

Foaming ability of zeolitic rocks as a function of their composition

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Samples of natural zeolites of different structural type, genesis, and cation composition (Ca and Mg- or Na and K-rich zeolites) were tested for their foaming ability at 1200 °C. The degree of foaming was estimated by the density of solid foamed material obtained after calcination. Thermally-induced foaming ability of natural zeolites was shown to be a function of the chemical composition. Only Ca and Mg-rich zeolites foam at 1200 °C calcination. The FTIR method showed that upon dehydration of the Ca and Mg-rich zeolites original water molecules transform into thermostable framework OH groups that became the source of high-temperature water vapor for foaming zeolite. Foamed material is formed if the temperature of OH group recombination into H₂O coincides with that of sintering, and the viscosity of the melt at 1200 °C is sufficient to enclose the H₂O vapor within the pores. Both the sintering and viscosity of the melt are functions of the chemical composition of a zeolitic rock.

Key words: foaming, natural zeolites, composition, cationes, sintering, melt viscosity, IR-spectroscopy.

Introduction

During the last 15-20 years, large deposits of zeolitic tuffs were discovered throughout the world, so only silica, feldspars, and clay minerals are more abundant than zeolites in the lithosphere [1]. About 50 structural types of natural zeolites are known so far. Zeolites are framework aluminosilicates, their structure consisting of interconnected channels and cavities lodging various cations (mostly Na⁺, K⁺, Ca²⁺, and Mg²⁺) and water molecules, which are able to be removed and reabsorbed without structural breakdown. Zeolite chemical formulae, as a rule, do not include OH groups connected to the framework with chemical bonds, but only molecular water [2, 3], in contrast to other water-containing aluminosilicates, e.g., clays, micas, vermiculite, and obsidian. In real zeolites the OH groups can be sited only on the defects of the crystal structure [4].

Over the past ten years, Kazantseva *et al.* [4-6] have shown that zeolitic tuffs are prospective source for porous building materials because many of them foam upon heating to a pyroplastic state. When developing the methods of production of porous zeolitic material, she came across the problem of the nature of the foaming gas at the melting temperature of zeolitic rocks, 1100-1200 °C. The ability of some zeolites to foam on rapid heating has been known practically since the discovery of the first zeolites [2, 3] (c.f., the name zeolite, *zeo* = to boil and *lithos* = stone). As the source

of the high-temperature foaming gas, molecular water was considered, retained due to the rapidity of heating. However, as experiments have shown [5], some natural zeolites foam also on slow heating (100 K^h⁻¹) up to the melting point, and even at long holding times (8-10 hours) at 900 °C. Under these heating conditions, molecular zeolitic water is fully removed from the structure before a mineral sinters. Nevertheless, chromatographic analysis of the gas from the pores of zeolitic material foamed on slow heating detected only water vapor, provided the only water-bearing mineral was zeolite [5].

In the present work, we aimed to discover the nature of high-temperature water vapor, to study the thermal evolution of H₂O molecules and framework OH groups in zeolites up to the pyroplastic state, and the effect of the cation composition on the thermally-induced foaming process. We also revealed the criteria for chemical composition of zeolitic rock defining the fusibility and viscosity necessary for pore retention in the porous melt. The results of investigations on most typical representatives of natural zeolites from various deposits are reported here below.

Experimental

Natural zeolites of different structural type, genesis, and cation composition from deposits of different localities were investigated, among them macrocrystalline samples from basalt and/or agate, and tuffs with a zeolite content of more than 50 wt.%. The chemical formulae of the macrocrystalline samples and bulk chemical composition of tuffs with a zeolite content of more than 70 wt.% are given in Tables 1 and 2 respectively, and the oxide compositions of all studied

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Table 1. Characteristics of original and calcined at 1200 °C macrocrystalline zeolites

