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# ZEOLITES IN TERTIARY BASALTOIDS FROM RĘBISZÓW (LOWER SILESIA, SW POLAND)

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## ABSTRACT

Several minerals from zeolite group have been found in Rębiszów basaltoid deposits: gobbinsite, natrolite, gismondine, garronite, thomsonite and phillipsite. For the first time gobbinsite has been recognized in basaltoids from Lower Silesia. Moreover, a new phase has been distinguished on the basis of some determined parameters (such as calculation of chemical formulae and X-ray diffraction patterns), belonging to zeolite group and occurring together with other zeolites. Origin of the whole assemblage of zeolite minerals can be related to hydrothermal activity of post-magmatic solutions within thermal contraction cracks of congealing basaltoid lava.

**Key words:** *basaltoid, zeolite, garronite, gismondine, gobbinsite, phillipsite, natrolite, thomsonite, new zeolite phase, Lower Silesia, Rębiszów*.

## INTRODUCTION

Scientific interest in minerals of zeolite group results mostly from their specific crystal structure (the presence of empty channels) which makes possible to use these minerals as molecular sieves. Due to this property, the mineral group finds their application in many different domains, like drainage and purification of gases and liquids, enrichment of the air with oxygen, recovering of metals from solutions and industrial sewages, animal breeding, growing plants, protection of natural environment and others. Such a broad range of applications results from physical and chemical properties of the zeolite group, and mostly from their ability of high molecular sieves adsorption, especially at low pressures. The demand for zeolites resulted in successful attempts of synthesis of these minerals (Donahoe *et al*. 1984, Gottardi 1989). Fly ashes were also proved to be a useful raw material for this purpose (Mondragon *et al*. 1990; Link

Cheng-Fang, Hsi Hsing-Cheng 1995; Querol *et al.* 1995, 1997; Amrhein *et al.* 1996; Michalik, Wilczyńska-Michalik 1998).

It seems thus, that the appropriate characterization of chemical and physical properties of natural zeolites leads not only to the recognition of their practical usefulness but also to determination of conditions of their formation. Recognition of their structure, in turn, makes possible to find their most appropriate application in the sphere of economic activity.

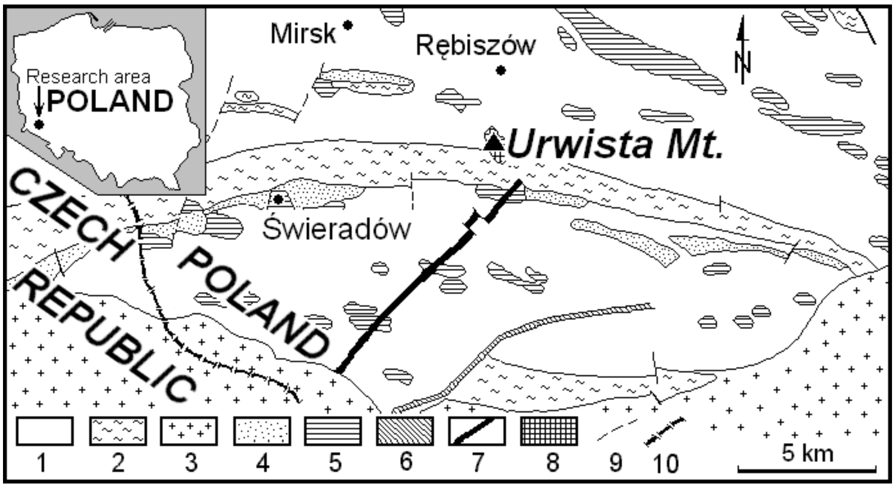



Fig. 1. Geological sketch map of Izera Mountains and Izera Upland with the localization of the Urwista Mt. basaltoid (Smulikowski 1972); 1 – Izera gneiss, 2 – mica and chlorite schist, 3 – Karkonosze granite, 4 – leucogranite, 5 – Izera granite-gneiss, 6 – Garby Izerskie silicified dislocation zone, 7 – vein microgranite, 8 – basaltoid, 9 – faults, 10 – state boundary.

