Properties and Application of Georgian Natural Phillipsite

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Abstract

Oceanic and terrestrial sedimentary phillipsites make up very large reserves, but the use of this natural zeolite is not so wide comparing to clinoptilolite, and purpose of our study was to characterize the phillipsites of the Georgian deposits and highlight their possible application. It is shown that natural phillipsite can be used as a raw material for the synthesis of phase-pure zeolite NaX with Si/Al~1.5-1.7 in the form of octahedral crystallites with uniform micrometric (2-7 µm) dimensions, characterized by high specific surface area (590-770 m²/g) and volume of pores (0.58 cm³/g) including uniform zeolitic micropores and channels with an average diameter of 55 nm, which opens up the prospect of its use in catalysis. It has been established that natural phillipsite is a suitable carrier of bioactive metals: silver-, copper-, and zinc-containing micro-mesoporous materials have been prepared using ion-exchange reactions between zeolite and a salt of a transition metal; the products contain up to 235 mg/g of silver, 85 mg/g of copper, and 87 mg/g of zinc, and in the Kirby-Bauer disk-diffusion test show strong bacteriostatic activity against such microorganisms as gram-negative bacterium Escherichia coli, gram-positive bacteria Staphylococcus aureus and Bacillus subtilis, fungal pathogenic yeast Candida albicans and a fungus Aspergilus niger. The use of bactericidal materials obtained on the basis of natural phillipsite is possible both for water purification and disinfection, and as fillers in the production of polymeric materials, paper and cardboard.

Keywords: properties, application, natural phillipsite, georgia

Introduction

The objectives of the work included a brief description of the chemical composition, structure and properties of Georgian natural phillipsite, as well as to show new possibilities for its application, based on the results of studying samples of this zeolite from two local deposits.

Phillipsite was first recognized in the mid-1870s during the expedition of the H.M.S. Challenger [1]. The content of phillipsite in siliceous sediments of the southeastern Pacific Ocean and in some areas of the Indian Ocean ranges from 3 to 12%, while in calcareous sediments phillipsite can be up to 50% [1]. Chemical analyzes of different samples show that oceanic phillipsites have Si/Al=2.3-2.8, while terrestrial hydrothermal phillipsites are low-silica (Si/Al=1.3-2.4) and phillipsites from sediments of saline alkali lakes are high-silica (Si/Al=2.6-3.4) [2]. The cationic composition of phillipsite varies over rather wide ranges, but it is one of the few zeolites in which potassium may be the most abundant exchangeable cation [3].

Phillipsite belongs to the PHI type (crystal chemical data $|K_2 (Ca, Na_2)_2 (H_2O)_{12}| [Al_6Si_{10}O_{32}]$-**PHI**, [4] and is structurally built up by layers of four- and eight-member rings forming double crankshaft chains, the framework contains three systems of channels parallel to a, b and c: [100] **8** 3.8 x 3.8* ↔ [010] **8** 3.0 x 4.3* ↔ [001] **8** 3.2 x 3.3*.

The field of application of phillipsite is not as wide as that of clinoptilolite, but phillipsite was used for ammonia adsorption [5], in removal of heavy metals [6] and other contaminants [7,8] from waste waters, and interest in faujasite-phillipsite and phillipsite-chabazite rocks has recently increased [9,10].

Phillipsite-containing Eocene rocks were discovered in Georgia firstly at the northern fringe of the Akhaltsikhe depression, along with other zeolites, and then, in the early 1970s, in the Gurian range. Chemical composition and properties of phillipsite samples from sites discovered in 1990s were described earlier [11], but research continued, and a more complete characterization of the natural phillipsites of the Georgian deposits was presented [12]. The purpose of our contribution is to give additional information and highlight the results of our research on their possible application.

