

UDC 551.14/16

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<https://doi.org/10.23939/jgd2022.02.092>

## THE CONNECTION OF CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES IN MOUNTAIN ROCKS OF THE EARTH'S CRUST AND MANTLE AND THEIR DYNAMIC CHANGES UNDER DIFFERENT THERMOBARIC CONDITIONS

Determining the physical parameters of geomaterials under high temperature and pressure conditions is necessary in connection with the fundamental issues of geology and geophysics. It is also aimed at solving applied problems, such as establishing relationships between physical parameters and chemical components of rocks under the earthly conditions of temperature and pressure. The purpose of the paper is to study the peculiarities of the influence of chemical components on the elastic and density properties of igneous and metamorphic rocks of the continental and oceanic lithosphere under high temperature and pressure conditions. The elastic and density characteristics of the rocks of the continental and oceanic lithosphere were determined by the ultrasonic pulse method. The experiments were carried out in a high-pressure solid-phase installation of a cylinder-piston type. The technique provides for the simultaneous determination of the longitudinal and transverse waves velocity and density in the course of one experiment on one rock sample at high temperature and pressure conditions up to 1.5–2.0 GPa. Based on an experimental study of the elastic and density properties of the rocks of the continental and oceanic lithosphere, the research revealed a qualitative connection between these parameters and chemical composition of the samples under high temperature and pressure conditions. It is first established that the studied rocks demonstrate regional dependence in the influence of oxides on the elastic wave velocity and density magnitude. Therefore they increase with the growing pressure in some areas, and decrease in others. This phenomenon is explained by the difference in the atomic structure of matter. It was revealed that in the section of the lithosphere, the speed and density of elastic waves increase with depth. Moreover, chemical composition of rocks changes from acid to medium, basic, and, finally, ultrabasic composition. The relationship of the chemical composition of rocks and minerals with elastic and density properties makes it possible to directly search for solid minerals.

*Key words:* ultrasonic pulse method; chemical components; velocity; longitudinal waves; transverse waves; solid-phase installation; density.

### *Introduction*

Determination of physical parameters of geomaterials under high thermobaric conditions is necessary both in connection with fundamental problems of geology and geophysics. It is also important for solving applied problems. The laboratory longitudinal and transversal wave velocity measurements play a significant role in lithology interpretation of the rocks [Birch, 1960; Smorodinov, et al., 1970; Freund, 1992; Boadu, 2000; Kahraman, & Yeken, 2008; Moradian, Behnia, 2009, Khandelwal, & Ranjith, 2010; Kurtulus, et al., 2015]. Rocks in the laboratory can be subjected to various defined positions and their process and mechanism can be examined in situ simulation conditions. Applied questions of geology and geophysics include the establishment of connections between physical parameters and chemical components of rocks under thermobaric conditions close to those

existing in the earth [Volarovich, et al., 1974; Dortman, 1992, Physicochemical..., 1999]. The use of these links opens up great opportunities for judging the patterns of chemical elements distribution and their behavior in the lithosphere. A comparative analysis evaluates the validity of certain geophysical models and corrects them. For this reason, when interpreting field and laboratory observations, it is necessary to consider the effects of geochemical rock components on the physical properties, as well as planning the search and discovery practice [Khandelwal, & Ranjith, 2010].

### *Purpose*

The aim of the work is to study the peculiarities of influence of chemical components on the elastic and density properties of igneous and metamorphic rocks of the continental and oceanic lithosphere under high thermobaric conditions.

### *Methodology*

#### *The procedure for measuring elastic wave velocities and density*

The experiments were carried out in a solid-phase cylinder-piston unit [Volarovich, et al., 1974], using a technique developed earlier by [Safarov, 1984, 2003]. This technique involves simultaneous determination of the longitudinal and transverse wave velocity and density in the course of one experiment on one rock specimen at high thermobaric conditions. A distinctive feature of the new design of the device is based on the azimuthal dependence periodicity of the longitudinal – P and transverse – S waves. This allows separating the effects: periodic – anisotropy and chaotic – rock heterogeneity. The velocities of longitudinal and transverse waves in samples of rocks and minerals were measured by ultrasonic pulse velocity method. Piezoceramic sensors with a natural oscillation frequency of 1 to 2 MHz are fixed to the polished surfaces of the conical staples to pass ultrasonic waves through the samples. The rock samples are prepared in the form of cylinders with a length of 20 mm and a diameter of 17.5 mm for the experiments.