Zeolite	Deposit	Chemical composition per formula unit	$\frac{Na+K}{Si+Al}$	$\frac{Ca+Mg}{Si+Al}$	Calcined sample
Na-rich zeolites					
Analcime	Nidym River, Russia	$Na_{15.04} [Al_{15.04}Si_{32.96}O_{96}] \cdot 16.0 H_2O$	0.31		Transparent glass
Natrolite	Khibin Mts., Russia	$Na_{15.04} K_{0.16} Ca_{0.32} [Al_{15.68}Si_{24.24}O_{80}] \cdot 17.0 H_2O$	0.38	0.008	Transparent glass
Na-rich zeolites					
Scolecite	Berufjord Iceland	$Na_{2.0}Ca_{6.9} [Al_{15.8}Si_{24.3}O_{80}] \cdot 23.7 H_2O$	0.05	0.17	Large pores 0.7-1.2 mm
Chabazite	Far East, Russia	$Na_{0.24}K_{0.10}Ca_{1.65} [Al_{3.79}Si_{8.25}O_{24}] \cdot 12.8 H_2O$	0.03	0.14	Large pores 0.9-1.5 mm
Stellerite	Trasbaikalia, Russia	$Na_{0.2}Ca_{3.8} [Al_{7.9}Si_{28.2}O_{72}] \cdot 27.5 H_2O$	0.005	0.10	Fine pores 0.1-0.4 mm
Stilbite	Nidym River, Russia	$Na_{1.17}Ca_{4.01} [Al_{9.22}Si_{26.69}O_{72}] \cdot 28.5 H_2O$	0.03	0.11	Isolated pores
Ca-Na zeolites					
Mesolite	Poona, India	$Na_{14.5}K_{0.2}Ca_{16.5} [Al_{48}Si_{72}O_{240}] \cdot 62.56 H_2O$	0.12	0.14	Fine pores 0.3-0.5 mm
Heulandite	Nidym River, Russia	$Na_{1.58}K_{0.19}Ca_{3.40} [Al_{8.35}Si_{27.59}O_{72}] \cdot 24.4 H_2O$	0.05	0.095	Isolated pores
Clinoptilo-lite	Tedzami, Georgian Republic	$Na_{2.68}K_{0.48}Ca_{1.6} [Al_{6.55}Si_{29.45}O_{72}] \cdot 20.8 H_2O$	0.088	0.044	Transparent glass

Table 2. Characteristics of original and calcined at 1200 °C zeolitic tuffs

Zeolite (wt.%)	Deposit	Bulk chemical composition calculated per zeolite formula unit	$\frac{Na+K}{Si+Al}$	$\frac{Ca+Mg}{Si+Al}$	Calcined sample (density, Γ/cm^3)
Clinoptilo-lite (90)	Dzegvi, Georgian Republic	$Ca_{1.9}Mg_{1.05}K_{0.64}Na_{1.02}[Al_{7.15}Fe_{0.99}Si_{28.5}O_{72}] \cdot 21.6 H_2O$	0.046	0.082	Porous (0.70)
Clinoptilo-lite (90)	Oregon, USA	$Ca_{0.91}Mg_{0.38}K_{2.38}Na_{1.34}[Al_{6.07}Si_{29.45}O_{72}] \cdot 21.0 H_2O$	0.10	0.036	Fused, dence (>1)
Heulandite (75)	Khongurruu, Russia	$Ca_{1.56}Mg_{0.98}K_{0.56}Na_{1.18}[Al_{6.76}Si_{29.56}O_{72}] \cdot 18.5 H_2O$	0.048	0.070	Porous (0.85)
Clinoptilo-lite (75)	Khongurruu, Russia	$Ca_{0.37}Mg_{0.64}K_{0.64}Na_{3.79}[Al_{6.18}S_{29.36}O_{72}] \cdot 18.8 H_2O$	0.125	0.028	Fused, dence (>1)

