

## **Structure-Properties Correlations in Original and Hydrothermally Altered Rocks: Pore-scale Modeling Study Using Element Mapping and X-ray**

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### **ABSTRACT**

Reactive transport and hydrothermal alteration of rocks depend not only on boundary conditions, e.g., pressure, temperature and solution chemistry, but is also influenced by original rock structure. By structure we mean not only pore morphology and connectivity, but also spatial correlations of pore space and chemical elements/mineral phases. In this work we combine detailed structure information obtained using X-ray microtomography scanning with high resolutions, element mapping with  $\mu$ XRF-spectrophotometer, laboratory measurements on rock samples, and pore-scale modeling to characterize structure-properties correlations in original and hydrothermally altered rocks. We use such modern methods as local porosity theory analysis (connectivity of the pore space), correlation functions (spatial correlations between pore space and different mineral phases), different pore-scale modeling approaches to determine permeability and mechanical properties and connect them to structure data (spatial correlations and pore morphology estimated from pore-network extractions). As a result, it was shown that pore space morphology and connectedness affect precipitation/dissolution patterns, which, in turn, affect changes in physical properties. Pore-scale modeling techniques were found to be invaluable tools in characterizing changes in physical properties of altered rocks based on 3D structure information obtained using non-destructive microtomography scanning.

### **1. INTRODUCTION**

At the moment the priority is the development of renewable energy sources, one of which is the heat contained within the Earth. This is especially actual in areas of active volcanism, where it is difficult to produce or deliver and use traditional energy sources (Kelly, 2011). In connection with the construction of geothermal power plants in the world for several decades been studying the composition, structure and properties of hydrothermally altered rocks. Hydrothermal transformations lead to activation of geological processes – on thermal fields confined to the slopes of volcanoes observed the landslides (Kristmannsdottir and Armannsson, 2003). One of the examples - June 3, 2007 in the Valley of Geysers in Kamchatka, where the change in rocks under the influence of hydrothermal activity has become one of the major factors contributing to the formation of a landslide (Leonov, 2008). Change of physical and physic-mechanical properties of rock the influences on the stress- strain state of massif (Frolova, Ladigin, Rychagov, 2011). At the Department of Engineering and Environmental Geology, Geological Faculty of Moscow State University studied more than 30 years of engineering-geological features of the hydrothermally altered rocks in the world (Ladigin et al., 1983); with a focus on the Kuril-Kamchatka region of Russia (Frolova et al., 2010). In the middle of the last century began to be conducted experimental studies aimed at exploring the transformation of minerals and rocks under the influence of hydrothermal processes (Karpov, 1969). Until now, most experimental studies devoted to changes in the mineral composition of rocks in hydrothermal processes, while modifying their properties in real time remains poorly studied, despite the fact that such research is particularly relevant in areas of existing geothermal power stations and affects the continuity wells and trouble-free operation of the equipment. Construction of new and modernization of existing geothermal power plants requires an expansion of research of hydrothermal processes and raises the question about the possibility of predicting changes in the composition, structure and properties of rocks under the influence of hydrothermal processes during the operation of geothermal power plant.

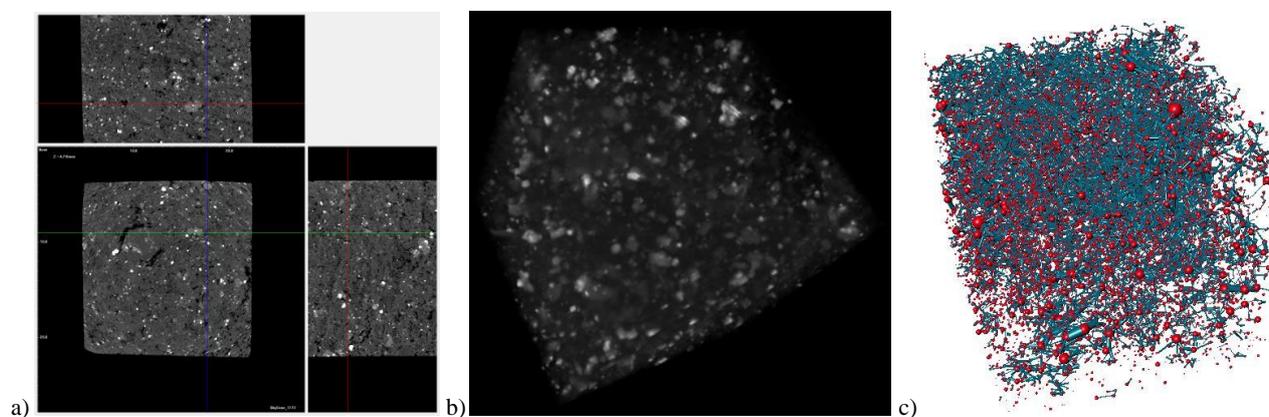
### **2. COMPREHENSIVE METHOD OF STUDYING CHANGES IN THE COMPOSITION, STRUCTURE AND PROPERTIES OF ROCKS UNDER THE INFLUENCE OF HYDROTHERMAL PROCESSES**