The elastic waves velocities and density of the samples are determined first at atmospheric pressure. The samples are then placed in a lead sheath and inserted into the cylindrical channel of the chamber between the pistons. After compression in a high-pressure chamber, the specimen with a sheath and sealing rings constitutes a solid cylinder, completely occupying the volume of the chamber channel between the pistons. After the experiment, the sample is carefully removed from the chamber and its length is measured in the lead cladding. The relative error in measuring the velocity of elastic waves under high-pressure conditions does not exceed 1.2–1.8 %.

### *Results*

The proposed work is devoted to the peculiarities of the influence of chemical components on the elastic and density properties of magmatic and metamorphic rocks of the continental and oceanic lithosphere under high thermobaric conditions. In addition to serpentinization, there are a number of other factors affecting the physical characteristics of rocks, age and structure, under high thermobaric conditions. Each one determines the appearance of the desired parameters to some degree [Volarovich, et al., 1974; Dortman, 1992; Physicochemical..., 1999]. One of such factors is the chemical composition of rocks [Safarov, 1984, 2003].

Studying the physical properties of rocks and minerals shows that the chemical composition influences the value of the elastic wave velocity and density both at atmospheric and high thermobaric conditions. It was noted earlier in [Volarovich, et al., 1974; Safarov, 1984, 2011]. The research established two types of dependencies between the velocity of elastic waves and density, determined by the

difference in the atomic structure of the substance. For the first type this dependence has the form  $V_p=f(\rho)$ , for the second type it is  $V_p=f(1/\rho)$ . The first type includes all the main rock-forming minerals, consisting predominantly of elements with a structure of the type SP (K; Na; Si, etc.). The velocity of elastic waves and the density of these minerals depend significantly on the magnitude of the atomic radii, which mainly determine the packing density of atoms in crystals, and their structures (with a subordinate effect of the atomic mass). The second type includes minerals and metals with a structure of type *d*, for which the influence on the physical parameters of the relative atomic mass (Fe, Co, U, magnetite, pyrite, etc.) is significant. The second type is characterized by a decrease in the velocity of elastic waves with increasing density [Volarovich, et al., 1974; Dortman, 1992].

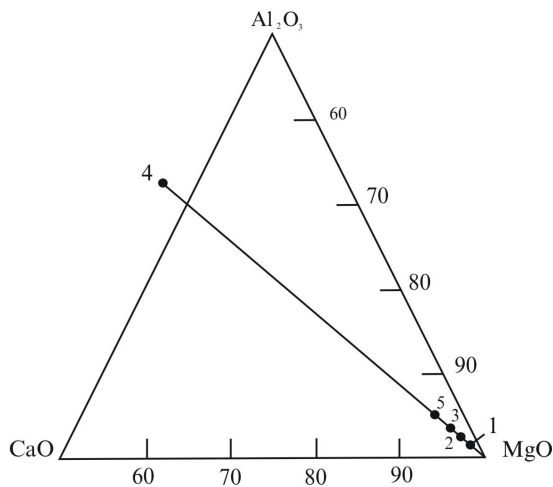
These types of bonds are preserved for such multicomponent systems as rocks. But naturally they are more complex. Depending on many other factors, they are not always unambiguous, little investigated, especially at high pressures [Safarov, 1984, 2003, 2011]. As shown by studies of the chemical composition of the continental crust and upper mantle [Lutz, 1975, 1980; Udovkina, 1985], during the formation of the mantle, the substance underwent a strong differentiation. When considering the data of silicate analysis of rocks, the relationship between their chemical composition and depth is traced. In the crust, the content of silica, alumina and calcium increases and the amount of magnesium, chromium, nickel, cobalt and vanadium decreases. Comparison of the average analyzes of the main representatives of mantle rocks from small-albino alpinotypes to the deepest garnet hyperbasites shows that they have a close silicate composition. At the same time, the distribution of chemical elements in the upper mantle is also differentiated in depth.