Table 3. Chemical composition of zeolitic tuffs

Deposit	Zeo-lite ¹	Oxide, wt.%									
		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Ignition loss	Σ
Zeolite \geq 90 wt.%											
Bowie, Arizona, USA	Chab	52.7	0.49	16.37	4.57	2.88	1.91	1.66	7.47	12.4	100.4
S. Severino, Quarry, Italia	Chab, Phil	59.1	0.55	12.3	4.06	3.88	2.99	2.53	4.96	9.65	100.0
Dzegvi, Georgian Rep.	Cpt	60.1	0.34	13.25	2.87	4.48	1.54	2.16	1.09	14.2	100.0
Tushleg, Mongolia	Cpt	63.1	0.21	13.02	1.08	2.10	1.85	2.90	1.93	13.83	100.0
Oregon, USA	Cpt	65.2	0.33	11.2	2.57	1.2	0.38	1.07	4.76	13.1	99.81
Wikieup, Arizona, USA	An	57.8	0.16	17.8	2.44	0.76	1.07	10.3	0.85	8.94	100.1
Pine Valley, Nevada, USA	Phil, Er	53.4	0.19	15.76	2.35	0.32	0.21	7.07	2.97	17.63	99.9
70-80 wt.% of zeolite											
Bania, Bosnia	Cpt	66.0	0.18	11.93	1.63	3.38	1.24	1.24	1.28	13.1	100.0
Khongurruu, Russia	Heul	67.3	0.12	11.12	1.55	3.31	1.49	1.39	1.00	12.3	99.6
Khongurruu, Russia	Cpt	68.6	0.19	12.24	1.33	0.82	1.01	4.57	1.18	9.96	99.9
Tsagan Tsab, Mongolia	Cpt	68.2	0.43	11.65	3.47	0.57	1.22	2.80	4.55	6.61	99.5
Bely Plast, Bulgaria	Cpt	65.7	0.13	11.12	0.87	2.83	0.76	0.56	3.22	14.69	99.9
Tedzami, Georgian Rep.	Cpt	53.9	0.36	11.9	2.96	7.8	1.82	2.0	1.48	17.34	99.6
65-50 wt.% of zeolite											
Seryodochnoe, Russia	Cpt	67.1	0.21	12.77	1.43	2.82	0.72	0.57	3.77	10.5	99.9
Shyvirtuiskoe, Russia	Cpt	61.4	0.33	13.20	1.21	3.28	1.35	1.56	2.66	14.2	99.2
Metaxades, Greece	Cpt	68.6	0.16	11.74	0.66	2.34	0.93	1.0	2.68	11.45	99.6
Lytutogskoe, Russia	Cpt	69.2	0.32	12.73	2.21	2.16	1.23	1.82	2.46	6.98	99.1

¹Chab-chabazite; Er-erionite; Phil-phillipsite; Mord-mordenite; An-analcime; Cpt-clinoptilolite; Heul-heulandite.

Table 4. Intensity of zeolitic tuffs foaming at 1200 °C

Deposit	¹ Content, wt.% CaO+MgO; Na ₂ O + K ₂ O; SiO ₂ + Al ₂ O ₃	CaO + MgO SiO ₂ + Al ₂ O ₃	² RO + R ₂ O SiO ₂ + Al ₂ O ₃	³ Mineral composition	⁴ Foaming ability
Zeolite ≥ 90 wt.%					
Bowie, Arizona, USA	4.79; 9.1; 69.07	0.069	0.20	Chab, Er. (traces)	+++
S. Severino, Quarry, Italia	6.87; 7.49; 71.4	0.096	0.20	Chab, Phil, fs	+++
Dzegvi, Georgian Rep.	6.02; 3.25; 73.35	0.082	0.126	Cpt, q	+++
Tushleg, Mongolia	3.95; 4.83; 76.12	0.052	0.115	Cpt, fs; q	++
Oregon, USA	1.58; 5.83; 76.4	0.021	0.097	Cpt, fs	–
Wikieup, Arizona, USA	1.83; 11.15; 75.6	0.024	0.172	An, q (traces)	–
Pine Valley, Nevada, USA	0.53; 10.04; 69.16	0.01	0.152	Phil, Er (traces)	–
70-80 wt.% of zeolite					
Bania, Bosnia	4.62; 2.52; 77.93	0.059	0.092	Cpt, mn, fs, q	+++
Khongurruu, Russia	4.8; 2.39; 78.42	0.061	0.092	Heul, fs, q	++
Khongurruu, Russia	1.83; 5.75; 80.84	0.023	0.094	Cpt, fs, q	–
Tsagan Tsab, Mongolia	1.79; 7.35; 79.85	0.022	0.114	Cpt, sm, fs, q	–
Bely Plast, Bulgaria	3.59; 3.78; 76.82	0.047	0.096	Cpt, anor, mn	–
Tedzami, Georgian Rep.	9.62; 3.48; 65.80	0.146	0.199	Cpt, calc., fs, q	–
65-50 wt.% of zeolite					
Seryodochnoe, Russia	3.54; 4.34; 79.87	0.044	0.099	Heul, mn, q, fs	++
Shyvirtuiskoe, Russia	4.63; 4.22; 74.6	0.062	0.119	Cpt, mn, fs, q	+++
Metaxades, Greece	3.27; 3.68; 80.34	0.041	0.086	Cpt, fs, q	–
Lyutogskoe, Russia	3.39; 4.28; 81.93	0.041	0.094	Cpt, q, fs	–