The subject of this research are zeolites found in Tertiary basaltoid deposits in the quarry at Urwista Mountain near Rębiszów in Izera Upland in Lower Silesia, SW Poland (Fig. 1) in form of white veinlets cutting the basaltoid rock. The veinlets were most probably formed due to post-magmatic activity of hydrothermal solutions within thermal contraction fissures in the rock.

The occurrence of zeolites near Rębiszów at the Urwista Mountain was pointed out earlier (Adamczyk 1998), however, detailed identification of the particular minerals was not performed. The aim of the present work was to identify zeolites from this deposit.

## EXPERIMENTAL

Thickness of white veinlets within the basaltoid does not exceed 1.5 mm. Investigations were made on the material mechanically separated from the veinlets. Samples were taken from several tens of the veinlets, however the original samples for testing were chosen from several relatively thick veinlets (numbers of these samples are 1–7). The rest of the material was blended together, what resulted in a significant volume of uniform and averaged material for the research (sample 8).

Identification of minerals was conducted with the use of:

**a)** X-ray diffraction analysis (XRD) – diffractometer Philips PW 1140 (for the averaged sample and for the original samples mechanically extracted from relatively thick veinlets), conditions of measurements: Cu lamp, Ni filter, field voltage of the lamp 35 kV, current 14 mA, recording $1^{o}$/20mm/1min, angle range $\Theta = 2–40^{o}$;

**b)** standard wet chemical analysis (for the averaged sample);

**c)** differential thermal analysis by use of a derivatograph of the Paulik-Paulik-Erdey system (for the averaged sample); conditions of measurements: TG – 200, DTA – 1/5. DTG – 1/5, T – $1000^{o}$C, atmosphere – air, sample mass 500 mg;

**d)** scanning electron microscope HITACHI S-4200 with cold cathode, combined with X-ray EDS unit by NORAN INSTRUMENTS (for individual grains of the averaged sample), conditions of measurements: voltage – 15 kV, measurement time adjusted individually for each record, quantitative analysis performed with the use of VOYAGER 3500 system.

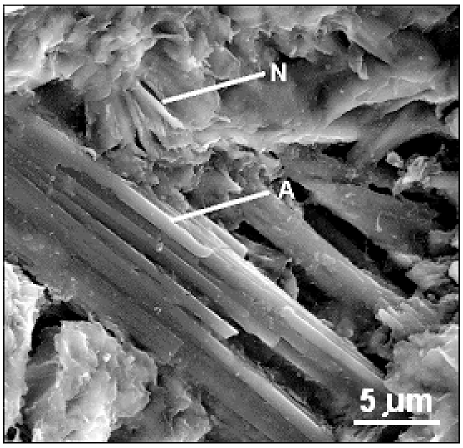
It should be marked that the complete wet-method analysis was performed on the averaged sample. The other samples (numbers 1–5) were studied by the X-ray diffraction for their identification and by use of a scanning electron microscope with the EDS unit to determine their chemical composition.

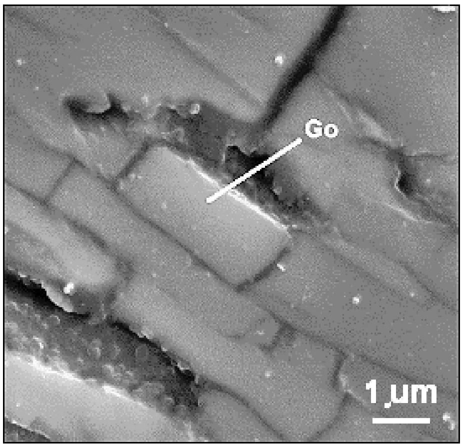
## RESULTS

Scanning microscopy made possible the description of the habits and kinds of aggregates of the examined zeolites, whereas the EDS analysis yielded their chemical composition. Two morphological types of zeolite crystals were found: crystals of prismatic, elongated habits (Figs 2 and 3) and these of platy shapes (Figs 3 and 4). Prismatic zeolites occur in two basic kinds of crystal clusters, in which they are either radial or parallel arranged. The slightly elongated platy crystals with two systems of approximately perpendicular cleavage form sometimes aggregates, in which the crystals are usually parallel to each other.