Shallow alpine-type, medium-deep spinel and the deepest pomegranate hyperbasites differ in their chemical composition. Alpinotype hyperbasites possess less silica than garnet, the amount of aluminum decreases 1.5 times, and calcium – 2 times mantle [Lutz, 1975, 1980]. There is a huge difference in the distribution of alkaline earth, rare earth and radioactive elements. Thus, when compared with garnet peridotites in spinel hyperbasites, the principal elements are reduced by a factor of 4, and in alpinotypic hyperbasites by a factor of 10–30.

In the mantle, there is a consistent increase in the content of CaO and Al<sub>2</sub>O<sub>3</sub> from the shallow alpine-type hyperbasites to the mid-deep spinel peridotites and then to the deepest garnet peridotites containing the maximum amount of alumina and lime. This pattern for mantle rocks is well traced on the diagram Al<sub>2</sub>O<sub>3</sub>-CaO-MgO (Fig. 1).

It was of interest to consider the relationship between the physical parameters of the rocks studied by us from different regions (the Siberian Platform,

the Tien Shan, the Urals, the Pacific, the Mediterranean, the Talysh fold zone and others). The research helped to observe a change in their chemical composition, in particular, the regularities in the distribution of oxides under high thermobaric conditions.



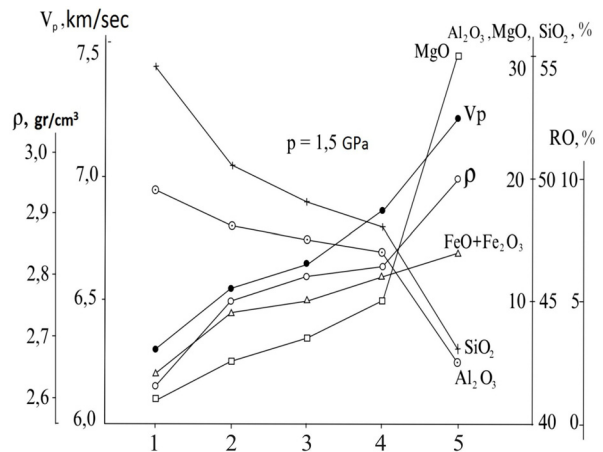
**Fig. 1.** Ratio of  $Al_2O_3 - CaO - MgO$  (mol %) in mantious rocks and chondrites:

1 – Alpinotype hyperbasite; 2 – spinel peridotite; 3 – garnet peridotite; 4 – mantle eclogite; 5 – Chondrite [Lutz, 1975, 1980].

It is known that the main chemical components of rocks are oxides of silicon, potassium, sodium, aluminum, calcium, magnesium and iron [Lutz, 1975, 1980; Azizbekov, et al., 1979; Mushkin, 1979; Udovkina, 1985].

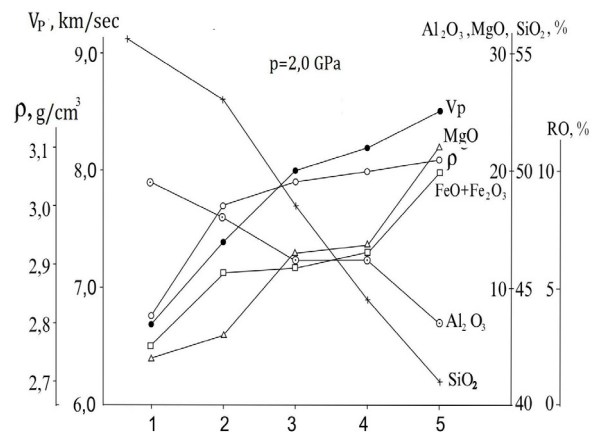
The ratio of the contents of these oxides largely determines the elastic characteristics of geological formations. The lowest velocity of elastic waves is characterized by rocks enriched in oxides of silicon, potassium, and sodium. With the increase in the content of calcium, magnesium and iron oxides, rocks become more high-velocity. However, the degree of influence of these oxides on the velocity of elastic waves and density in rocks is different and can be divided into three groups. The first group includes the rocks of the Talysh folded zone and the Tien Shan.

