

## Hydrothermal Alterations and Petrophysical Properties: A Case Study of Yagodninskoe Zeolite Deposit, Kamchatka Peninsula

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### ABSTRACT

The paper describes the secondary alteration and petrophysical properties of the host rocks in Yagodninskoe zeolite deposit (Kamchatka Peninsula). The deposit has hydrothermal origin where vitric tuffs and perlites have been transformed to zeolite-bearing rocks. Intensity of zeolitization varies from moderate to almost totally altered rocks where glassy matrix is totally recrystallized to fine-grained zeolitic aggregate. Clinoptilolite and mordenite are the most abundant among zeolites; smectites and silica minerals are also presented in secondary mineral assemblage. The relationship between petrophysical properties of the rocks and petrographic features such as composition, structure and secondary alteration were studied. The special attention is given to intensity of hydrothermal alterations and their influence on the rock properties.

### 1. INTRODUCTION

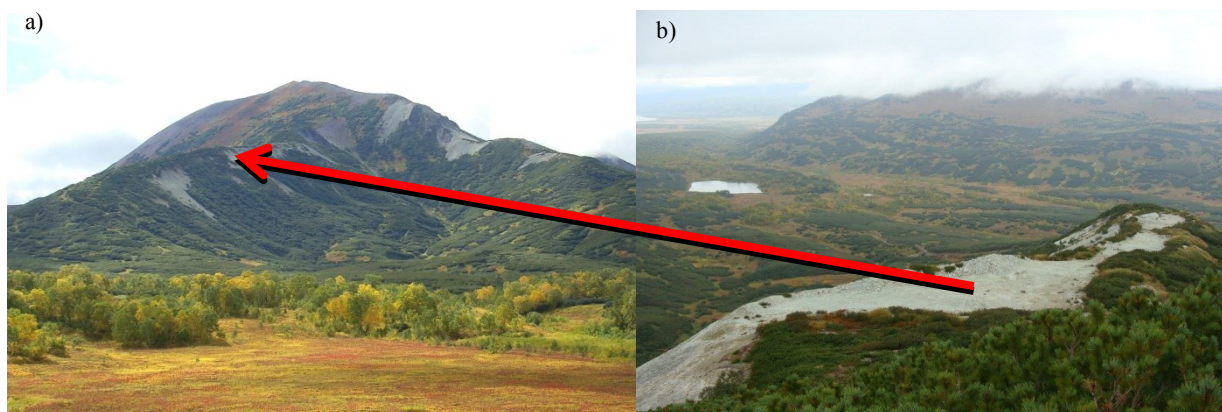
The study of natural zeolites and their deposits are of great interest in science and technology and remain relevant nowadays due to the special properties of these minerals and their wide usage in various sectors of the industry. Yagodninskoe deposit is a large deposit of natural zeolite, which has been prospected in Kamchatka Peninsula. It attracts many researchers due to the propagation of contrasted rock compositions, wide occurrence of ignimbrites and rhyolite tuffs, formation of large calderas, and dome-ring structures. A detailed study of the deposit area is important for better understanding of the evolution of magmatism, volcanic and hydrothermal activity in the area of Banno-Karymshinkii district.

The main target of the presented research is to study alteration of volcanic rocks, to identify types and morphology of zeolites, to determine petrophysical properties of the host rocks and to assess the effect of hydrothermal alteration on rock properties. The samples were collected in 2011-2012 by the staff of Institute of Volcanology and Seismology during the field work. Forty samples of various alteration degree were selected from outcrops for laboratory studies.

### 2. GEOLOGICAL SETTING

Yagodninskoe deposit of zeolite materials and perlites is confined to an extrusive-subvolcanic complex (elevation 1081m, fig.1a) of Miocene-Pleistocene age and has the same name with the ore-forming hydrothermal-magmatic system. Several large lava flows and relatively small extrusive domes are identified within the deposit area. The central parts of flows are composed of fluidal rhyolite, while the edges consist of volcanic glass. Crater phase of extrusion and edge zones of short flows are composed of spherulitic and dark green perlite, which is intruded by dikes of Quaternary basalts (Nasedkin, 1988).

The studied zeolite-bearing productive stratum was formed under the intense heating of perlites and tuffs in the upper part of the hydrothermal system (fig.1b). More than 100 m thick stratum of vitro-lithoclastic tuffs contains clinoptilolite, mordenite, and other high-silica zeolites comprising up to 80-90% of the rock volume.