X-ray diffraction of the averaged sample revealed on diffraction patterns the presence of the reflections characteristic of the following zeolite minerals: gobbinsite, gismondine, thomsonite, phillipsite and natrolite (Fig. 5 and Table 1).

High intensity of the reflections 7.20, 6.56, 3.20 and 2.28 Å as well as the presence of individual lines for gobbinsite and natrolite point to the predominant presence of these two minerals, whereas other zeolite minerals occur in minor amounts. More than ten individual reflections (those with d values: 8.22, 6.45, 5.41, 3.98, 3.94, 3.29, 2.58, 1.8924, 1.5514, 1.5472, 1.3843,



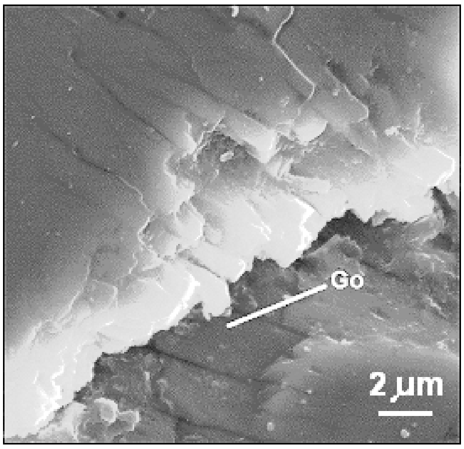




Fig. 2. (*Upper left*) Clusters of prismatic zeolites: *N* – natrolite, *A* – unidentified zeolite; SEM image.

Fig. 3. (*Upper right*) Cluster of elongated platy zeolite: *Go* – gobbinsite; SEM image.

Fig. 4. (*Left*) Clusters of prismatic and platy zeolites: *Go* – gobbinsite; SEM image.

1.3380 and 1.3153 Å) have not been attributed to any of the above listed minerals or to any known mineral, thus they can be related to the presence of a new phase.

Many of the reflections, related to particular zeolites, interfere on diffraction pattern, so additional analyses were performed for the original samples from individual veinlets (Table 1).

These diffraction patterns showed the lines characteristic of the following zeolite minerals: garronite (samples 4 and 5), natrolite and gobbinsite (sample 5), gobbinsite (sample 7) and phillipsite (sample 1). Remarkable are the samples showing monomineral composition of the veinlets built by garronite (sample 4), gobbinsite (sample 7) and phillipsite (sample 1). The material from sample 5, although extracted from an individual veinlet, showed the presence of three zeolite minerals: natrolite, gobbinsite and garronite.

X-ray diffraction analysis of the averaged sample was also performed on the material primarily heated at the temperature of 1000ºC. The diffraction pattern shows the reflections characteristic of nepheline and wollastonite (Table 2)

– the phases, which were formed as a result of decomposition of natrolite and gobbinsite, and recrystallization of the new-formed substance.