The technique of studying the changes in the composition, structure and properties of volcanic rocks under the influence of hydrothermal processes in real time in the deep and surface conditions, which consists of blocks: 1) field study of hydrothermal fields (temperature survey, geochemical sampling), sampling thermal water, sediments and samples of unaltered rocks, 2) laboratory study of the chemical and mineral composition, structure, physical and physic-mechanical properties of the investigated rocks, chemical composition of the thermal waters and sediments; 3) in-situ research aimed at understanding the changes in the composition, structure and properties of volcanic rocks in real time: a) in natural manifestations of thermal waters, plums from wells, b) in hydrothermal clay soils, 4) laboratory experiments in autoclaves using natural and model solutions at temperatures and pressures characteristic of the studied hydrothermal systems.

#### **2.1 Methodology of laboratory determination of composition, structure and properties of investigated rocks**

The mineral composition of the studied volcanic and volcano-clastic rocks determined in thin sections using a polarizing microscope, spot chemical analyzes of minerals and study the morphology of the pore space using a scanning electron microscope. For an illustration of the changes made pictures original and modified rocks and thin sections. To determine the composition of new minerals conducted quantitative X-ray analysis. Composition of ore minerals can be clarified by studying the magnetic properties of samples (stepwise thermal demagnetization to temperatures of 540-700 °C). Chemical analysis of rocks can be determined by X-ray crystal diffraction spectrometer.

To determine the percentage of the ore minerals and the most detailed study of the pore space rocks is advisable to use the method of X-ray computer microtomography ( $\mu$ KT). During scanning, the object to rotate around its axis, thereby accumulating batch of images of the hundreds of shadow projection, which upon mathematical reconstruction of two-dimensional images obtained stack (Fig. 1 a). Using specialized software, you can build any sample section or section combining together to get a bulk of his computer model. Segmentation (binarization the average value between the peaks of the intensity histogram), obtaining three-dimensional images (Fig. 1 b) and some quantitative estimates obtained X-ray picture of the density of processed programs SkyScan and ImageJ. Using a specially designed software packages (Korost, Gerke, 2012) of the hollow space allocated grid models where using clustering inscribed spheres (Dong, Blunt 2009), you can allocate large education - pores and channels connecting them (Fig. 1 c). In addition to the statistics of pore size distribution on the selected model calculates the absolute permeability and porosity. In the first case, assuming that the sample was completely saturated with fluid, the pressure drop is given. Flow is calculated according to the hydraulic radius of the channel (which is calculated hydraulic conductivity), the permeability is determined according to Darcy's law (Oren et al., 1998).



