

# Dependence of Electrical Conductivity of Mica on Interlayer Cations

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**Abstract**—Relationship between the electric conductivity of mica minerals and content in them of interlayer cations is studied by researching the geoelectrical properties of dielectric materials. Conductivity isotherms have been obtained for biotite, phlogopite and muscovite at 200 and 950°C, respectively. For phlogopite and muscovite, decrease in conductivity with increasing in sodium content has been found. This is due to the fact that the radius of the sodium ions are smaller than potassium ones that results in a significant compression of a space around the sodium interlayer, which complicates migration of ions. The availability of potassium in the mineral results in a higher conductivity. It is concluded that the correlation between sodium and potassium in mica, depending on the physical and chemical conditions of their genesis, determines the magnitude of their conductivity.

**Keywords**—biotite; phlogopite; muscovite; electrical conductivity; potassium; sodium; temperature

## I. INTRODUCTION

Solution of fundamental and applied problems in Earth sciences requires a comprehensive study of the physical properties of geological materials. There is a widespread use of electrical methods to determine the composition and structure of the Earth's crust and upper mantle, and the temperature distribution, as well to identify the petrophysical nature of anomalous zones at different depths, determine the physical nature of electrical precursors of earthquakes, etc. It takes place due to high sensitivity of the electrical conductivity of minerals and rocks to changes in temperature, material composition, and to physicochemical and phase transformations. Knowledge of the electrical properties of minerals and rocks is also required to increase the efficiency of geophysical survey, applicable also in mining and metallurgy, as well for mathematical and physical modeling of processes in rocks - this is not a complete list of problems requiring a comprehensive study of electrical conductivity for mineral substance of the earth.

Study of the interrelation between the property of a substance and its composition is a fundamental problem of science. Such investigations for the mineral substance of the Earth are one of the most important tasks of petrophysics. In the case studies, to determine the physical nature of the laws governing the change in the electrical properties of rocks under high thermodynamic parameters, one must know the data on the dependence of the electrical conductivity of rock-forming minerals on their crystal chemical features. In [6], the

characteristic dependences of electrical conductivity on chemical composition had been determined for a number of mineral groups. In this regard, the mica was found to be the least studied, although it is a common mineral in the earth's crust (about 3.8%). The micas are often rock-forming minerals for many igneous, metamorphic and partly sedimentary rocks. The interest of researchers to micas is due to both the singularity of their structure and the wide practical application.

Dependence of mica electrical conductivity on the main petrogenic elements content had been investigated in the octahedral and tetrahedral layers [11]. It was found that the same nature of changes in electrical conductivity depending on the chemical composition indicates the decisive role of defects that occur in the mineral due to deviations from the stoichiometric composition.

The purpose of the current work is to investigate the genetic relationship between the crystal chemical features and electrical conductivity of minerals from the mica group: biotite, phlogopite, and muscovite. Namely, it is a searching of the correlation of the specific electrical conductivity  $\sigma$  for these minerals and the content of interlayer cations.

## II. OBJECTS AND RESEARCH METHODS

The electrical conductivity of mineral samples was measured in a DC mode. The installation and the research method was similar to that described in [13]. The mineral samples were prepared by the method of pressing from mineral powder in view of needed small their geometrical dimensions (diameter of 10 mm and thickness of about 1 mm). The fabricated sample was placed in a measuring cell located in a quartz glass chamber in which a vacuum of about 0.10 Pa was created. This prevented the sample and an electrode block from oxidizing, and also eliminated sorbed moisture which according to [8] is the main cause of surface conductivity. The electrical resistance was measured with an E6-13A teraohmmeter and a P-4053 high-resistance bridge with an uncertainty not exceeding 3%. The sample was heated in the range of 100-1000 °C by means of a tubular electric furnace with a bifilar heater winding; the temperature was measured with a chromel-alumel thermocouple. To obtain reliable reproducible results, measurements were made with stabilized for 5-10 min sample temperature. To eliminate the influence of polarization effects, the electrical conductivity of the studied minerals was determined by two values obtained when

passing the current in mutually opposite directions. The practice of laboratory studies of electrical conductivity shows that high-voltage polarization of mineral substance is not observed, as a rule, at temperatures above 300 °C, and therefore the real values of resistance are obtained during measurements. To check the possible penetration of the electrode material inside the sample at high temperatures, the measurements of the electrical conductivity of the same mineral sample were carried out during several heating and cooling cycles. An increase in electrical conductivity, indicating the penetration, was not observed.