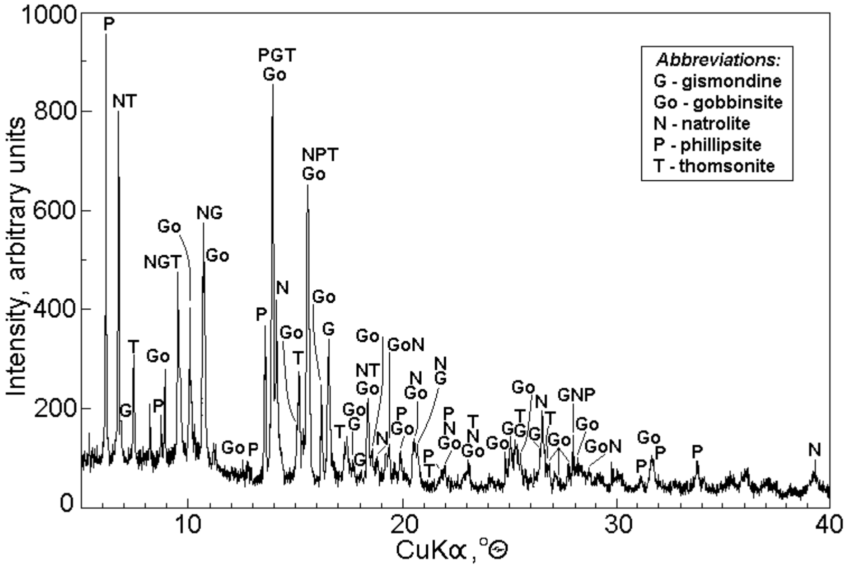



Fig. 5. X-ray powder pattern of the averaged sample of zeolites from Rębiszów

Table 1. X-ray powder patterns of zeolites from Rębiszów

| Sample No. 1 | | | Sample No. 4 | | | Sample No. 5 | | | Sample No. 7 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $d_{hkl}$ | I | Mineral | $d_{hkl}$ | I | Mineral | $d_{hkl}$ | I | Mineral | $d_{hkl}$ | I | Mineral |
| 7.16 | 4 | P | 7.16 | 4 | Ga | 7.15 | 4 | Ga | 7.11 | 8 | Go |
| 4.99 | 3 | P | 4.94 | 3 | Ga | 7.12 | 4 | Go | 4.41 | 4 | Go |
| 4.29 | 3 | P | 4.11 | 8 | Ga | 6.57 | 3 | N | 4.12 | 7 | Go |
| 4.12 | 4 | P | 3.21 | 10 | Ga | 5.90 | 4 | N | 3.20 | 10 | Go |
| 3.28 | 6 | P | 3.13 | 7 | Ga | 5.04 | 3 | Go | 3.10 | 6 | Go |
| 3.19 | 10 | P | 2.69 | 6 | Ga | 4.94 | 3 | Ga | 2.96 | 5 | Go |
| 3.13 | 6 | P | 2.67 | 6 | Ga | 4.65 | 2 | N | 2.70 | 6 | Go |
| 2.92 | 4 | P | 2.13 | 1 | Ga | 4.40 | 5 | Go | 2.20 | 3 | Go |
| 2.90 | 2 | P | 1.770 | 1 | Ga | 4.12 | 5 | Go,Ga | | | |
| 2.75 | 7 | P | | | | 4.09 | 4 | N | | | |
| 2.69 | 8 | P | | | | 4.04 | 3 | Go | | | |
| 2.66 | 5 | P | | | | 3.27 | 4 | N | | | |
| 2.56 | 1 | P | | | | 3.21 | 8 | Ga | | | |
| 2.53 | 1 | P | | | | 3.20 | 10 | N,Go | | | |
| 2.34 | 1 | P | | | | 3.18 | 10 | N,Go | | | |
| 2.24 | 1 | P | | | | 3.12 | 6 | Go,N | | | |
| | | | ***Abbreviations*:** | | | 2.88 | 5 | Ga | | | |
| | | | Ga – garronite | | | 2.85 | 6 | N | | | |
| | | | Go – gobbinsite | | | 2.76 | 3 | Go | | | |
| | | | N – natrolite | | | 2.70 | 4 | Go,Ga | | | |
| | | | P – phillipsite | | | 2.38 | 2 | Go | | | |
| | | | | | | 2.34 | 1 | Ga | | | |