**Figure 1: Images basalt samples: a) orthogonal sections (unmodified sample HK-100-1-34); b) visualization of the location of ore minerals (shown in white) in a sample of basalt HK-102-30; c) grid model pore space of basalt sample HK-102-30 (red - pores, blue - channels)**

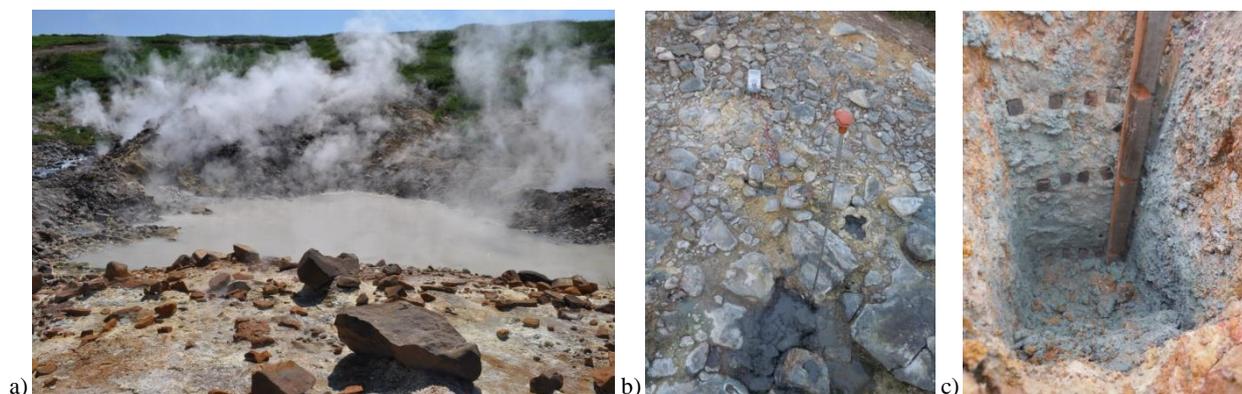
To study the physical and physic-mechanical properties of rock samples were prepared prior to the experiments (stone-cutting machine to cut into rectangular parallelepipeds and polished). Sample size is selected with the possibility of holding them in situ investigations and laboratory experiments (diameter of autoclaves and cups). After preparation of the samples identified density of the rocks and its solid components, total porosity, open porosity, water absorption, moisture absorbent, propagation velocities of elastic waves (longitudinal and transverse), magnetic susceptibility, uniaxial compression strength and tensile. All work is done according to standard methods of studying the physical and physic-mechanical properties of rocky, described in various textbooks and manuals (Laboratory work on the soil, 2008).

## 2.2 Methodology of field in-situ research on the geothermal fields

At selected sites for field studies conducted temperature survey, which allows you to select various areas of thermal field, and they reach the maximum number of manifestations of hydrothermal activity in the form of water and mud pots. Samples of the rocks studied the composition, structure and properties are placed in wooden cups with drilled holes in their walls to interact rocks with the solution. Using cups first need for active thermal fields, where the bottom of the boiling cauldron piled plenty of rock fragments, where is easy to lose the sample. Cups also allow experiments even in deep pots. The choice of material for the cups due to economic reasons and ease of manufacture, and the lack of secondary contamination of samples and thermal springs. In the experimental points (Fig. 2 a, b) are determined by physic-chemical parameters of the solutions: temperature, pH, Eh, salinity. During fieldwork conducted sampling of water and sediments to determine the chemical composition of natural solutions and features of the concentration of elements in sediments of different sources as well as for laboratory experiments.

To study changes in the composition, structure and properties of rocks without the active effects of the thermal waters, conducted research in an array of hydrothermal clay soils where traversed pits (Fig. 2 c) and at depths corresponding to the zones of the sulfuric acid leaching and carbon acid leaching laid studied samples. Locations of field investigations attached by GPS.

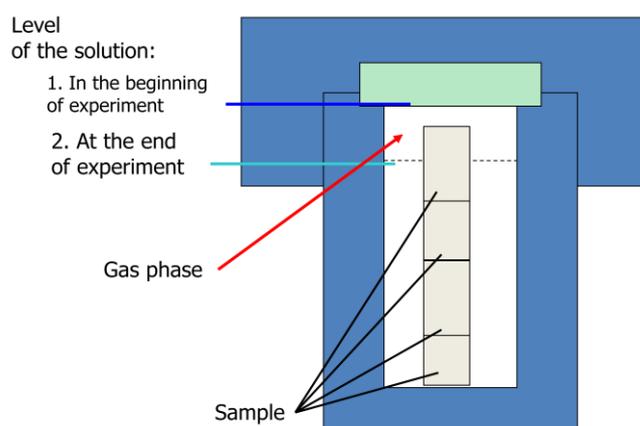
When removing the samples from water boilers used special gloves that are resistant to high temperatures. After extracting the samples, they are weighed on scales up to 0.01 g then hermetically packaged to save water saturation prior to arrival at the laboratory, which is controlled by subsequent weighed on analytical scales. In laboratory conducted the above complex definition composition, structure and properties already altered rocks.