Materials and Methods

Phillipsite samples were collected at the lower Tsinubani plot of the Akhaltsikhe deposit, the zeolite phase content in them is up to 70%, major impurities are chlorite and montmorillonite [12], chemical composition is described by empirical formula $(Na_{1.4}K_{0.7}Ca_{0.7}Mg_{0.35})Me_{0.10}[Al_{4.3}Si_{11.7}O_{32}]\cdot 11.2H_2O$, $Me^+ = {}^1/_3Fe^{3+}$, $\frac{1}{2}Cu^{2+}$, $\frac{1}{2}Mn^{2+}$, etc. The yellow-green rock from the upper plot of the Shukhuti manifestation is an aggregation of micrometric crystallites with an average size of about 5 μm bound together by clay minerals, zeolite phase content is up to 80%, main impurity is heulandite [12], chemical composition corresponds to formula $(Na_{1.30}K_{2.0}Ca_{0.30}Mg_{0.25})Me_{0.10}[Al_{4.50}Si_{11.50}O_{32}]\cdot 11.4H_2O$, $Me^+ = {}^1/_3Fe^{3+}$, $\frac{1}{2}Cu^{2+}$, $\frac{1}{2}Zn^{2+}$, etc.

Processing of raw in target material

Phillipsite-containing rock was crushed in the planetary micro mill Pulverisette 7 (Fritsch Laboratory Instruments, Idar-Oberstein, Germany) to a size less than 0.063 mm (250 BSS mesh). Phillipsite powder was suspended in Teflon flack placed in shaking water bath OLS 26 Aqua Pro (Grant Instruments, Cambridge, UK) controlling temperature at 90-95℃; suspension was processed with a 12% hydrochloric acid solution at the rate of 5 mL per gram of the solid raw material; activated suspension was diluted with water and treated by adding of a 25% sodium hydroxide solution, followed by the formation of a homogeneous gel. The molar ratio of components optimal for obtaining zeolite X from phillipsite is $2.9Na_2O : 0.26Al_2O_3 : SiO_2 : 150H_2O$, duration of the gel aging at room temperature was 96 hours, crystallization in temperature-controlled water bath adjusted to prepare micrometric single crystals lasted up to 55 hours. Beginning of crystallization after 16 hours was detected by sampling and X-ray diffraction analyses. Separation of produced crystalline material was carried out by filtration of mother solution, solid material was cleaned by distilled water until pH 8.0-8.5, and dried at 90-100 ℃.

Ion exchange reactions

Ion exchange reactions on crushed and sieved phillipsite-containing rock were carried out in 1N solutions of silver nitrate, copper and zinc chlorides at a solid : liquid ratio of 1 : 10 at room temperature with stirring for 6 hours; the prepared samples were dried at 100-110 °C. Analytical grade silver (I) nitrate $AgNO_3$, copper (II) chloride dihydrate $CuCl_2\cdot 2H_2O$, and zinc (II) chloride $ZnCl_2$ were purchased from Merck KGaA (Darmstadt, Germany) and used without any further purification.

Instrumentation

Chemical composition of samples was calculated from the X-ray energy dispersive (XRED) spectra obtained from high performance scanning electron microscope JSM6510LV (Jeol, Japan) equipped with X-Max 20 analyzer (Oxford Instruments, UK). The crystalline phase was identified by powder X-ray diffraction (XRD) patterns obtained from a Dron-4 X-ray diffractometer (Russia) employing the Cu-K$_\alpha$ line (λ = 0.154056 nm), scanning in the 2Θ range of 5° to 50° with a speed of 1°/min. Fourier transform infrared spectra (FTIR) were collected by a 10.4.2 FTIR spectrometer (Perkin-Elmer, UK) over the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1} using the KBr pellet technique for sample preparation. Nitrogen adsorption-desorption isotherms were measured at 77 K using an ASAP 2020 Plus analyzer (Micromeritics, Norcross, GA, USA), after evacuation of the samples at 350℃ during 2 hours; water adsorption capacity was measured under static conditions.