**Figure 1: The elevation of 1081m (a) and Yagodninskoe zeolite deposit (escarpment is approx. 750m high) (b)**

### 3. ANALYSIS AND TESTING METHODOLOGY

About 40 samples have been collected, studied and processed. The samples were obtained from natural outcrops. In the laboratory, each sample was separated into several specimens (from 1 to 10) for physical and mechanical measurements. Specimens had

cylindrical shape with a length-to-diameter ratio from 1:1 to 2:1. Several tests were carried out for each property and the mean values were obtained representing the sample.

The measurements were made in accordance to the standard testing procedures (Trophimov & Korolev, 1993), which is similar to the International Society for Rock Mechanics standards (ISRM, 2007). Physical properties include bulk density ( $\rho$ ), grain density ( $\rho_s$ ), open (no) and total (n) porosity, gas permeability, hygroscopic moisture (Wg), water absorption (W), velocity of ultrasonic P- and S-waves ( $V_p$ ,  $V_s$ ), and magnetic susceptibility ( $\chi$ ). The gas permeability was measured by the steady state method. Ultrasonic wave velocity (both P- and S-waves) was measured by ultrasonic pulse transmission technique (State Standard 21153.7-75).

Mechanical parameters refer to the strength characteristics of rocks and their deformability, and include dynamic and static elastic modulus (E), Poisson's ratio ( $\nu$ ), uniaxial compressive ( $\sigma_c$ ) and tensile ( $\sigma_t$ ) strength in air-dry and water-saturated states. The uniaxial compressive strength test was conducted by standard testing procedures in accordance with State Standards 21153.2-84 (1984) and ASTM D7012 (2013). The tensile strength was determined by cleavage of cylindrical samples based on State Standard 21153.3-85 (1985). The elasticity constants were calculated from the measured wave velocities and the bulk density based on the ASTM D2845 (2008).

The composition and structure of the rocks were also analyzed. All samples were described macroscopically and studied in thin sections with transmitted light microscopy using optical microscope "Olympus" BX-41. Mineral composition was identified by DRON-3 diffractometer. Electron microscopy with microprobe analysis was conducted for a portion of the samples in order to study morphology of pore space and chemical alterations (equipment is electron microscopes Camebax SX-50 and LEO 1450VP with microprobe apparatus INCA 300).

## 4. RESULTS AND DISCUSSION

### 4.1. Petrology of the host rocks

All collected samples were divided into the following groups:

- 1) Tuffs with different degree of alteration
  - 1.1) almost totally altered
  - 1.2) highly altered
  - 1.3) moderately altered;
- 2) Perlites with different degree of alteration: slightly and highly altered.
- 3) Other volcanic rocks including basalts, basaltic andesites, andesites, phylolites, and clastolava.

Classification of tuffs into the groups was conducted on a qualitative level. To *moderately altered samples* attributed those rocks in which secondary changes subjected to volcanic glass, whereas lithoclasts and crystals of Pl and CPx are remained unchanged. Size of lithoclasts reaches to 5-6 mm, rarely up to several cm (fig. 2). Matrix is composed of fine-grained quartz-feldspar-zeolite aggregate (fig. 3a) or zeolite-smectite aggregate (figs. 3b, 4a). Crystals of the zeolites fill pores of different shape and often completely replace clasts of glass (fig.4b). The content of zeolite minerals varies in the range of 12-36%, the amount of clay minerals reaches to 21%. Majority of the samples of this group were taken close to the top of the deposit (i.e. 1081 m), some researchers call them "crater" tuffs.