**Figure 2: Experimental points on the Lower-Koshelevsky thermal anomaly: a) HK-15; b) HK-9; c) HKG-3**

### 2.3 Autoclave methodology for modeling the impact of solutions, temperature and pressure on the changes in the composition, structure and properties of rocks

For high temperature experiments is advisable to use autoclaves (Fig. 3), consisting of titanium alloy VT-8, each of which contains from 2 to 6 rock samples studied composition and properties, which are filled with natural or model of hydrothermal solutions. Closed autoclaves kept in an oven at a temperature characteristic of the studied hydrothermal system. The temperature can be regulated by means OWEN TPM 10 to within  $+1$  °C and monitored by thermocouples. After the experiments the autoclave was cooled with running water and disclosed. In hardening solutions measured the pH.



**Figure 3: Autoclave scheme**

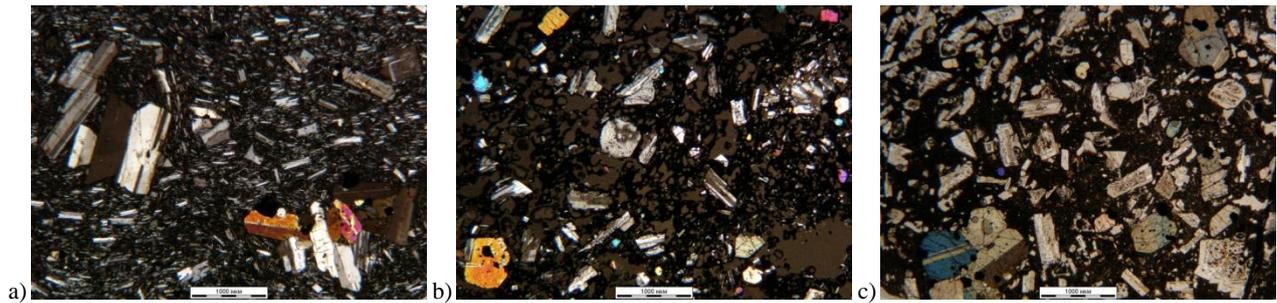
Thus, the developed methodology consists of four blocks and is conducting parallel investigations of field and laboratory experiments and the optimal combination of modern methods to study the composition, structure and properties of rocks (X-ray computer microtomography, scanning electron microscopy, quantitative X-ray analysis, determination of density of the solid components and absorbent humidity rocks, etc.) The methodology has been perfected in the study of changes in the composition, structure and properties of andesites and basalts Koshelevsky volcano, tuffs Pauzhetskoe geothermal field (Southern Kamchatka) and basalts volcano Krafla (Iceland). This is due to research Lower-Koshelevsky thermal anomaly as a promising field for the production of thermal waters, the presence of existing (1966 Pauzhetskaya and 1978 Krafla) geothermal power plants, and the core material, respectively, to compare the results of experimental transformation of rocks with natural analogues and practical significance of the data.

### 3. FEATURE ROCKS STUDIED

As the rocks under study were selected volcanics rocks of Koshelevsky volcano selected when the field work of the South Kamchatka expedition of the Institute of Volcanology and Seismology, associated with long-term studies of Lower Koshelevsky thermal anomaly, as a promising field for the production of thermal waters. Koshelevsky volcanic massif consists of several volcanic centers, Lower Koshelevsky thermal anomaly located on a slope West Koshelevsky volcano from which preserved part of the somme (or ledge caldera).

Petrographic thin sections described (sample HK-1/09-1 and-1c) - andesite with porphyritic structure (Fig. 4 a), fine-grained. On the background of the bulk of observed phenocrysts presented plagioclase, pyroxene and ore minerals (presumably magnetite). Groundmass is composed of plagioclase, clinopyroxene, ore mineral and glass.