¹Oxide content corresponds to the data of chemical analyses in Table 3

²RO + R₂O = CaO + MgO + Na₂O + K₂O

³Chab-chabazite; Er-erionite; Mord-mordenite; An-analcime; Cpt-clinoptilolite; Heul-heulandite; fs-feldspar; sm-smectite; mn-montmorillonite; q-quartz; calc-calcite

⁴Foaming ability is: +++-good ($d < 1.0 \text{ g/cm}^3$); ++-mediate ($d = 11.5 \text{ g/cm}^3$); -samples do not foam ($d > 1.5 \text{ g/cm}^3$).

tuffs is given in Table 3. The analyses were performed by X-ray fluorescence (XRF) using a Karl-Zeiss VRA-20R spectrometer. Mineral composition of the tuffs studied (Table 4) was obtained by a quantitative X-ray powder diffraction method (XRD) using a “DRON-3” diffractometer (CuK α radiations, graphite monochromator).

To estimate the foaming ability of the zeolites, coarsely crushed samples, 5-10 mm in size, were heated (500 Kh⁻¹) in a muffle furnace, kept at 1200 °C for 15 minutes and then abruptly cooled to room temperature. The degree of foaming was estimated in calcined tuff samples by the density (Tables 2, 4), and in macrocrystalline samples by the pore size and propagation visually by optical and scanning electron microscopy (SEM) (Table 1). (The latter could not be immersed into a liquid as they had no surface crust and got soaked).

Thermal evolution of H₂O molecules and framework OH groups in zeolites was followed by an IR spectroscopy method. Typical representatives of macrocrystalline zeolites (heulandite from basalt (Nidym), clinoptilolite from agate (Tedzami), chabazite from basalt (Khilok)

(Table 1), and heulandite and clinoptilolite tuffs (Khongurruu and Oregon, respectively, Table 2) were examined. Self-supported pellets (18-30 mg/cm²) of pulverized samples were placed in a quartz cell connected to a vacuum unit, evacuated to 10⁻⁴-10⁻⁵ torr for two hours and then heated to 200, 400, 600, and 800 °C, with an exposure of 1 hour at each temperature. The rate of heating was 500 Kh⁻¹. The samples were cooled to room temperature and spectra were recorded on a Karl-Zeiss UR-20 spectrometer in the ranges of 1580-1700 and 3200-3800 cm⁻¹, i.e. covering the bending and stretching OH group vibrations. The intensities of absorption bands in the spectra were normalized to the same pellet thickness.

To expose the OH groups that actually cause foaming, upon calcining in air, and not in vacuum, we recorded the IR spectrum for heulandite tuff (Khongurruu, Russia) calcined at 900 °C in air for 30 minutes. Self-supported pellets were heated to 500 °C in air and evacuated for 1 hour to remove absorbed water, and spectra were taken on a Bruker spectrophotometer. The intensities of absorption bands were not normalized as previously (Fig. 3).