Bacteriostatic activity test

Bacteriostatic properties of zeolite samples were determined by the disk diffusion (Kirby-Bauer) method using the cultures of gram-negative bacterium *Escherichia coli* (strain ATTC 8739), gram-positive bacteria *Staphylococcus aureus* (ATTC 6538) and *Bacillus subtilis* (ATTC 6633), fungal pathogenic yeast *Candida albicans* (ATTC 10231) and a fungus *Aspergilus niger* (ATTC 16404 – *A. brasiliensis*) placed (10^9 CFU/ cm^3) on Mueller–Hinton agar (3 mm deep) poured into 100 mm Petri dishes. Before testing the antibacterial activity, all dry zeolite products were sterilized at 70 °C for 2 hours in a dry sterilizer. No microbial contamination of the prepared samples was found. 0.2 g of zeolite in the form of pellets with 8 mm in diameter was placed into the plates. The plates contaminated with *E. coli*, *St. aureus* and *B. subtilis* were incubated at 37 °C over 5% CO$_2$ medium and the width of inhibition zone of each sample in the plates was measured at the end of the first day, while the plates contaminated with *C. albicans* and *A. niger* were incubated at 25 ℃ during 3-4 days. All experiments were done in triplicate, the values obtained were averaged to give the final data with standard deviations.

Results And Discussions

Hydrothermal transformation of the sodium-rich phillipsite from the Akhaltsikhe field was described previously [13], here are the new results obtained using the rich in potassium and having a higher content of the zeolite phase phillipsite from Shukhuti (PS). Preparation, chemical characterization and bacteriostatic activity against *Escherichia coli* of silver-, copper-, and zinc-containing phillipsites obtained by "solid-state" ion-exchange reactions is described in [14], here are the new results on metal-containing phillipsites obtained by conventional "liquid" reactions and on their bacteriostatic activity against a wider range of microorganisms.

Zeolite X recrystallized from phillipsite

The technique and conditions of rock processing, gel preparation, its aging, hydrothermal crystallization and product separation are the same, as for phillipsite from Akhaltsikhe, some differences are in the chemical composition and structure of the product recrystallized from the Shukhuti sample PS.

Chemical composition, XRD and FTIR

According to the data of the XRED spectrum, counted on total 192 T-atoms and 384 oxygen atoms in the unit cell, the empirical formula of the phillipsite recrystallization product is $|Na_{62(5)}K_{6(1)}Me_{2(0.5)}(H_2O)_{240(10)}|[Al_{70(5)}Si_{122(7)}O_{384}]$ ($Me^+ = \frac{1}{2}Ca^{2+}$, $\frac{1}{2}Mg^{2+}$, trace amounts of $\frac{1}{2}Cu^{2+}$, $\frac{1}{3}Fe^{3+}$. and $\frac{1}{2}Zn^{2+}$). In contrast with the almost monocationic zeolite NaX obtained from Akhaltsikhe phillipsite, the product contains a small amount of potassium, which is due to the high content of this metal in the initial mineral raw material. The molar ratio of silicon and aluminum Si/Al=1.74 is higher than in previously obtained zeolite (Si/Al=1.46) and closer to the value according to the crystal chemical data (Si/Al=2.31 [4]). Comparison of the recorded XRD pattern with the simulated one for the hydrated zeolite NaX [15] showed their complete coincidence (Fig. 1), which made it possible to unambiguously assign the peaks and confirm the receipt of the target zeolite of the FAU type.

The mid infrared peak pattern in FTIR spectrum testifies formation of zeolite structure: the bands of (i) the internal deformation vibration modes of T-O-T bridges (462 cm^{-1}), (ii) asymmetric external vibration of double 4-rings (562 cm^{-1}), (iii) internal vibration of T-O symmetric stretching (668 cm^{-1}), (iv) valence T–O–T vibrations (752 cm^{-1}), (v) internal vibration of T-O asymmetric stretching (976 cm^{-1}) are observed as well as bands at ~1650 and ~3470 cm^{-1} corresponding to the presence of water and hydroxyls, respectively. The observed FTIR bands are in good agreement with those reported [16], further proving the successful synthesis of zeolite X from the Shukhuti phillipsite.