Scoria (Fig. 4 b) composition basalt ( $\text{SiO}_2$  50,30-50,75%) and basalts (Fig. 4 c) ( $\text{SiO}_2$  50,75% -53,10%) - with porphyritic structure. Plagioclase phenocrysts are presented, pyroxene (clinopyroxene predominates) and ore minerals (magnetite). Groundmass is composed of plagioclase, clinopyroxene, olivine, ore mineral and glass structure hyaline. Vesicular texture.



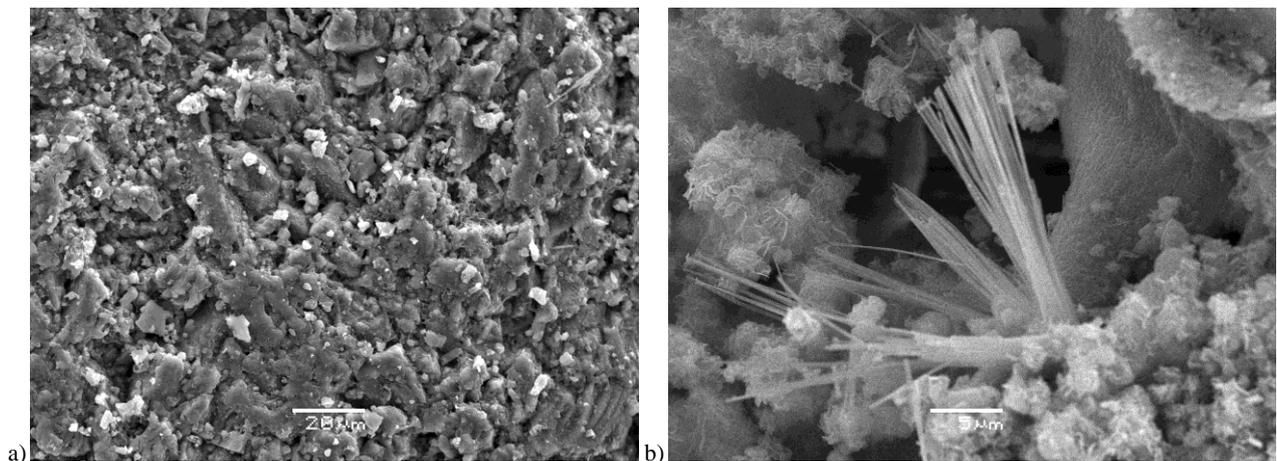
**Figure 4: Rocks studied: a) andesite; b) scoria; c) basalt**

By the properties of the studied rocks are divided into three groups: 1) andesites (HK-1/09-1 and -1c) - the most dense ( $2,50-2,51 \text{ g/cm}^3$ ) with a minimum density of the solid component ( $2,68-2,69 \text{ g/cm}^3$ ), porosity (6-7 %) and the moisture absorbent (0,1-0,2 %) with a maximum uniaxial compression strength (151-168 MPa); 2) basalts (NK- 100-1 and -3) - medium density ( $2,23-2,25 \text{ g/cm}^3$ ), porosity (21-24 %), absolute permeability ( $0,3 \cdot 10^{-11} \text{ m}^2$ ) such higher values up to  $10e^{-10} \text{ m}^2$  for a typical highly porous basaltic tuff (Zhatnuev et al., 1996, Ostapenko et al., 1987, Saar and Manga, 1999, Smith and Sharp, 2006), a hygroscopic moisture content (0,4-0,5 %) and strength (39-55 MPa); 3) scoria (NK-102 and NK-110) - the lowest density ( $1,73-1,07 \text{ g/cm}^3$ ) and strength (7-12 MPa), maximum porosity (40-65%), the length of the channel (0,37 mm) and their number in a single pore (5,8) by the average values of absolute permeability ( $3,9 \cdot 10^{-11} \text{ m}^2$ ) and hygroscopic moisture content (0,6-0,7 %) with minimum velocities of the elastic waves (longitudinal 2,65-2,75 km/s and transverse 1,65-2,00 km/s).