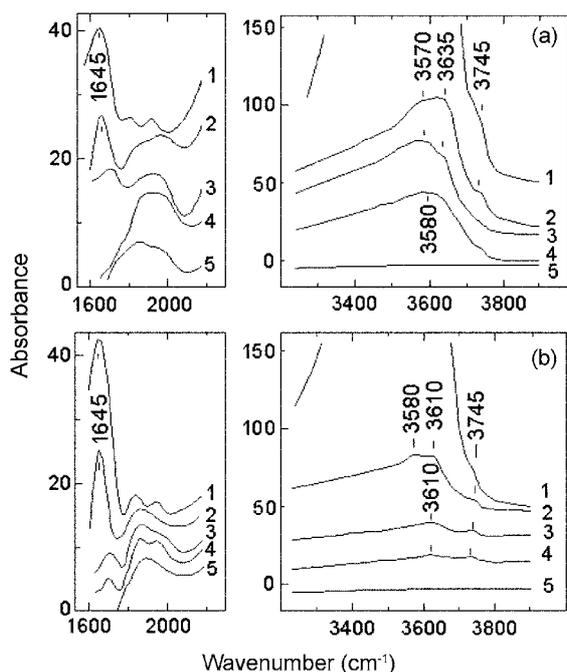


Fig. 1. Infrared spectra of the pellets prepared from zeolitic single crystals, after heating in vacuum at: (1) 25°; (2) 200°; (3) 400°; (4) 600°; (5) 800 °C. (a) Ca-rich heulandite; (b) Na-rich clinoptilolite.

Results and Discussion

The Nature of High-temperature Foaming gas in Natural Zeolites

The IR spectroscopy study of macrocrystalline zeolites from basalt and agate and zeolitic tuffs revealed the similarity of thermal evolution of H₂O molecules in them (Figs. 1 and 2). When heated in vacuum, they practically lost all their water by 400 °C (the absence of bending H₂O vibration in the IR spectra after 400 °C). Therefore, the bands in the region of stretching OH group vibrations in the IR spectra are conventionally allotted only to the framework OH groups in different structural positions [2, 7, 8]. Peaks at 3560-3570, 3610-3635, and 3740-3745 cm⁻¹ can be discerned on the broad band in the range of 3500-3800 cm⁻¹ in the spectra of all samples studied after heating to 200 °C (Figs. 1, 2). The peak at about 3745 cm⁻¹ is conventionally ascribed to the terminal OH groups at Si atoms at the end of Al-O-Si chains [7, 8]. It is weak for all samples and does not depend on the chemical composition of a sample. Isostructural heulandite-clinoptilolite samples demonstrate that the intensity of the two remaining bands depends on the valence of the predominating cation in a sample: only in Ca and Mg-rich heulandites the bands are strong, and in Na and K-rich clinoptilolites they are weak. In the spectra taken after heating to 600 °C, the band at 3580-3600 cm⁻¹ was detected only for the Ca and Mg-rich zeolites. After heating to 800 °C in vacuum, practically a full dehydroxilation was observed in all the samples studied.

If calcined in air, zeolite samples are dehydroxilated

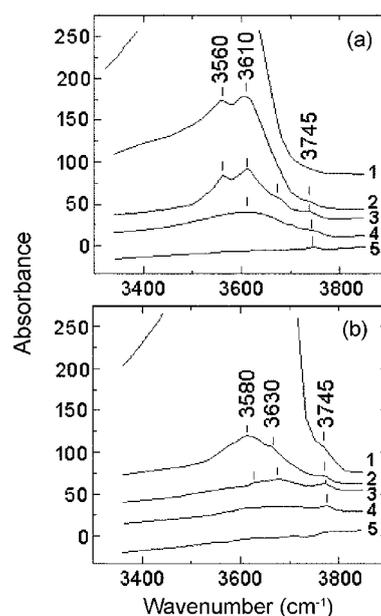


Fig. 2. Infrared spectra of the pellets prepared from zeolitic tuffs, after heating in vacuum at: (1) 25°; (2) 200°; (3) 400°; (4) 600°; (5) 800 °C. (a) Ca-rich heulandite tuff from Khonguruu (Russia); (b) K-rich clinoptilolite tuff from Oregon (USA).