Figure 2: Moderately altered tuffs

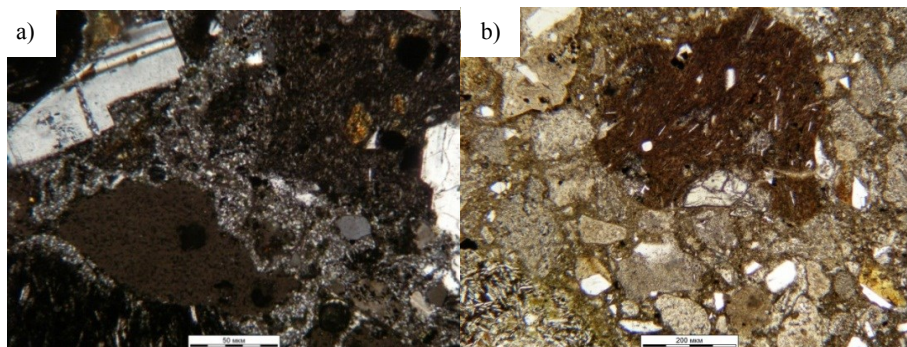
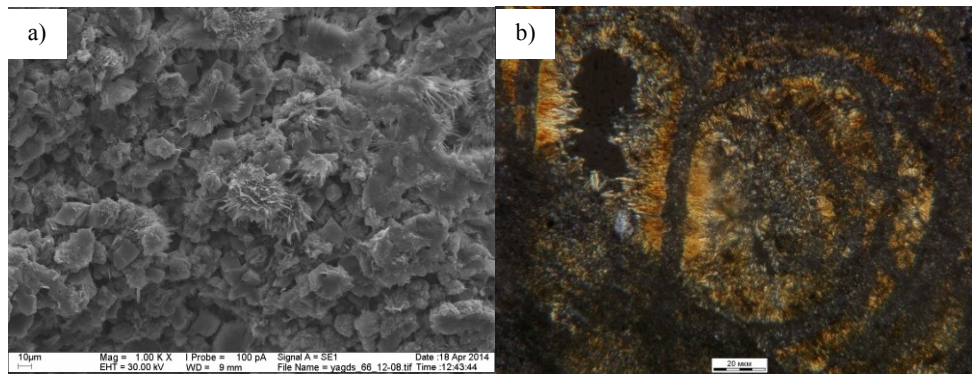


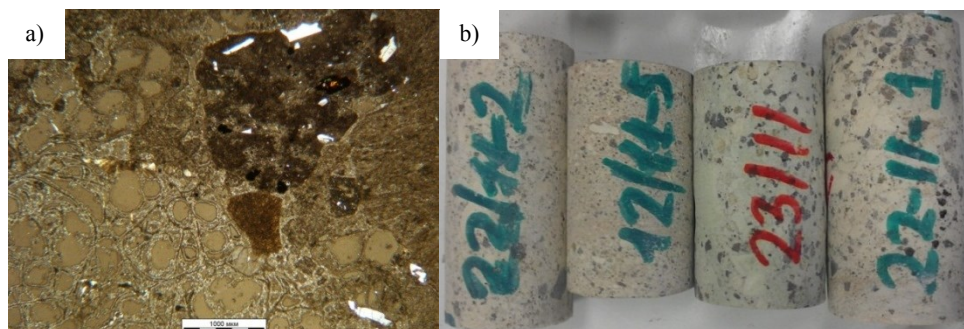
Figure 3: Moderately altered tuffs. Photomicrographs of thin sections: a) Quartz-feldspar-zeolite aggregate and b) Zeolite-smectite aggregate



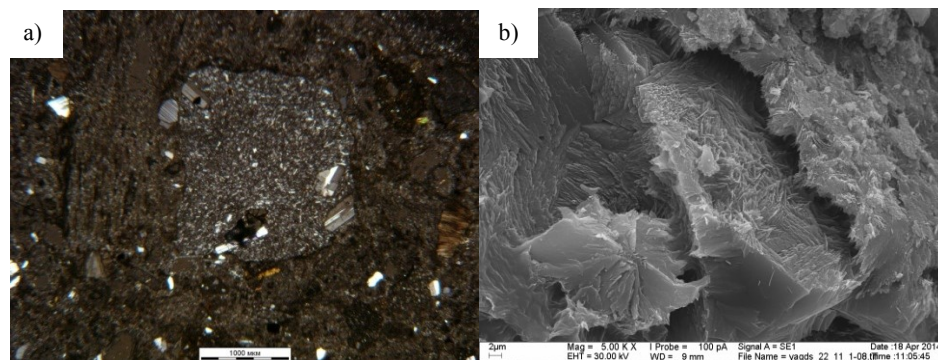


**Figure 4: a) SEM-image of zeolite-smectite aggregate, b) Photomicrograph of thin section showing replacement of vitroclast by zeolites and smectites**