Figs. 2 and 3 show the dependence of the elastic wave velocities as well as the density of the content percentage of the chemical components ( $SiO_2$ ,  $Al_2O_3$ ,  $MgO$ ,  $FeO$ ,  $Fe_2O_3$ ) in the rocks of the Talysh zone and the Tien Shan at pressures up to 1.5–2.0 GPa. An important factor in the evolution of the subalkaline basal and ultrabasic complexes of the Talysh region is the existence of temporary differences between them. In the intrusive massifs of Talysh the corresponding  $SiO_2$  respiration is noted. The following sequence is observed there: the subalkaline peridotite-subalkaline gabbro, gabbrosienite;  $Al_2O_3$ ;  $N_2O$ ;  $K_2O$ ;  $CaO$  with decreasing  $MgO$ ;  $Fe_2O_3$ ;  $FeO$ . Moreover, the subclaved gabbro is not distinguished as an independent phase, but as a transition between subalkaline peridotites and gabbro-syenites [Azizbekov et al, 1979].



**Fig. 2.** Dependence of the longitudinal ( $V_p$ ) wave velocity and density ( $\rho$ ) in samples of rocks of the Talysh zone on the content of silica ( $SiO_2$ ), alumina ( $Al_2O_3$ ), magnesium oxide ( $MgO$ ), and iron oxide ( $FeO$ ) at a pressure of 1.5 GPa:

1 – trachianandesitis; 2 – trachydolerite; 3 – trachybasalts; 4 – gabbroids; 5 – ultrabasites.



**Fig. 3.** Dependence of the longitudinal wave velocity ( $V_p$ ) and density ( $\rho$ ) in samples of mountain rocks of the Tien Shan on the content of silica ( $SiO_2$ ), magnesium oxide ( $MgO$ ), aluminum oxide ( $Al_2O_3$ ) and iron oxide ( $FeO$ ) at a pressure of 2.0 GPa:

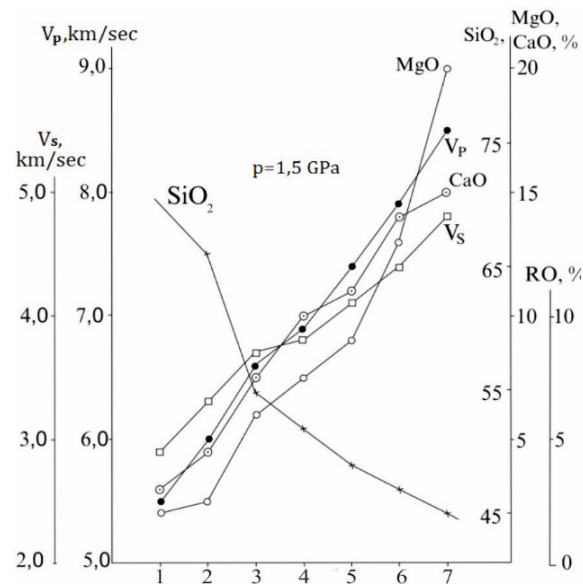
1 – graphite pyroxenites; 2 – bipyroxene gneisses; 3 – olivine spinel pyroxenites; 4 – olivine pyroxenites; 5 – spinel pyroxenites.