Mica refers to layered aluminosilicates. Their main structural unit is a layer in which the network of cations in octahedral coordination lies between two grids of silicon-oxygen tetrahedrons. The oxygen atoms located at the vertices of the tetrahedrons are bound to the atoms of the octahedral layer; this is Al in the case of muscovite and Fe or Mg in the case of biotite or phlogopite. Inside the octahedral network, there are also hydroxyl groups bound up only with Al, Mg, or Fe atoms. Due to this arrangement of cations in the grids, a doubled strongly connected silicate packet is formed; both of its external surfaces are represented with bases of tetrahedrons. In the silicon-oxygen network, a part of silicon ions can be replaced by aluminum that resulted in an unbalanced negative electric charge in the layer.

Such layers are bonded to each other by interlayer cations K, Na, Ca, etc. that are charge compensators and perform the function of preserving the electroneutrality of the crystal [1]. The forces acting inside the layers are much stronger than between them; therefore, mica is characterized by perfect cleavage along planes parallel to the layers.

Due to the uniformity of the structure, all the mineral varieties of micas have a number of common properties. All of them are crystallized in the monoclinic system and have a hexagonal form of crystals. They have low hardness and are high-resistant dielectrics.

The chemical composition of mica is quite complex, isomorphous substitutions are widely manifested in them. The overall composition for the minerals of mica group can be expressed by the formula  $X_2Y_{2-4}Z_8O_{20}(OH, F)_4$ . The tetrahedral group Z consists of Si and Al cations, the octahedral Y is Al, Mg, Fe, Li, the interlayer cations X are K and Na. In the general case, the filling of octahedral positions in micas varies from two to three; one of the most common divisions of micas into dioctahedral (muscovite, glauconite) and trioctahedral (biotite, phlogopite) is based on this.

As rock-forming minerals in the form of inclusions, mica is found in many igneous rocks; in the form of large crystals it is most often observed in pegmatite seams.

The mica samples studied were taken from various deposits (the Urals, Siberia, Baikal, the Kola Peninsula, the Aldan Shield, and the Himalayas).

### III. RESULTS AND DISCUSSION

The layered silicates (kaolinite, montmorillonite, mica, chlorites, etc.) have structures in which the bonding forces inside the layers are much stronger than the forces of

interlayer interaction, and the weakness of the forces acting between the layers often results in various structural disturbances. Such types of disorder are characteristic mainly for structures in which the layers are connected by weak hydrogen (kaolin and serpentine minerals, chlorites) or van der Waals (pyrophyllite, talc) bonds. The disorder in the overlay of layers is less pronounced in the case of micas, in the structure of which the layers are connected with strong electrostatic interaction through interlayer potassium cations and sodium cations replacing them isomorphically [9].

In this regard, we consider the relationship between the electrical conductivity of biotite and potassium content in them. This dependence for two temperatures of 200 and 950°C does not demonstrate a specific relationship between variations in the amount of  $K_2O$  in biotite samples and the magnitude of their conductivity, although potassium ions are considered to be the main charge carriers in mica [2]. The reaction of biotite chloritization is an evidence of the relatively high mobility of potassium in biotite: potassium is being taken out, but Ti, Si, Al, Fe, Mg remain in place [10]. We can assume that at such large concentrations of potassium, its amount significantly exceeds the concentration of lattice defects providing the vacancy mechanism of ionic conductivity in the crystals. Therefore only a small part of potassium ions contained in biotite is involved in charge transfer. For ionic crystals, the characteristic initial relative concentration of vacancies  $n/N$  is about  $10^{-6}$  (here  $n$  is the number of vacancies and  $N$  is the number of ions per unit volume) [4].

