characterized by a definite hypogene zoning. In particular, clinoptilolite has a propensity for the upper part of a zone. Such a zoning is characteristic for a series of other clinoptilolite deposits, and was noted by Takahisa (1961), Sudo *et al.* (1962), Hideo and Minori (1971), and Lijima (1971) who studied the deposits of Japan.

The above given results of the investigation of clinoptilolite from the Aydag deposit allow us to determine more precisely the chemical nature, thermal peculiarities, structure, and other physico-chemical peculiarities of this remarkable mineral from the clinoptilolite–heulandite group of zeolites. These data can be adopted as standard for clinoptilolite, taking into consideration that the data existing in the literature cannot serve as a base for a complete characterization of clinoptilolite at all.

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