Sorption properties and porous structure

The adsorption of water vapor at a relative pressure p/p$_o$=0.4 is ≈16 mmol/g, and such a high value indicates the presence of a developed system of micropores in the recrystallization product. The N$_2$ adsorption-desorption plot at 77 K for the obtained zeolite (Fig. 2) up to relative pressure p/p$_o$~0.9 corresponds to typical Langmuir isotherm attributed to the filling of micropores. The adsorption isotherm is perfectly described by the Brunauer-Emmet-Teller (BET) equation at relative pressures up to p/p$_o$=0.35. The specific surface area calculated from the BET equation is 780 m^2/g, which is larger than the surface area of zeolite NaX obtained by recrystallization of Akhaltsikhe phillipsite (590 m^2/g [13]), but the total pore volume (0.578 cm^3/g) and the volume of micropores with a diameter of less than 0.8 nm (0.3 cm^3/g) for both samples coincide within the measurement and calculation errors. At high relative pressures (0.92<p/p$_o$<0.99), a narrow hysteresis loop is observed, corresponding to the filling of well-defined cylindrical channels [17]. Pore size distribution curve (Fig. 2) calculated from desorption isotherm by the Barrett-Joyner-Halenda method shows average channel diameter of 53 nm (55 nm in [13]); the specific volume of the channels is 0.28 cm^3/g, approximately half of the total adsorption capacity of the zeolite.
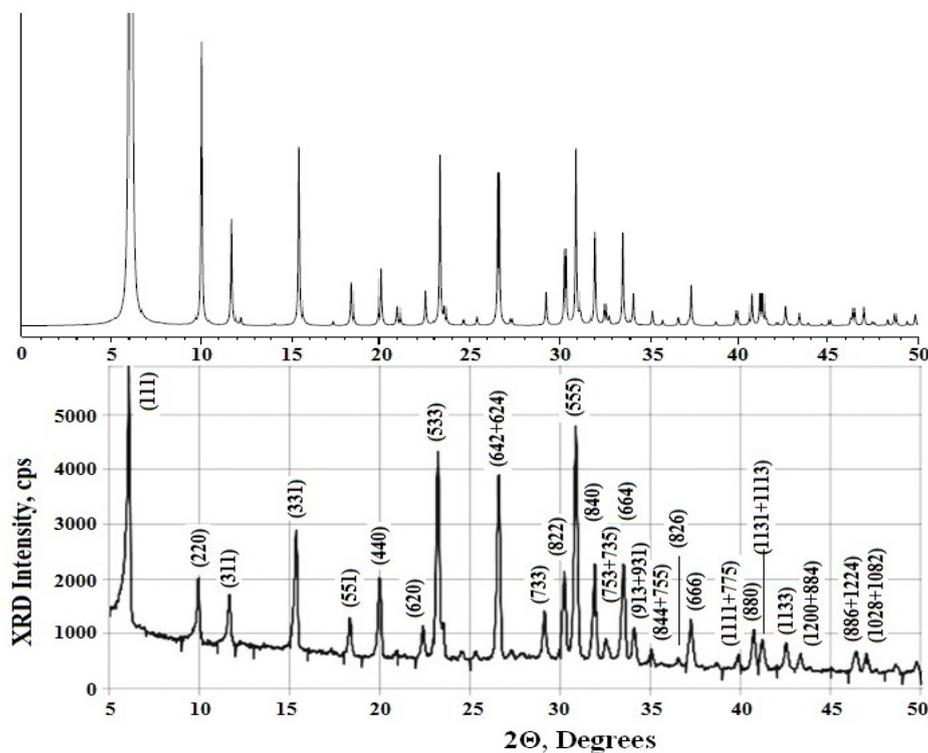