An analysis of the relationship between the content of  $Na_2O$  and the electrical conductivity of biotite shows the presence of some positive correlation, although the scatter of points around the middle line is very significant and makes this relationship very vague. Conductivity isotherms at 200 and 950°C, respectively, are described by the expressions:

$$\lg \sigma = -9.83 + 1.36 (Na_2O) \text{ and } \lg \sigma = -4.25 + 0.74 (Na_2O).$$

We will show later that in phlogopite and muscovite the dependence of  $\lg \sigma$  on the content of  $Na_2O$  is just opposite, i.e. with increment of  $Na_2O$  the conductivity tends to decrease. The causes of this phenomenon will be analyzed when considering phlogopite and muscovite.

For the results describing the nature of the effect of potassium and sodium interlayer cations on the conductivity of biotite, we can propose the following explanation. Values of the electrical conductivity of biotite and montmorillonite [12, 13] are found to be close to each other at 1000 °C (about  $10^{-4} \Omega^{-1} \text{ cm}^{-1}$ ). But, there are significant differences in the structure of their interlayer gaps. As known, montmorillonite is a three-layer mineral, that is, in its lattice, there is one aluminohydroxyl layer in two tetrahedral silica-oxygen layers; it is similar to the structure of biotite. The composition of these layers is not constant due to isomorphous substitutions. The resulting negative charge of the layers is compensated by exchange cations K, Na, H, Ca, etc., located between them. Montmorillonite are characterized by a high content of interlayer water; therefore the interplanar space expands as hydration increases [5]. Thus, the montmorillonite lattice is mobile. This feature of the interlayer space, i.e. the dynamic

nature of interlayer cations, is a distinctive feature of montmorillonite compared with biotite. It, nevertheless, does not result in significant differences in the magnitude of their electrical conductivity.

The given considerations make it possible to conclude that the conductive properties of layered silicates are formed by the ions of the octahedral and tetrahedral layers. The graphs of the dependence of electrical conductivity on the composition of minerals demonstrate this fact clearly. More dynamic nature of the interlayer space in montmorillonite, as compared with biotite, does not lead to a radical change in the magnitude of electrical conductivity. The observed difference in the electrical conductivity between biotite and kaolinite can be explained from the standpoint of the fact that during kaolinization of biotite, according to [7], a decrease in the K and Fe content and an increase in Al and Si occur.

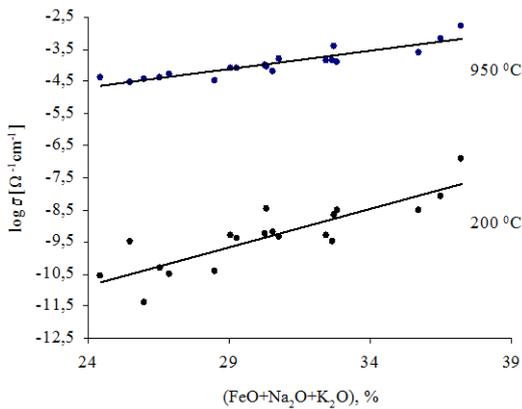


Fig.1. Dependence of  $\lg \sigma$  of biotites on the content of (FeO, K<sub>2</sub>O, Na<sub>2</sub>O)