Table 2. X-ray powder patterns of the averaged samples of zeolites from Rębiszów

| Raw sample* | | | Sample heated at 1000°C | | |
|---|---|---|---|---|---|
| $d_{hkl}$ | I | Mineral | $d_{hkl}$ | I | Mineral |
| 8.22 | 1 | | 7.68 | 2 | Wo |
| 7.20 | 10 | P | 4.96 | 2 | Ne |
| 6.56 | 8 | N, T | 4.50 | 3 | Wo |
| 6.45 | 2 | | 4.33 | 6 | Ne |
| 5.96 | 3 | G | 4.29 | 7 | Ne |
| 5.93 | 3 | T | 4.16 | 8 | Ne |
| 5.41 | 2 | | 4.06 | 1 | Wo |
| 5.08 | 2 | P | 3.84 | 9 | Wo |
| 4.98 | 3 | Go | 3.82 | 10 | Ne |
| 4.66 | 5 | N, G,T | 3.32 | 3 | Wo |
| 4.41 | 4 | Go | 3.25 | 7 | Ne |
| 4.16 | 6 | G | 3.22 | 6 | Wo |
| 4.15 | 6 | N | 3.17 | 2 | Ne |
| 4.14 | 5 | Go | 3.16 | 1 | Wo |
| 3.98 | 1 | | 3.04 | 1 | Ne |
| 3.94 | 1 | | 2.99 | 7 | Ne |
| 3.55 | 1 | Go | 2.98 | 10 | Wo |
| 3.48 | 1 | P | 2.87 | 8 | Ne |
| 3.29 | 4 | | 2.79 | 3 | Wo |
| 3.21 | 9 | Go, P | 2.57 | 1 | Ne,Wo |
| 3.19 | 8 | Go, G, T | 2.48 | 2 | Wo |
| 3.16 | 5 | N | 2.44 | 1 | Wo |

*Only selected reflections listed; G – gismondine, Go – gobbinsite, N – natrolite, Ne – nepheline, P – phillipsite, T – thomsonite, Wo – wollastonite.

Chemical analysis of the averaged sample showed unambiguously that apart from such basic components as $SiO_2$, $Al_2O_3$ and $H_2O$, this sample contained also $Na_2O$ in amount exceeding 10 wt % as well as admixtures of CaO, MgO and $K_2O$ (Table 3).

Chemical compositions of the individual crystals extracted from the relatively thick veinlets, determined by the X-ray EDS analysis, are shown in Table 4.

The chemical compositions of the individual crystals differ from the composition of the averaged sample of the zeolite by the absence of MgO and $K_2O$. A conclusion can be hence drawn that the zeolites from Rębiszów basaltoid contain sodium and calcium, however, the admixtures of magnesium and/or potassium occur in minor phases, other than the zeolite minerals. The determined chemical compositions of the zeolites, with cation content calculated on 32 atoms of oxygen show clear similarity, especially the samples Nos 1 – 5, to the composition of gobbinsite from Tertiary basalts of the Northern Ireland. (Nawaz, Malone 1982). The sample No. 6 has different chemical composition than the other five samples analyzed by means of the EDS method. The differences concern the amounts of $SiO_2$, $Al_2O_3$ and $Na_2O$. This suggests the presence of another mineral from the zeolite group. Morphology of its crystals is characteristic of the prismatic type habits of zeolites (Fig. 2).

Chemical analysis of the samples shows also the presence of potassium-containing minerals among the discussed zeolites. This has been confirmed by X-ray diffraction analysis.

Differential thermal analysis of zeolites is important for determination of their sorptive and catalytic properties. The main process recorded by this method is dehydration (Fig. 6).

The analysis was performed only on the averaged zeolite sample. As it appears from Fig. 6, the DTA curve is of complicated shape with distinct endothermic effects visible at 90, 190,

Table 3. Chemical composition of the averaged zeolite sample

| Component | wt % |
|---|---|
| $SiO_2$ | 39.76 |
| $Al_2O_3$ | 27.96 |
| $Fe_2O_3$ | 0.00 |
| CaO | 3.95 |
| MgO | 1.47 |
| $Na_2O$ | 10.36 |
| $K_2O$ | 0.72 |
| $H_2O^-$ | 2.87 |
| $H_2O^+$ | 12.52 |
| Total | 99.61 |