Fig. 1. Comparison of powder XRD pattern of the phillipsite recrystallization product with simulated pattern; numbers in parenthesis are Miller indices *hkl*.
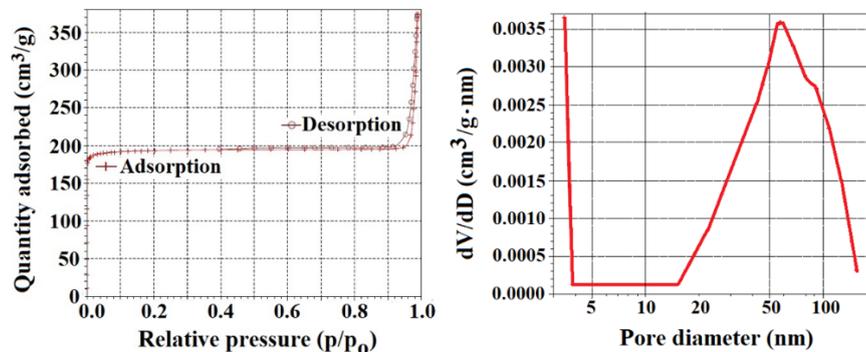

FIG. 2. N$_2$ adsorption-desorption isotherms (left) and pore size distribution dV/dD curves (right) of the phillipsite recrystallization product.

Morphology

More than 95% of NaX crystallites obtained by recrystallization of Akhaltsikhe phillipsite are octahedral and have sizes within 2 – 7 μm (Fig. 3a [13]), crystallites obtained from Shukhuti phillipsite have the same habit and sizes within 3 – 6 μm (Fig. 3b). In both cases, a small amount (<2-3wt.%) of spherical or ellipsoidal nano (0.1 – 0.25 μm) crystallites is also formed during crystallization.

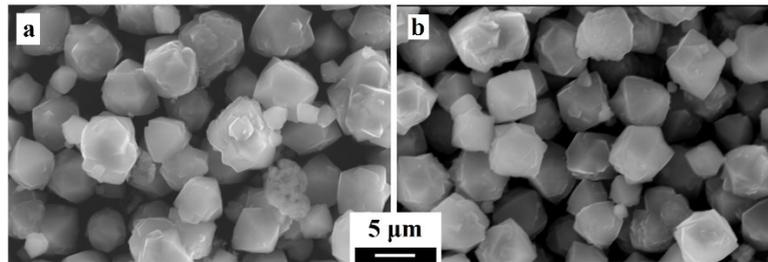FIG. 3. SEM images of the Akhaltsikhe (**a**) and Shukhuti (**b**) phillipsites recrystallization products.

Metal-containing phillipsites

Silver-, copper-, and zinc-containing phillipsites obtained by liquid ion exchange reaction are characterized by XRED spectra, powder XRD patterns, FTIR spectra and nitrogen adsorption-desorption isotherms; their bacteriostatic activity is tested by the Kirby-Bauer dick diffusion method.

Chemical composition

Chemical composition of ion-exchanged Shukhuti phillipsites with a maximum silver, copper or zinc content is given in Tab. 1 in terms of the empirical formulas, where Me^+ ion corresponds to the remaining impurity of iron and other metals, for example, copper and zinc in silver-rich phillipsite AgPS.

There is no significant difference between the chemical composition of the samples obtained by the "solid" or "liquid" method: introduction of silver, copper, and zinc ions are into the framework of phillipsite does not change the Si/Al molar ratio, the number of water molecules in the crystal lattice increases, the degree of substitution (the contribution of introduced transition metal ions to compensate for the negative charge on the aluminum atoms) is remained at the level of 80%, the specific content of silver and zinc can be considered unchanged within the measurement and calculation error (230 and 235 mg/g for silver, 86 and 87 mg/g for zinc), but the copper content increases from 66 to 85 mg/g.