In the group of *highly altered rocks*, the secondary alterations were subjected to vitreous matrix as well as numerous clasts of volcanic rocks that are partially or completely replaced by microcrystalline zeolite-smectite mass (fig. 5a). Primary components are mostly (> 70%) replaced by secondary minerals. The centers of perlite clasts are often presented by blank pores, which are contoured by zeolite films. Some clasts of volcanic rocks are unaltered, their sizes reach up to 2-10 mm (fig. 6a). "Empty rim" is often observed between clasts and cement (fig. 6b). The content of zeolites varies in the range of 70-90% and the amount of clays reaches to 10%. Samples selected for this group contain two tuff stratum underlying the northern and north-eastern flows of perlite (fig. 5b).

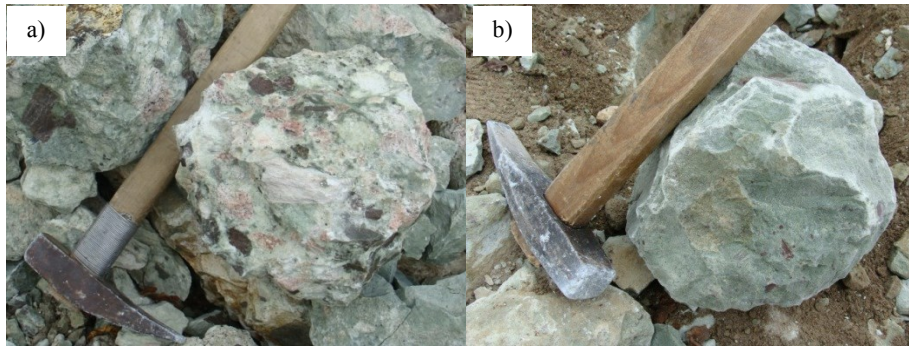


**Figure 5: Highly altered tuffs: a) Photomicrographs of thin sections: replacements of lithoclasts and matrix; b) View of samples**

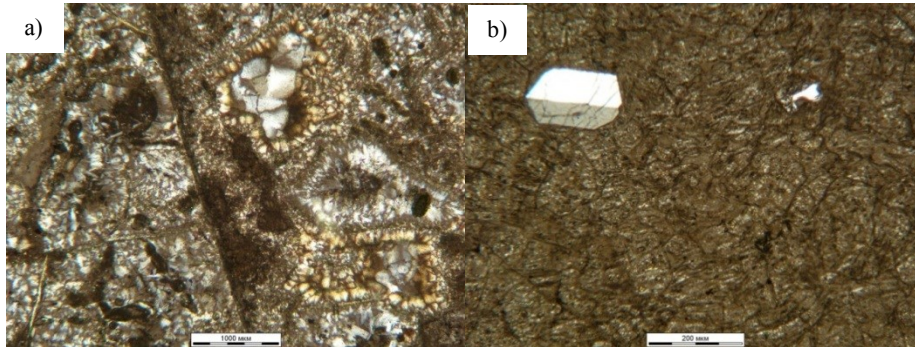


**Figure 6: Unaltered lithoclast (a) and SEM-image of the "empty rim" between clast and cement (b)**

About 90-100% of primary minerals are subjected to secondary changes in *almost totally altered tuffs*. The primary clastic structure of tuffs is occasionally invisible due to alteration process. There are allocated samples with lots of visible clasts in which the matrix, glass and clasts of effusive and extrusive rocks are almost completely replaced by zeolite-smectite mass (figs. 7a, 8a) and the samples of apocrystal tuffs in which clasts are difficult to distinguish, and the cement and clasts are completely redesigned by hydrothermal processes in the solid mass (fig. 7b, 8b). The content of zeolite minerals varies in the range of 90-100%, the amount of clay mineral (e.g. smectite) reaches to 10%. Tuffs of this group were selected from the productive zeolite stratum underlying northeast perlite lava flow, in various parts of the walls of the quarry.