Fig. 2 demonstrates different character of the dependence of the longitudinal waves velocity and density on the percentage of individual chemical components of rocks in the Talysh zone at a pressure of 1.5 GPa. The longitudinal wave velocity in rocks decreases with the growing concentrations of  $SiO_2$  and  $Al_2O_3$  and increases with the growing content of  $MgO$ . The greatest influence on the elastic wave velocity and density is done by changes in the content of aluminum oxide. It demonstrates itself in the prevailing gradient of the change in the velocity magnitude. However, as

can be seen from these figures, the total content of iron oxides  $\text{FeO} + \text{Fe}_2\text{O}_3$  has a predominant effect on the density of rocks [Safarov, 2003].

Within the Southern Tien Shan along the zones of deep faults, there are massifs of mafites and ultramafites. They are regarded as derivatives of the upper mantle and they are mainly represented by olivine clinopyroxenites of poor  $\text{Al}_2\text{O}_3$ , olivine-spinel clinopyroxenites rich in  $\text{Al}_2\text{O}_3$ , and less often pomegranate clinopyroxenite [Mushkin (1979)]. Fig. 3 shows that the relationship between the values of the velocities of elastic waves and the density of the percentage of oxides at pressures of 2.0 GPa has a different character for the rocks of the Tien Shan (Safarov, 1984; 2003). In the pressure range up to 2.0 GPa, elastic waves and density in  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  rocks are decreasing and MgO content is increasing with the increasing content. It can be seen from Figs. 2 and 3 that the content of iron oxides in the rocks provides the first type of velocity dependence on the density, namely,  $V_p = f(\rho)$ . Consequently, with a growth of iron oxides –  $\text{FeO} + \text{Fe}_2\text{O}_3$  in the total content, the magnitude of the elastic wave velocity and density increases.

The second group includes mountain rocks of ophiolite complexes of Cyprus and the Urals. Figs. 4 and 5 show the dependence of longitudinal and transverse waves on the chemical composition of the rocks in Cyprus and the Ural up to 1.5 GPa.



**Fig. 4.** Dependence of  $V_P$  and  $V_S$  waves on silica ( $\text{SiO}_2$ ), magnesium oxide (MgO) and calcium oxide (CaO) contents at 1.5 GPa pressure in rock samples in Cyprus:

1 – andesites; 2 – plagiogranites; 3 – basalts; 4 – toliies; 5 – amphibolites; 6 – gabbroites; 7 – pyroxenitites.

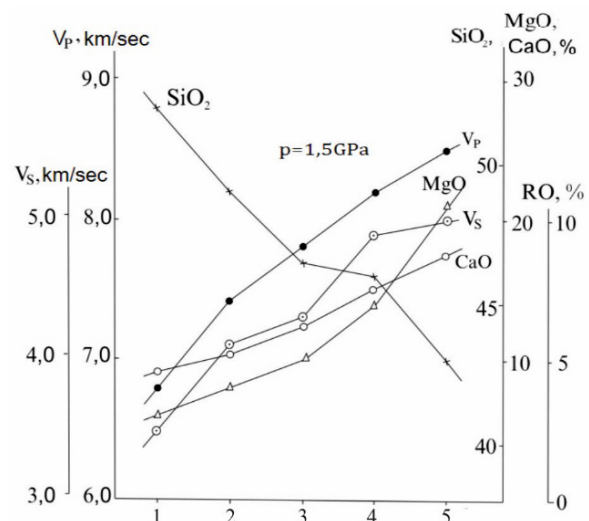
It should be noted that an essential relationship between the longitudinal ( $V_P$ ) and transverse ( $V_S$ ) wave velocities towards decreasing or increasing

under high thermobaric conditions is established in the investigated rocks of the Troodos Island. The decrease in the velocity of longitudinal –  $V_P$  and transverse –  $V_S$  waves in rocks is well correlated with the change in the chemical component –  $\text{SiO}_2$ . Rocks with an increased content of  $\text{SiO}_2$  in the sample are accompanied by a decrease in the velocity of longitudinal and transverse waves (Fig. 4).

Sufficiently high values of the longitudinal and transverse wave velocities are characteristic of rocks containing elevated components of MgO and CaO, and high densities are characterized by an elevated content in the  $\text{FeO} + \text{Fe}_2\text{O}_3$  sample [Safarov, 2003].