Tab. 1. Chemical composition, degree of substitution and metal content of ion-exchanged samples.

	Empirical formula	Degree of substitution (%)	Metal content	
			mg/g	mmol/g
AgPS	$Ag_{3.5}(Na_{0.01}K_{0.07}Ca_{0.25}Mg_{0.20})Me_{0.02}[Al_{4.5}Si_{11.5}O_{32}]\cdot14.2H_2O$	78±2	235±7	2.18±0.07
CuPS	$Cu_{1.8}(Na_{0.14}K_{0.12}Ca_{0.20}Mg_{0.12})Me_{0.02}[Al_{4.5}Si_{11.5}O_{32}]\cdot14.3H_2O$	80±2	85±0.3	1.33±0.04
ZnPS	$Zn_{1.8}(Na_{0.12}K_{0.14}Ca_{0.17}Mg_{0.15})Me_{0.02}[Al_{4.5}Si_{11.5}O_{32}]\cdot14.6H_2O$	80±2	87±0.3	1.33±0.04

Structure

On the powder XRD patterns of the ion-exchanged samples, the most pronounced phillipsite peaks (see Fig. 4) are preserved, only their intensities change, as shown in Tab. 2.

Tab. 2. Miller indices, 2Θ angles and relative intensities (%) of the most pronounced peaks in powder XRD patterns of natural PS and ion-exchanged phillipsites.

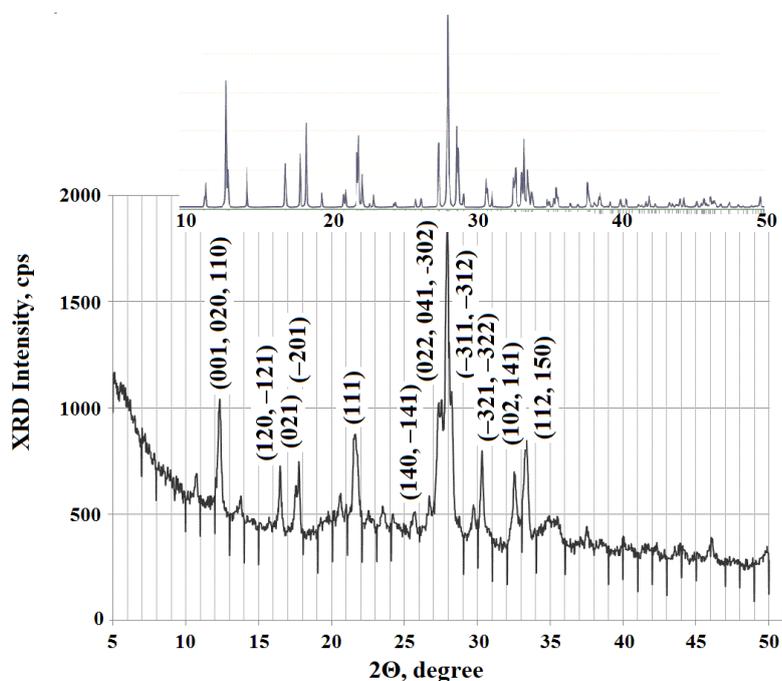| Hkl	2Θ (º)	Natural PS	AgPS	CuPS	ZnPS
001, 020, 110	12.4	56	52	50	61
120, −121	16.5	37	35	41	38
021	17.5	29	25	23	27
−201	18.0	40	41	36	39
111	21.5	45	44	47	46
140, −141	27.3	52	53	57	50
022, 041, -302	27.9	100	100	100	100
−311, −312	28.5	53	48	56	50
−321, −322	30.2	32	32	30	28
102, 141	32.4	30	33	35	33
112, 150	33.1	40	36	37	38

Fig. 4. Powder XRD pattern of PS with Miller indices of the most pronounced peaks compared with simulated pattern of phillipsite $|K_2Ca_{1.648}(H_2O)_{12}||Si_{10.7}Al_{5.3}O_{32}|$ from [15].