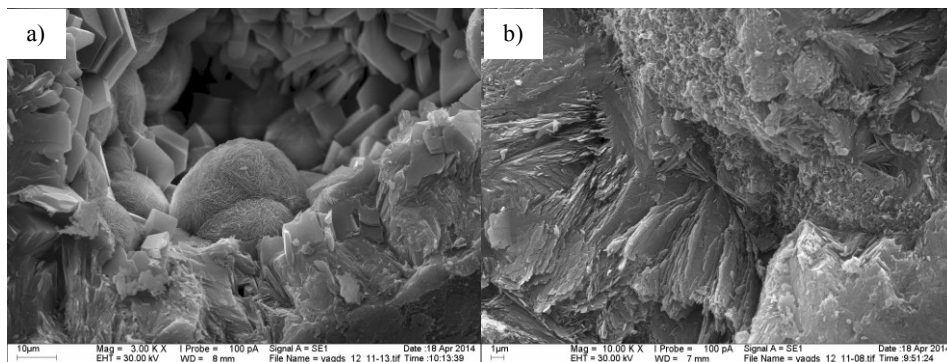


**Figure 7: Almost totally altered tuffs: with lots of visible clasts (a) and with apocrystal structure (b)**



**Figure 8: Almost totally altered tuffs. Photomicrographs of thin sections: replacement of vitroclast by zeolites (a) and apocrystal structure of tuffs (b)**

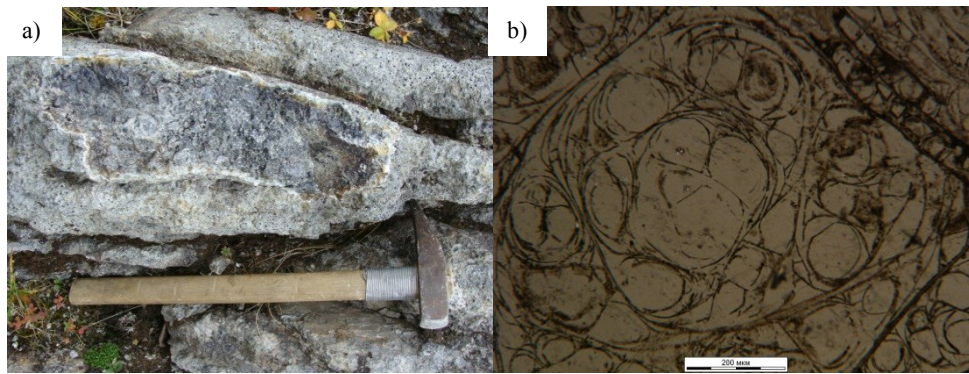
Zeolites, which are developed in pores and fractures, form crystals of regular geometric shape such as tabular, prismatic, fibrous, and needle-like (fig. 9a). This is facilitated by conditions of free growth. Zeolites, which replace volcanic glass (in cramped conditions) are characterized by lamellar and scaly aggregates where the density of crystals packing is significantly higher (fig. 9b).



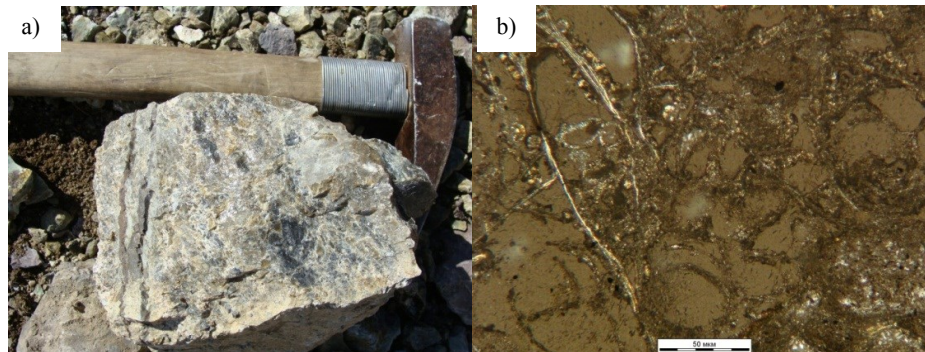
**Figure 9: SEM images. Zeolite crystals of regular geometric shape fill pore in perlite clast (a) and replacement of glassy matrix by scaly zeolite aggregate (b)**

Perlites were selected from the northeastern lava flow. They are subdivided into slightly and highly altered types. The slightly altered perlites are located at the lower part of the flow situated above the zeolite tuffs stratum. They have dark color, massive texture, large concentric perlitic structure and average degree of fracturing (fig.10a). Hydrothermal transformation of perlites begins from development of zeolites in fractures (fig.10b). Zeolites are represented by small secretions up to 10% and mainly characterized by clinoptilolite and heulandite. The clay minerals (smectite and hydromica) are also often developed in the fractures. Highly altered perlites were selected from the top part of the lava flow near the tectonic fault zone. They are characterized by light, greenish color with layered texture caused by interlayers of zeolite tuff and the perlite with small-scaled structure and intensive fracturing. Zeolitization of glass extends to the perlitic globules, expanding from the concentric fractures to the center of globules (zeolite content is about 20%) (figs.11a and b).