#### 4. RESULTS

In the experiments studied unaltered volcanics rocks confined to Western Koshelevsky volcano. On the territory of the Lower Koshelevsky thermal field under the action of bicarbonate water (pH 6,8,  $T = 95 \text{ }^\circ\text{C}$ ) andesites gradually converted to montmorillonite clay (Lucko et al., 2009). Changes in the properties of andesites in nature start with rocks to reduce the density of  $2,05 \text{ g/cm}^3$ , with a slight decrease in the density of solid particles (up to  $2,65 \text{ g/cm}^3$ ), increasing to 23% porosity and moisture absorbent to 1%.

As a result of the high temperature ( $300 \text{ }^\circ\text{C}$ ) and pressure (86 bar) and the chemical composition of different solutions have changed the composition, structure and properties of the studied volcanics rocks. Hydrothermal processing, primarily affected clinopyroxene phenocrysts, which started at the edges turn into serpentine, and ore minerals, which began to collapse. Similar changes have been reported in the West Thermal field within Uzon-Geyser depression in Kamchatka, where regardless of the intensity of hydrothermal alteration bulk varied less than phenocrysts (Naboko, 1974). On the exposed surface of the samples and in large pores was the formation of new minerals in alkaline solution - a minor amount of chlorite (Fig. 5 a), in acid - a large number of actinolite, fibrous aggregates which contributed to the closure of pores and channels (Fig. 5 b), which is reflected in reduction of open porosity and porosity calculated from 3D images (scoria NK-102-30). Change in pore space affects the absolute permeability of the rocks, in the slag is reduced by  $5,8 \cdot 10^{-12} \text{ m}^2$ .

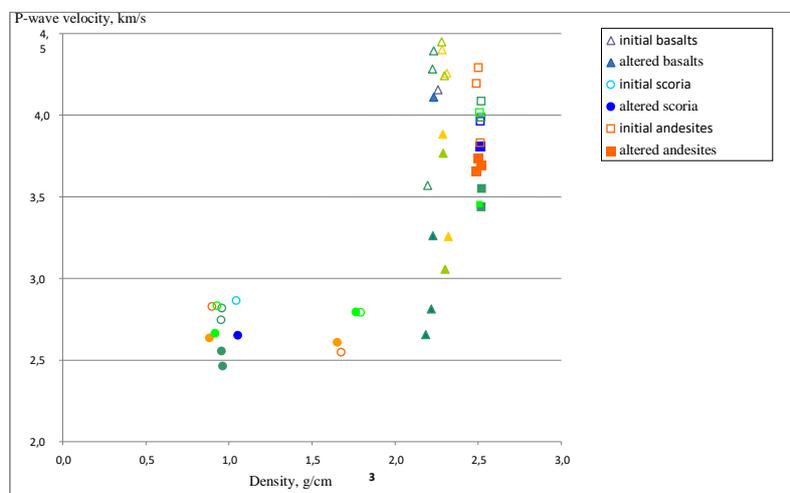


**Figure 5: The newly-formed minerals: a) chlorite on a sample of andesite, b) actinolite (sample scoria NK-102-30). Photo V.O. Yapaskurt**