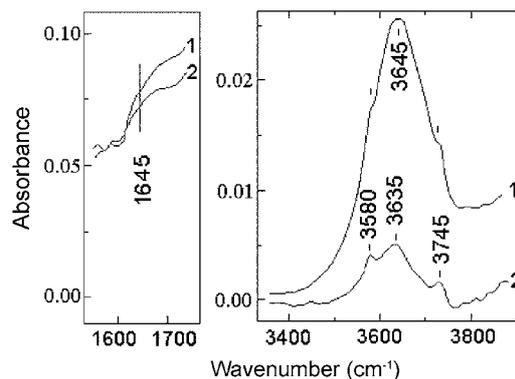


Fig. 3. Infrared spectra of Ca-rich heulandite tuff from Khonguruu (Russia) after air calcination of coarsely crushed tuff fragments (15-20 mm) at 900 °C for 30 minutes. Spectra were recorded after heating of the spectrum pellets at 500 °C for 2 hr: (1) in air; (2) in vacuum.

in a higher temperature range: after thermal treatment at 900 °C, heulandite tuff (Khonguruu, Table 2) still manifested the same bands (3580, 3635, and 3745 cm⁻¹) in its IR spectrum (Fig. 3), in the absence of the bands of bending H₂O vibrations.

However, the spectra of tuff samples calcined in air at a still higher temperature, 1100 °C, is different, containing bands at 3430, 3600, and 3680 cm⁻¹. The band at 3740-3780 cm⁻¹ is retained (Fig. 4).

Thus, our results show that I) bivalent cations promote framework OH group formation in natural zeolites under thermally-induced dehydration and II) these groups undergo some transformations under further heating of samples to the temperature of their collapse at sintering.

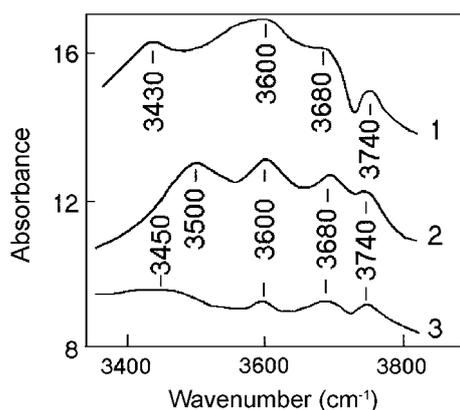


Fig. 4. Infrared spectra of zeolitic tuffs after air calcination of coarsely crushed tuff fragments (15–20 mm) at 1100 °C for 30 minutes. Spectra were recorded after heating of the spectrum pellets at 500 °C in vacuum: (1) Ca-rich clinoptilolite tuff from Dzegvi (Georgian Republic); (2) Ca-rich heulandite tuff from Khongururu (Russia); (3) K-rich clinoptilolite tuff from Oregon (USA).

The first inference supports the common belief obtained mainly from research on synthetic zeolites. Similar bands of OH group stretching vibrations are typical of alkaline earth forms of synthetic faujasites under thermally-induced dehydration, whereas they have not been found in the alkaline forms [7, 8]. The only available data on natural zeolites, Ca-bearing scolecite and Na-bearing natrolite, support the same hypothesis [9]. The role of the bivalent cation on framework OH group formation has been recognized since the 1960-ies. Some schemes for the split of the H₂O molecule under the polarizing effect of the cation, resulting in framework OH group (AlO-(H)-Si) formation and cation transformation into a calciumoxygen complex were advanced by Ward and Uytterhoeven *et al.* [8, 10]. However, the detailed mechanism of framework OH group formation remains in dispute till now [11].