**Figure 10: Slightly altered perlites: the sample (a) and photomicrograph of thin section: zeolites in pore and fracture (b).**



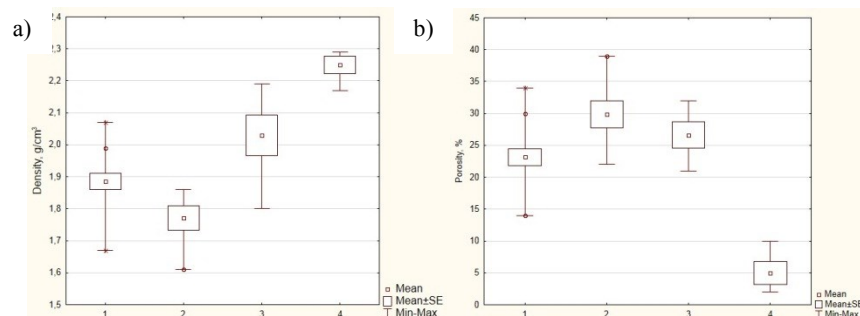
**Figure 11: Highly altered perlite: the sample (a) and photomicrograph of thin section: zeolites and clay minerals in fractures (b).**

Petrographic and petrophysical properties of other rocks of the deposit were also studied. The rocks include rhyolites, underlying the stratum of zeolitic tuff, andesites/andesibasalts, effusive basalts, and clastic lavas from the crater of the elevation 1081 m. Effusive and extrusive rocks are unaltered. It is assumed that they were formed later than the stage of zeolitization, or that the hydrothermal processing was located in a small area.

#### 4.2. Petrophysical properties

Petrophysical properties depend mainly on the primary rock features (e.g. composition, structure, grain size, and heterogeneity) and secondary alteration.

Rocks density decreases regularly from 2.72 to 1.61 g/cm<sup>3</sup> in the series of perlites → tuffs (moderately - almost totally altered - highly altered) (fig.12a). The total porosity increases from 5% to 30% in the series of perlites → tuffs (almost - average - highly altered).



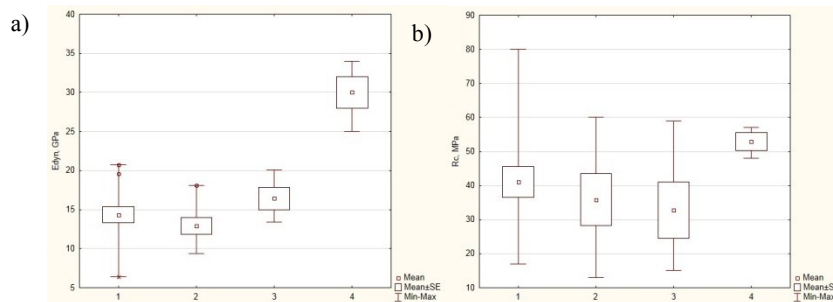
**Figure 12: Box diagram: density (a) and porosity (b). Symbols: 1 – almost totally altered, 2 – highly altered, 3 – moderately altered, 4 - perlites**

As a result of hydrothermal alteration, these rocks become more homogeneous in structure, up to the formation of apotuffs, with a number of small-sized isolated pores. Thus, at the first stage of alteration, zeolites replace volcanic glass, and this process is accomplished by leaching and formation of secondary porosity. The final stage (when the glass is completely altered) is characterized by zeolite sedimentation in the pores that causes reduction in porosity and permeability.

Acoustic and elastic properties decrease with increasing porosity and decreasing density in accordance with the increase of alteration degree. The lowest elastic characteristics are of typical for highly altered tuffs ( $E_d = 6,4$  GPa), whereas perlites have the highest values (32GPa) (figs.13a, 14a).