Table 4. Chemical compositions of the zeolites from Rębiszów and reference zeolite analyses, wt %

| Compo-nent | Zeolites from Rębiszów, sample numbers | | | | | | Gobbinsite (Nawaz *et al.* 1982) | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | data from 3 analyses | values without water |
| $SiO_2$ | 57.52 | 56.39 | 55.46 | 55.25 | 54.50 | 63.89 | 52.17 – 49.21 | 57.26 – 61.81 |
| $Al_2O_3$ | 27.27 | 27.84 | 28.27 | 29.64 | 30.04 | 26.97 | 23.64 – 20.52 | 24.31 – 27.51 |
| MgO | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 – 1.00 | 0.00 – 1.16 |
| CaO | 0.00 | 1.44 | 2.19 | 2.23 | 3.82 | 3.43 | 0.66 – 1.58 | 0.78 – 1.84 |
| $Na_2O$ | 15.21 | 14.33 | 14.08 | 12.88 | 11.64 | 5.71 | 9.85 – 10.71 | 11.46 – 12.69 |
| $K_2O$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 – 0.98 | 0.00 – 1.16 |
| $H_2O$ | – | – | – | – | – | – | 13.55 – 15.29 | – |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | | |
| Si | 10.3 | 10.1 | 10.0 | 9.9 | 9.8 | 11.1 | | 10 |
| Al | 5.7 | 5.9 | 6.0 | 6.3 | 6.4 | 5.5 | | 6 |
| Ca | 0.0 | 0.3 | 0.4 | 0.4 | 0.7 | 0.6 | | 1 |
| Na | 5.3 | 5.0 | 4.9 | 4.5 | 4.1 | 1.9 | | 4 |
| O | 32.0 | 32.0 | 32.0 | 32.0 | 32.0 | 32.0 | | 32.0 |

*Note*: the analyses recalculated to 100% by weight (without water).

370, 590, 790 and 870°C as well as exothermic effect at 970°C. Complexity of this curve results from polymineral composition of the sample, since it consists of a mixture of five zeolite minerals (indicated by X-ray analyses). Nevertheless, thermal curves point to predominant presence of gobbinsite and natrolite in the examined material.

The first thermic effect at the temperature of 90°C is related to the loss of moisture by the sample. The endothermic effect at 370°C is characteristic of natrolite due to its dehydration. It can be presumed that the remaining effects (190, 590, 790 and 870°C) are related to the presence of gobbinsite. It is commonly known (*cf. e.g.* Ciciszwili *et al.* 1990) that the thermic resistance of zeolites increases with:

**a)** increasing Si/Al ratio (for gobbinsite the ratio is low – 1.66),

**b)** increasing content of $K^+$ ions (there are mainly $Na^+$, $Ca^{2+}$ ions in gobbinsite, sporadically $K^+$),

**c)** increasing pore size in minerals (gobbinsite is the narrow-porous one).

The above characteristics indicate that the number and temperature of thermic effects distinguished on the DTA curve of the averaged zeolite sample point to the predominant presence of thermally low-resistant zeolite – gobbinsite.

Exothermic effect observed at the temperature of 970°C is related to crystallization of the new phases identified by X-ray diffraction as nepheline and wollastonite. It seems that the ascertained presence of wollastonite additionally evidences the primary presence of gobbinsite since the latter mineral contains calcium, which is necessary for formation of wollastonite.

Interesting conclusions can be drawn from the percentage balance of water amount related to dehydration of the sample. Total loss of water by natrolite