**Discussion**

It should be noted that the rocks of the Urals and Cyprus have the same chemical components of the samples and influence the magnitude and the density of longitudinal –  $V_P$  and transverse –  $V_S$  waves. The greatest effect on the magnitude of the elastic waves velocity is caused by a change in the oxides content of  $\text{SiO}_2$ ; MgO; CaO. The Urals samples were examined with pressure in the order of increasing the longitudinal velocities –  $V_P$  and transverse –  $V_S$  waves. Comparing them with the chemical composition, it was found that an increase in the  $\text{SiO}_2$  content in the rock is accompanied by a decrease in the elastic wave velocity and their increase with the growth in the content of MgO and CaO (Fig. 5). The density rises with increasing  $\text{FeO} + \text{Fe}_2\text{O}_3$  in the rock. The studied rocks from these regions show that for iron oxide they belong to the second type of dependence, i.e. when the elastic wave velocity decreases and the density increases [Safarov, 2003].

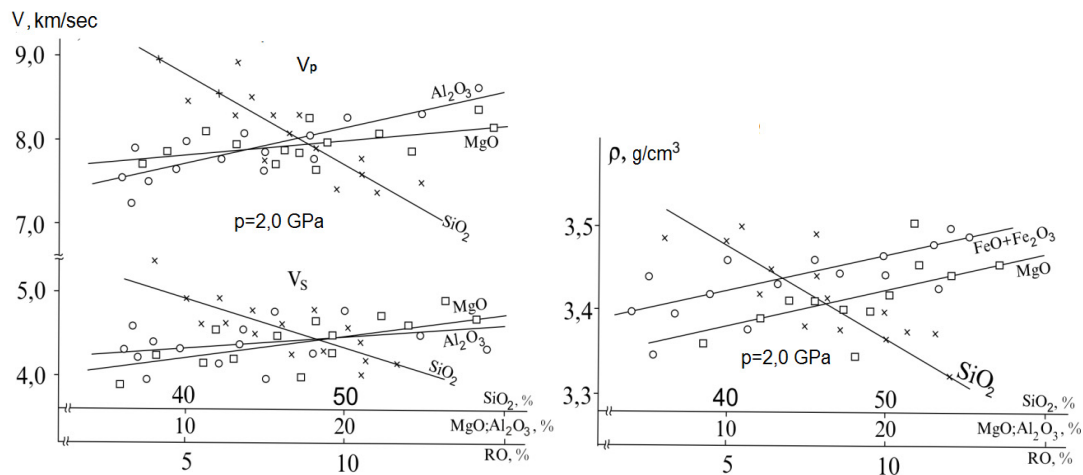


**Fig. 5.** Dependence of  $V_P$  and  $V_S$  waves in the Ural rocks on the content of silica ( $\text{SiO}_2$ ), magnesium oxide (MgO) and calcium oxide (CaO) at a pressure of 1.5 GPa:

1 – migmatites; 2 – amphibolites; 3 – eclogites; 4 – gabbroids; 5 – harzburgites.

The third group includes mantle eclogites from kimberlite pipes of Siberia and basaltoids of the Philippine Sea. Figs. 6 and 7 illustrate dependences of the longitudinal –  $V_p$  and transverse –  $V_s$  waves, as well as the density of the chemical components of mantle eclogites of Siberia and the basalts of the Philippine Sea at a high pressure of 1.5–2.0 GPa. A chemical analysis of mantle eclogites distinguishes two types of these rocks: troctolitic and basaltic [Sobolev, V. S., & Sobolev, N. V., 1964; Lutz, 1975; Udovkina, 1985]. Trocholite-type eclogites are close to different gabbros and troctolites and have low alkalinity (Na up to 2 % by weight), high magnesium ( $MgO/\Sigma FeO > 2$ ) and a low  $TiO_2$  content of between 0.1 and 1 % by weight.