The complicated IR spectra of calcined samples at 1100 °C (Fig. 4) can be interpreted as follows: the band at 3430 cm⁻¹ is typical of hydrogen-bonded hydroxyls in H₂O clusters [12], and the band at 3680 cm⁻¹ is similar to those from the OH groups linked to Al atoms [13]. This may be taken as evidence of structure collapse, accompanied by the closest approach of OH groups and probable hydration of Al-bearing debris in the insulated pores of sintered tuffs.

Thus, IR spectroscopy studies inferred that the original H₂O molecules in zeolites (zeolitic water) could not be the source of the gaseous phase for thermally-induced foaming. The dehydration of alkaline earth forms of natural zeolites, similarly to synthetic zeolites, results in the formation of structural OH groups, which on further heating can be rearranged into H₂O molecules enclosed in the micropores during zeolite dehydroxylation at sintering.

A primitive calculation shows that theoretically one Ca²⁺ per formula unit (pfu) of zeolite is enough to

ensure rich foaming: one Ca²⁺ is able to generate one framework OH group, and two OH groups produce one water molecule on further thermal dehydroxylation [7]. So, one mole of zeolite may produce 0.5 moles H₂O gas, the volume of one mole of ideal gas being 22.4 lit.

Thus, the correlation between the cation composition and the intensity of foaming proves that the structural OH groups, formed at dehydration of Ca- and Mg-rich natural zeolites, are the source of foaming. Tables 1 and 2 demonstrate that, upon heating up to 1200 °C, the intensity of foaming is a function of the (Ca²⁺ + Mg²⁺)/(Si + Al) ratio, diminishing as the value of the ratio decreases from 0.17 to 0.07. If a comparison is made of the zeolite-rich tuffs with the macrocrystalline samples having the same values of the (Ca²⁺ + Mg²⁺)/(Si + Al) ratio, the intensity of foaming is noticeably higher in the first ones, most probably, due to their lower crystallinity and melting temperatures. In reality, the foaming ability of zeolitic tuffs is limited, in addition to the cation composition, by several factors shortly discussed below.

Estimation of Foaming Ability for a Zeolitic Tuff

Zeolitic tuffs are polymineral rocks. Most common admixtures in zeolitic tuffs are water-bearing smectites and micas, and anhydrous feldspars, calcite, and dolomite with the same cations that are present in zeolites (Ca, Mg, Na, and K). This hinders the accurate determination of cation composition of the zeolite itself. But, with all this, a thermal test for the foaming ability of tuffs containing more than 50 wt.% of zeolite demonstrated that the main factor defining this ability is again the concentration of (CaO + MgO) in a tuff. Our results show that the rocks with (CaO + MgO) > 3 wt.% foam, and those with (CaO + MgO) < 2 wt.% sinter without pore formation (Table 4) (3 wt.% of CaO is equivalent to about 1.5 Ca²⁺ pfu of, e.g., clinoptilolite or mordenite). In tuffs containing about 90 wt.% of zeolite, this factor defines the foaming ability most directly, independently of structural type and genesis (Table 4). The foaming ability of tuffs with a zeolite content less than 80 wt.% depends also on the nature of the admixtures. The sample from Bely Plast, e.g., does not foam, even though its (CaO + MgO) content is 3.6 wt.% (Table 4). The main content of its admixture is anortite (calcium feldspar), and CaO makes up 25 wt.% or ¼ of anortite weight. Hence, 4 wt.% of anortite will add 1 wt.% of CaO to the bulk rock analysis, and the zeolitic part actually contains less calcium than the summary rock oxide composition shows. Thus, the requirements for foaming of tuffs with a zeolite content of 70–80 wt.% are (CaO + MgO) > 3 wt.% and Ca- and Mg-bearing anhydrous admixtures in a rock, not exceeding 3–4 wt.%.