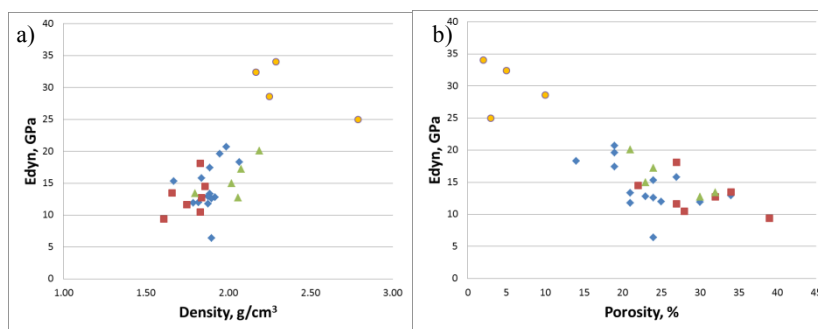
Influence of the degree of hydrothermal alteration on the strength is not traced clearly; the primary difference and heterogeneity of the individual samples (e.g. the amount and size of the clasts, fracturing, and also differences in the mineral composition of the

cement).play defining role. UCS decreases from 69 to 33 MPa in the series of perlites → tuffs (almost totally - highly – moderately altered) (Figs. 13b, 14 b, 15 a).

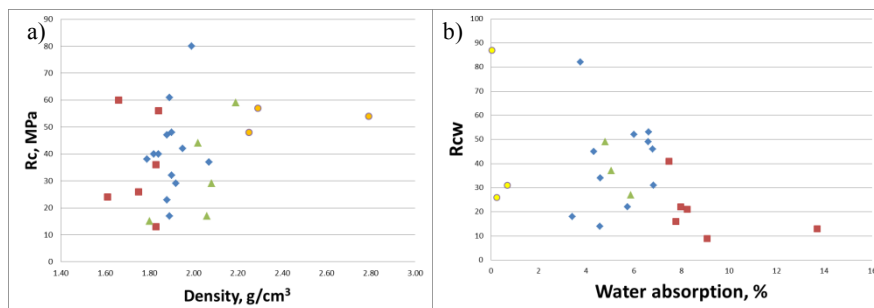


**Figure 13: Box diagram: dynamic elastic modulus (a) and UCS (b). Symbols: 1 – almost totally altered, 2 – highly altered, 3 – moderately altered, 4- perlites**

Strength in water saturated condition generally decreases with increasing of water absorption (Fig. 15b) and open porosity varies in a range of 10-82 MPa. Extremely altered tuffs with the highest values of water absorption, open porosity, and clay mineral content have the lowest values of unconfined compressive strength in saturated condition.



**Figure 14: Scatter plots: Dynamic elastic modulus versus density (a) and porosity (b).**



**Figure 15: Scatter plots: a) UCS in air-dry state versus density; b) UCS in water-saturated state versus open porosity**

**Symbols: ◆ - almost totally, ▲ - highly, ■ - moderately, ● perlites**

**5. CONCLUSIONS**

The main zeolite-bearing rocks of Yagodninskoe deposit are tuffs in which volcanic glass is completely replaced by zeolites such as clinoptilolite and mordenite. Vitric tuffs are the most altered in comparison with lithic and crystal-rich tuffs. High porosity and permeability contribute significantly to the intense transformation of tuffs. Perlites also have traces of zeolitization, however, due to the low porosity and permeability, they are altered in minor degree when compared to tuffs. Smectites, hydromica and silica minerals are also presented in secondary mineral assemblage of tuffs and perlites with minor contents. Most of effusive and extrusive rocks are unaltered because they have been obviously formed later than zeolitization.

Intense zeolitization and argillization basically reduce density, strength and elastic characteristics of tuffs, and increase porosity and water absorption properties. It was concluded that at the first stage of alteration, zeolites replace volcanic glass, and this process is accomplished by leaching and formation of secondary porosity. The final stage (when the glass is already completely altered) is characterized by precipitation of zeolites in the pores, which causes reduction in porosity and permeability. Thus, highly altered tuffs are characterized by the lowest density and mechanical properties, whereas totally altered tuffs have slightly higher values.

The strength characteristics depend not only on the degree of secondary alteration, but to a large extent on the structural and textural features and secondary fractures. Most of the tuffs are resistant to water saturation; highly altered tuffs are softened due to the high amounts of clay minerals (i.e. high open porosity and water absorption value).

## ACKNOWLEDGEMENTS

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