According to the composition, basaltic eclogites are close to different basalts (plateau basalts, oceanic basalts). Containing  $Na_2O > 2$  weight %, are richer than  $Ti_2O$  – up to 7 weight % and less magnesian than the trocholite type eclogites. As can be seen from Fig. 6, the relationship between the values of the elastic wave velocities and the density of the percentage of oxides content for mantle eclogites is ambiguous. With an increase in silica content –  $SiO_2$ , the elastic wave velocities  $V_p$  and  $V_s$  decrease. They are increased by growing  $MgO$  and  $Al_2O_3$  content. Moreover, change in the content –  $Al_2O_3$ , and transverse wave velocity of  $MgO$  significantly affect the longitudinal waves velocity magnitude [Safarov, 1984, 2003].

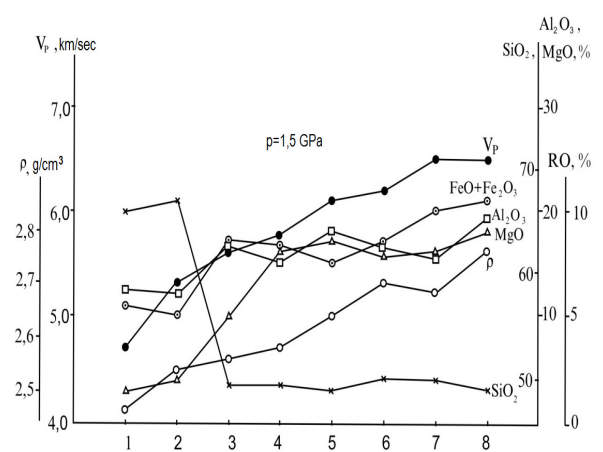


**Fig. 6.** Dependence of waves and density- $\rho$  in mantle eclogites of Yakutia on the content of silica ( $SiO_2$ ), magnesium oxide ( $MgO$ ), aluminum oxide ( $Al_2O_3$ ) and iron oxide ( $FeO + Fe_2O_3$ ) at 2.0 GPa pressure.

An analogous relationship between  $SiO_2$  and  $MgO$  with the density of rocks is observed. As for iron oxides, as noted above, iron refers to the second type of velocity vs. density, namely  $V_p = f(1/\rho)$ . Consequently, with growing  $FeO$  content, the velocity decreases and the density increases. As can be seen from the graph, the predominant effect on the increase in density is exerted by the total content of  $FeO + Fe_2O_3$  [Safarov, 1984, 2003].

The investigated basalts were selected by dredging in the Philippine Sea, at depths from 4150 to 7400 m. Among the dredged rocks, the ferrous basalts and andesite-basalts are shallow, and the vitrophilic and plagioclase basalts are the most profound. It should be noted that there is a direct decrease in the  $SiO_2$  content and an increase in the  $MgO$  content among oceanic basalts from the shallow aether basalt to plagioclase [Lutz, 1980].

Such a variation of the chemical composition in the samples of basaltoids is associated with changes of their origin in the depth. As for mantle eclogites, reduced elastic wave velocities and densities are noted with increasing content in rocks- $SiO_2$  (Fig. 7). With an increase in the content in rocks –  $Al_2O_3$ ;  $MgO$  and  $FeO + Fe_2O_3$ , the velocity and density increase, and this connection is more unambiguous under pressure [Safarov I. B., 1984, 2003].



**Fig. 7.** Dependence of the longitudinal velocity –  $V_p$  of waves and density –  $\rho$  in the basaltoids of the Philippine Sea from the content of silica ( $SiO_2$ ), magnesium oxide ( $MgO$ ), aluminum oxide ( $Al_2O_3$ ) and iron oxide content ( $FeO + Fe_2O_3$ ) at a pressure of 1.5 GPa:

1 – aetherian basalts; 2 – andesite-basalts; 3 – polyphyre basalts; 4 – glomeroporphyr basalts; 5 – metabasalts; 6 – vitrophire basalts; 7 – porphyryphanite basalts; 8 – plagioclase basalts.

One should pay attention to the difficulty in elucidating the effect of FeO on rocks. When the content of FeO is increased in the rock-forming minerals, the velocities decrease. Then, in determining the FeO effect on the velocity in rocks, this pattern is not always obvious, and for certain types of rocks it is reversed.