An estimation of the foaming ability of low-zeolitic tuffs (65–50 wt.%) shows that this content of zeolite is not enough to create the concentration of high-

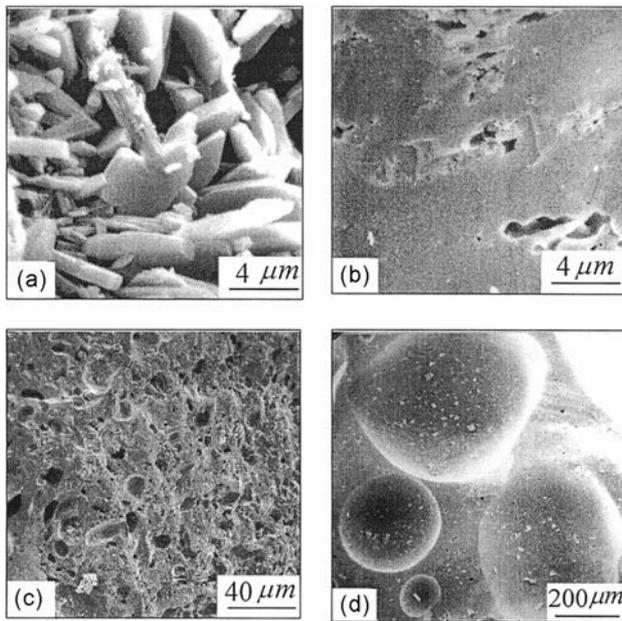


Fig. 5. Scanning electron micrographs showing changes on heating of Ca-rich clinoptilolite tuff from Dzegvi (Georgian Republic) to: (a) 900°C; (b) 1000°C; (c) 1100°C; (d) 1200 °C.

temperature water vapor necessary for foaming, so the foaming ability is defined not only by the zeolite, but by the different rock components. Such zeolite-poor tuffs foam if they contain, in addition to the zeolitic minerals, water-bearing admixtures, such as montmorillonite and micas, that can supply some additional water vapor. To ensure a foaming ability, the common content of all the water-bearing minerals including zeolite in a rock, has to be not less than 70 wt.%. The requirements of $(\text{CaO} + \text{MgO}) > 3$ wt.% and low content of Ca- and Mg-bearing anhydrous admixtures remain valid. The foaming ability of tuffs containing less than 50 wt.% of zeolite is out of the scope of the present work.

To retain the pores up to solidification, certain technological properties of the melt are required, also being functions of the chemical composition. Porous melt formation necessitates well-timed rock sintering to capture the gas, and optimal melt viscosity to allow pore expansion under gas pressure. For zeolitic rocks, the optimal viscosity range is 10^{-5} - 10^{-7} Pa·s [14]. Electron-microscopic analysis of textural thermal-induced transformations (Fig. 5) showed that sintering of the foamed samples occurred at 1000-1100 °C, pore nucleus formation at 1100-1150 °C, and pore expansion at 1200 °C. The temperature of the processes is controlled mainly by the particular chemical composition of a sample.

Our experimental results, in accordance with the calculations based on the correlation between the rock chemical composition and its viscosity [14], show that the melts with optimal viscosity in the above-mentioned temperature range are formed if the summary $\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ content lies within the range of

4.5-15.0 wt.%, whereas the sum of alkaline earth oxides should not exceed 6 wt.%. This last limitation is caused by the ability of bivalent cations, especially Ca^{2+} , to lower the melt viscosity at 1200 °C. For example, the Ca-rich sample Tedzami (Table 4) does not foam because it contains 7.8 wt.% CaO and its calculated viscosity (10^{-3} Pa·s) is beyond the lower limit of the optimal viscosity range.

Conclusions

The foaming ability of natural zeolites is a function of the chemical composition. Water vapor is the only source of the foaming gas during zeolite sintering, and it results from the multistep transformation of the original H_2O molecules in the alkaline earth forms of zeolites. During the first step, loosely bound H_2O molecules partly transform into firmly-bound thermostable framework OH groups. On further heating, the latter recombine into H_2O gas. Provided the temperatures of zeolitic rock sintering and melt formation are not higher than 1100 °C and 1100-1200 °C, respectively, the water vapor is trapped in the melt, if it is in the pyroplastic state, and pores can be formed and expanded under the water vapor pressure. The ranges of zeolitic rock chemical composition have been established to ensure solid porous material formation.

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