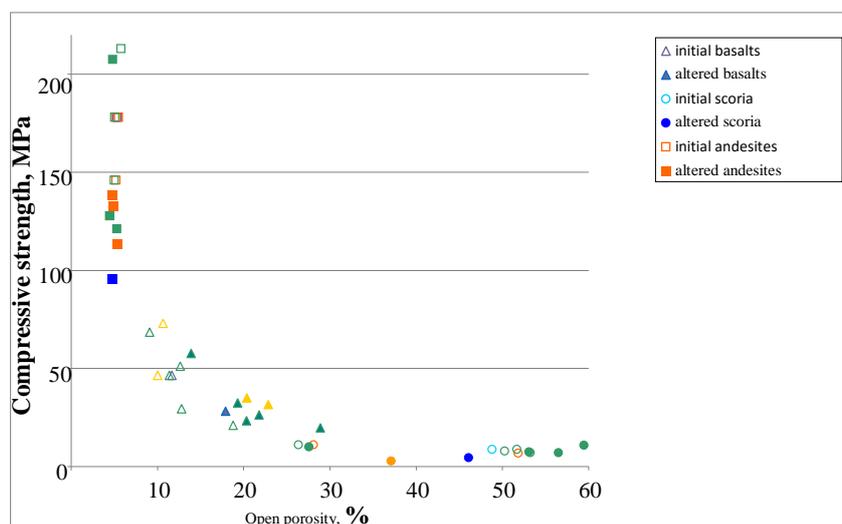
For studies using computer x-ray microtomography were selected four samples which were studied before and after experiments. However, given the small sample of andesite NK-1/09-1c-24 porosity (7,1 %) and a small characteristic pore size , the performance of quantitative estimates of porosity and permeability for 3D-model has too low accuracy. Obtained by standard techniques porosity evaluation are in general agreement with the calculated values from the images, but it is impossible to achieve absolute accuracy, since the physical volume of the sample exceeds the dimensions of the image being laid for the construction of 3D models, as well as part of microporosity is outside the resolution of the device, thereby obtained low values of porosity. Both the methods used show a decrease in porosity scoria exerted hydrothermal impact and increase the porosity of the basalts. In scoria significantly decreased the average number of connections of pores and channels that resulted in reduction of absolute permeability rocks.

High-performance computing in conjunction with X-ray microtomography can serve as a fast and accurate tool for modeling the physical properties of various natural porous materials and thus compete with traditional laboratory methods . The accuracy of calculations based on the data on the structure of the void space has been demonstrated previously by us on the basis of two different numerical methods: solution of the Stokes equation finite difference method and pore-network model (Gerke and Korost, 2011). Precisely because of this modern approach was possible to determine the filtration properties of the samples as the standard laboratory methods would change the internal structure unaltered rocks before experiments with autoclaves and were difficult to achieve on the samples in the form of rectangular parallelepipeds. On a separate note, that such research can be conducted on the sludge generated by the drilling , and the calculated electrical properties correlate with the data obtained by logging well.

The most significant impact on the change in the properties of the investigated rocks species have their primary features. Andesites have undergone the least dense transformation , aided primarily by their low open porosity (up to 5 %) , which after hydrothermal exposure has been narrowed. Maximum changes occurred in the middle group of rocks (basalts) , which is primarily due to the increase of open porosity of 60-80 % conversion occurred pore space structure affected the deterioration of the strength and deformation properties of rocks, even under steady density (Fig. 6 and 7). Increase and decrease in the open porosity of rock strength uniaxial compression associated with increased fracture due to the disjoining pressure of the solution and interacting Rebinder effect , which exposed primarily ultra- microcracks . Increase in the magnetic susceptibility of the rocks associated with the replacement of mafic minerals scaly hydromica minerals to form magnetite.



**Figure 6: The ratio of the velocity of longitudinal waves in the studied rocks and their density**



**Figure 7: Dependence of uniaxial compression strength of rocks from their open porosity**

## 5. CONCLUSIONS

New data on the nature of the changes in the properties of rocks during hydrothermal process:

1. The determining factor in the dynamics of transformation composition, structure and properties of the studied volcanics rocks are the primary features of the breed, so the least changes occurred in properties dense andesites with low values of open porosity (less than 5%).
2. At the same duration interaction-breed solution, temperature and pressure, a significant impact on changes in the properties of rocks has a pH of the solution by increasing the mineral in acidic conditions.
3. Conversion pore space rock impact on the change of open porosity and absolute permeability, deterioration of deformation and strength properties of rocks.
4. Numerical calculation of the filtration properties of the samples according to the X-ray microtomography has shown its effectiveness in the experimental work, when laboratory measurements cannot be made, or they lead to structural failure of the study of the porous medium. There is no doubt a great potential of this approach for solving various problems of engineering and environmental geology.
5. Composition, structure and properties of the studied volcanic rocks changed under the influence of temperature, pressure and composition of different solutions in a very short period in geological terms experiments. It is important that similar changes are going on in the modern hydrothermal systems where the pumping of waste thermal waters.

Ongoing changes of rock properties must be considered in the construction and operation of geothermal power plants, wells and pipelines, as well as the study of foundation soils of various structures in the areas of active development of hydrothermal processes.

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