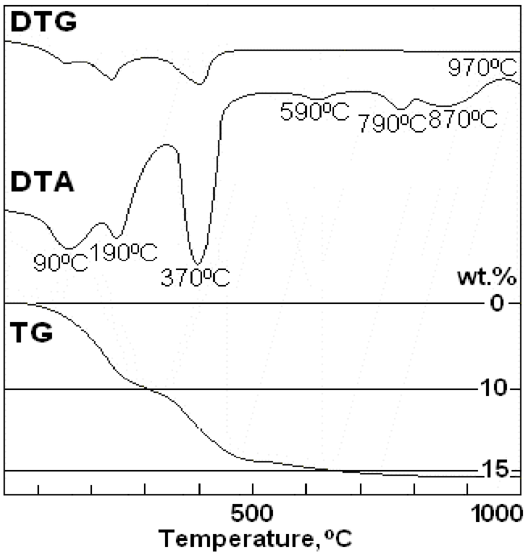



Fig. 6. Thermogramme of the averaged zeolite sample from Rębiszów

occurs at approximately 370°C, and the loss in mass due to this effect, according to theoretical calculations, should be approximately 9.50 wt %. In case of the averaged zeolite sample from Rębiszów, the loss of mass related to this effect was 4.80%; it can be hence concluded that natrolite content in the sample equals to 50%, the remaining 50% is gobbinsite. Total loss of mass referring to dehydration of gobbinsite at the temperature of 190°C would amount then about 4.60%. From comparison, in turn, of losses of masses related to moisture content (thermic effect at 90°C), which may be equal to about 2.00% in pure natrolite and was found to be 2.80% in the examined sample, it can be stated that the presence of gobbinsite within this mineral sample increases its hygroscopic properties.

## DISCUSSION

The zeolite minerals occurring in the veinlets in Tertiary basaltoid rock from Rębiszów are present in forms of prismatic crystals or columnar and platy crystals. Prismatic zeolites occur in two basic forms of crystal clusters which are either radial or parallel. The columnar and platy crystals are usually parallel to each other, forming compact aggregates; these crystals sometimes show two perpendicular planes of cleavage.

The following minerals have been distinguished among zeolites: gobbinsite, natrolite, gismondine, garronite, thomsonite and phillipsite. Predominant role is played by zeolites containing mainly sodium and calcium.

The following formulae of gobbinsite have been given in the published references:

$Na_4(Ca,Mg,K)Al_6Si_{10}0_{32} \cdot 12H_2O$ (Ciciszwili *et al.* 1990)

$Na_4CaAl_6Si_{10}O_{32} \cdot 12H_2O$ (Nawaz, Malone 1982)

$(Ca_{0,6}Na_{2,6}K_{2,2})(Si_{10}A_{l6}0_{32}) \cdot 12H_2O$ (McCusker *et al.* 1985)

$Na_5[Al_5Si_{11}O_{32}] \cdot 11H_2O$ (Bolewski, Manecki 1993)

$Na_4(Ca,Mg,K_2)[Al_6Si_{10}O_{32}] \cdot 12H_2O$ (Gaines *et al.* 1997).

Content of water, calculated from the above formulae, ranges between 15.61 and 16.12 wt %, with tendency to be higher for potassium-containing gobbinsite varieties. After consideration of the content of water in natrolite as well as the estimated contents of natrolite and gobbinsite in the averaged zeolite sample from Rębiszów, the total theoretical content of water in this sample should amount 12.45 to 12.70 wt %. The latter values are almost identical with the total loss of mass recorded on the TG curve for the averaged sample (15.40 wt %, including 2.80 % wt moisture). It seems from these considerations that the proportion of both minerals in the sample is approximately 1: 1.

For the first time gobbinsite, zeolite occurring very rarely in nature, has been recognized in basaltoids from Lower Silesia. On the basis of the determined chemical composition, the formula of gobbinsite has been established (recalculated to 32 atoms of oxygen) as follows:

$$Na_{5,3\text{-}4,1}Ca_{0,0\text{-}0,9}[Al_{5,7\text{-}6,3}Si_{10,1\text{-}9,8}O_{32}] \cdot nH_2O.$$

Simultaneously, the following probable formula has been proposed for the new phase, belonging to zeolite group and occurring together with other zeolites:

$$Na_{1,9}Ca_{0,6}[Al_{11,1}Si_{5,5}O_{32}] \cdot nH_2O.$$

It can be presumed that the non-interpreted reflections of the X-ray diffraction pattern for the averaged zeolite sample (reflections 8.22, 6.45, 5.41, 3.98, 3.94, 3.29, 2.58, 1.8924, 1.5514, 1.5472, 1.3843, 1.3380 and 1.3153 Å) may origin from this new phase, occurring in the habit of thin-prismatic crystals.

Origin of the whole paragenesis of zeolite minerals can be related to hydrothermal activity of post-magmatic solutions within thermal contraction cracks of congealing basaltoid lava.

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