In general, the establishment of dependencies between physical parameters and individual chemical components of rocks under high thermobaric conditions is important not only for explaining physicochemical processes occurring in the Earth, but also for predicting the material composition at great depths.

### Originality

This technique provides for the simultaneous determination of the velocities of longitudinal and transverse waves, as well as the density in the course of one experiment on a single rock sample under high temperature and pressure conditions. For the first time it was proved that in oceanic basaltoid rocks, all the elastic parameters (longitudinal and transverse wave velocity and density) and the content of oxides (FeO + Fe<sub>2</sub>O<sub>3</sub>), Al<sub>2</sub>O<sub>3</sub>, MgO increase simultaneously.

### Practical significance

The relationship of the chemical composition of rocks and minerals with elastic density properties makes it possible to directly search for solid minerals. This also allows you to specify the material composition of the mantle and lithosphere.

### Conclusions

1. On the basis of an experimental study of the elastic and density properties of rocks of the continental and oceanic lithosphere, a qualitative relationship between these parameters and their chemical composition was revealed under high thermobaric conditions.

2. The study revealed that, in the lithospheric section, the elastic wave velocity and density increase with depth, changing the chemical composition of rocks: from acidic to medium, basic and ultrabasic composition.

3. It has been established that in the studied rocks the effect of oxides on the elastic wave velocity and density magnitude depends on the regions; therefore, with the growing pressure in some areas, they increase, and in others they decrease. This phenomenon is explained by the difference in the atomic structure of matter.

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#### ЗВ'ЯЗОК ХІМІЧНОГО СКЛАДУ І ФІЗИЧНИХ ВЛАСТИВОСТЕЙ ГІРСЬКИХ ПОРІД КОРИ І МАНТІЇ ЗЕМЛІ ТА ЇХ ДИНАМІЧНІ ЗМІНИ В РІЗНИХ ТЕРМОБАРИЧНИХ УМОВАХ

Визначати фізичні параметри геоматеріалів у високих термобаричних умовах необхідно в зв'язку з фундаментальними проблемами геології і геофізики, а також для вирішення прикладних завдань, де особливо важливим є встановлення зв'язків між фізичними параметрами і хімічними компонентами гірських порід у термобаричних умовах, близьких до умов в надрах Землі. Метою роботи є вивчення особливостей впливу хімічних компонентів на пружні й густинні властивості магматичних і метаморфічних порід континентальної та океанічної літосфери за високих термобаричних умов. Пружні й густинні характеристики порід континентальної та океанічної літосфери визначено ультразвуковим імпульсним методом. Експерименти проводилися в твердофазній установці високого тиску типу циліндр-поршень за методикою, яка передбачає одночасне визначення швидкостей поздовжніх і поперечних хвиль, а також густини під час одного досліду на одному зразку гірських порід у високих термобаричних режимах до 1,5–2,0 ГПа. На підставі експериментального дослідження пружних і густинних властивостей порід континентальної й океанічної літосфери виявлено якісний зв'язок між цими параметрами і хімічним складом зразків в умовах високих термобаричних режимів. Вперше встановлено, що в досліджених гірських породах вплив оксидів на швидкості пружних хвиль, а також на густини залежить від регіонів, тому з підвищенням тиску в одних районах вони збільшуються, а в інших – знижуються. Таке явище пояснюється відмінністю в атомній будові речовини. Виявлено, що в розрізі літосфери швидкості пружних хвиль і густина з глибиною зростають зі зміною хімічного складу гірських порід: від кислого складу до середнього, до основного, і нарешті, ультраосновного складу. Взаємозв'язок хімічного складу гірських порід і мінералів з пружними і густинними властивостями уможливорює прямий пошук твердих корисних копалин.

*Ключові слова:* ультразвуковий імпульсний метод; хімічні компоненти; швидкість; поздовжні хвилі; поперечні хвилі; твердофазна установка; густина.

Received 24.01.2022