No noTab. changes were observed in the FTIR spectra of the modified phillipsites as compared with the vibration bands of raw zeolitic mineral (Tab. 5), only the maximum of broad peak at 1520 cm^{-1} corresponding to the bending vibration of bridging –OH-O– groups shifts to lower frequencies (1450 cm^{-1} for CuPS), and the intensity of the broad band at 3200 – 3700 cm^{-1} corresponding to the asymmetric stretching of OH group is slightly increased due to the larger number of water molecules in the samples containing silver, copper, and zinc.

Adsorption and porosity

Small water molecules with a kinetic diameter of 0.266 nm freely pass through all three entrance windows into the phillipsite channels, and the adsorption of water vapor at a relative pressure $p/p_o=0.4$ is a measure of the free volume of micropores, and adsorption at a pressure of saturated water vapor ($p/p_o \approx 1$) is a measure of the total pore volume. According to the measurement results (Tab. 3), the adsorption capacity of micropores for water vapor decreases when biometal ions are introduced into the zeolite cages, and this is apparently due to an increase in the number of water molecules in the crystal framework that reduce the free volume. In the original phillipsite, the free volume of micropores is 46% of the total pore volume; with the introduction of metals, especially silver, this ratio decreases.

TAB. 3. Water vapor adsorption capacity (cm^3/g) in phillipsites.

	Natural PS	AgPS	CuPS	ZnPS
Adsorption in micropores	0.130±0.06	0.100±0.05	0.120±0.008	0.118±0.06
Adsorption in all pores	0.285±0.015	0.282±0.012	0.286±0.018	0.290±0.015

The low-temperature N_2 adsorption-desorption isotherms on natural phillipsite (Fig. 5) and its modified forms demonstrate a hysteresis loop with a jump at $p/p_o= 0.4-0.5$ indicating the presence of mesopores including disordered pores and slit-shaped pores in non-rigid aggregates of particles (H_2 and H_3 type hysteresis loops, respectively [17]).
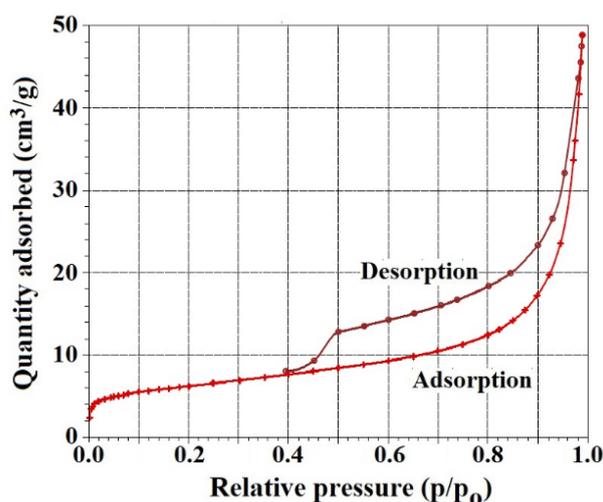
Fig. 5. N$_2$ adsorption-desorption isotherms of natural phillipsite.

The BET model equation well describes the adsorption isotherm only up to a relative pressure $p/p_o < 0.2$, the calculated values of the specific surface area and micropore volume are small (Tab. 4). Thus, the volume of micropores available for nitrogen molecules in the original phillipsite is only 18%, and for ion-exchange forms 12.5–13.6% of the total pore volume, which is much lower than the volume of micropores available for water molecules. Apparently, this is due to the fact that the kinetic diameter of a nitrogen molecule N$_2$ (0.364 nm) is comparable to the size of only one entrance window (8-membered ring 0.38 x 0.38 nm [4]) into the phillipsite cages and channels.

Tab. 4. Porosity parameters according to N$_2$ adsorption-desorption isotherms on phillipsites.

	Natural PS	AgPS	CuPS	ZnPS
BET surface area (m^2/g)	22.3	20.0	26.7	24.2
Total volume of pores (cm^3/g)	0.0755	0.0779	0.1115	0.0970
Volume of micropores (cm^3/g)	0.0139	0.0106	0.0139	0.0128
BJH adsorption/desorption average	16.7	19.0	21.8	19.8
pore diameter (nm)	10.8	12.7	11.4	12.8

A slight decrease in the surface area of the silver-containing sample, as well as an increase in the surface area of the copper- and zinc-containing phillipsites, may be related to the radius and charge of these metal ions replacing potassium and sodium. The pore size distribution dV/dD curves (Fig. 6) show that the main volume of mesopores falls on pores with a diameter of 2-3 nm, ion-exchange reactions lead to a change in the distribution in the region of 10-30 nm, which also follows the pore diameters calculated by the BJH method (Tab. 4).
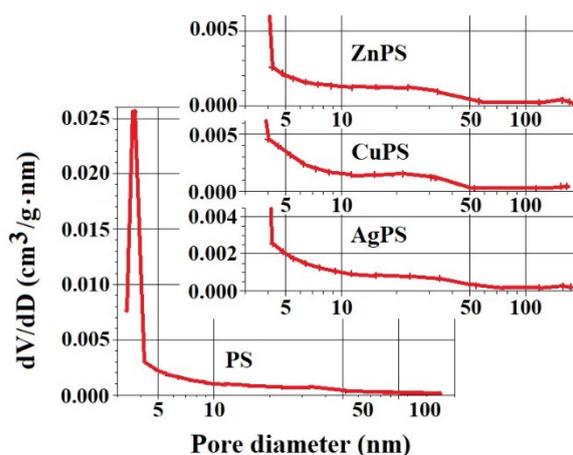

Fig. 6. Pore size distribution dV/dD curves of phillipsite PS and its ion-exchanged forms.

Bacteriostatic activity
Results of the Kirby-Bauer test are given in the Tab. 5. No antibacterial action was observed for the original phillipsite. Despite the differences in the diameters of the zones of *Escherichia coli* growth inhibition under the action of metal-containing phillipsites obtained by different methods, activity in the AgPS>ZnPS>CuPS series is preserved. As for gram-positive bacteria, the copper form is most active, the zinc form is inactive against staphylococcus, but very active against hay bacillus. The copper form does not affect

the growth of fungal microorganisms, and the zinc form inhibits the growth of *Aspergillus niger* even slightly more than the silver form.

Tab. 5. Diameter (mm) of the zone of inhibition of the growth of microorganisms by the original and modified phillipsites.

	PS	AgPS	CuPS	ZnPS
Escherichia coli	0	20±0.7	11±0.7	15±0.7
Staphylococcus aureus	0	19±0.7	20±0.7	0
Bacillus subtilis	0	16±0.7	23±0.7	22±0.7
Candida albicans	0	29±0.7	0	18±0.7
Aspergillus niger	0	27±0.7	0	28±0.7

Conclusions

Natural phillipsites can be used to obtain valuable zeolite products – their hydrothermal recrystallization results in phase-pure zeolites of the FAU type with Si/Al~1.5, characterized by high specific surface area (up to 770 m^2/g) and volume of pores (0.578 cm^3/g) including uniform zeolitic micropores and cylindrical channels with an average diameter of ≈50 nm, which opens up the prospect of its use in catalysis. Natural phillipsites are good carriers of bioactive metals – with the help of ion exchange reactions, a rather high amount of silver, copper and zinc can be introduced into them, and the resulting forms have high bacteriostatic activity against bacteria and fungal microorganisms, so their use is possible both for water purification and disinfection, and as fillers in the production of polymeric materials, paper and cardboard.

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