Nevertheless, the role of potassium and sodium ions in stimulating the electrical conductivity of a number of silicates is actively manifested when they are combined with ions of iron [6]. An analysis of the experimental results also shows the dependence of the electrical conductivity on the content of the total amount of alkali metals oxides and iron. Fig.1 shows the dependence of  $\lg \sigma$  on the total content of FeO, Na<sub>2</sub>O and K<sub>2</sub>O in biotite. There is a clear relationship between the increment of these oxides content and the growth of electrical conductivity in the region of impurity conductivity (200°C). This pattern for intrinsic conductivity (950°C) becomes more distinct. The effect of alkaline cations Na<sup>+</sup> and K<sup>+</sup> on the increase in electrical conductivity is explained by their relatively small ionic radius and high polarizability with a low charge. This, in total, results in a significant decrease in the energy of their fixation at the lattice nodes. According to the obtained results, the integral effect of iron, potassium, and sodium ions on the electrical conductivity of biotite is manifested as a rise of the correlation coefficients R for the dependence  $\lg \sigma = f(\text{FeO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$  (at 200°C,  $R = 0.86$  and at 950°C,  $R = 0.98$ ) compared with the dependence  $\lg \sigma = f(\text{FeO})$  (at 200°C and 950°C,  $R$  respectively 0.84 and 0.78) [11].

A characteristic feature of the correlation between sodium content and electrical conductivity in phlogopite, shown in

Fig. 2, is a slight reduction of  $\lg \sigma$  with increasing Na<sub>2</sub>O, while there is a significant scatter of points relative to the midline. Averaging lines are described by the following expressions, respectively, at 200 and 950°C:

$$\lg \sigma = -11.57 - 0.82 (\text{Na}_2\text{O}) \text{ and } \lg \sigma = -5.06 - 1.06 (\text{Na}_2\text{O}).$$

This result, at first glance, is unexpected, since it is believed that sodium raises the conductivity of silicate minerals [6]. The analysis of our results and the published data makes it possible to conclude the following. Known, Na<sup>+</sup> isomorphically replaces K<sup>+</sup> in the interlayer space in mica. Since the ionic radius of sodium is less than that of potassium, the structure of the mineral is compressed in local areas of Na<sup>+</sup> distribution. This compression leads to the energy growth in the lattice; therefore, with an increment of the sodium content, we observe some lowering the electrical conductivity of phlogopite.

The question naturally arises—why this mechanism does not work in biotite, after all an increase in conductivity with a growth of sodium content is observed in them. The following explanation can be given here. Octahedral positions in biotite are occupied by larger in size cations Fe<sup>2+</sup> compared to Mg<sup>2+</sup> in phlogopite. Therefore, in biotite Fe<sup>2+</sup> ions expand the crystal lattice, compensating for its compression in the regions of Na<sup>+</sup> penetration.

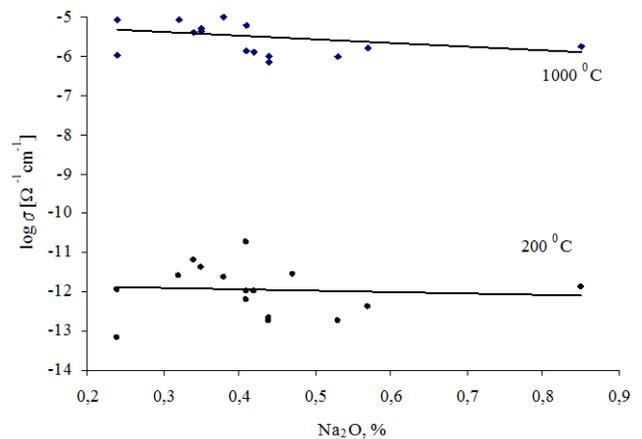


Fig. 2. Dependence of  $\lg \sigma$  of phlogopites on the content of Na<sub>2</sub>O

The results of the study show a very weak direct interrelation between the magnitude of  $\lg \sigma$  and the content of K<sup>+</sup> ions in muscovite at low and especially at high temperatures. The similar nature of the effect of potassium on the electrical conductivity is also observed in biotite and phlogopite; we have analyzed the causes of this phenomenon when considering these minerals.

The analysis of the influence of sodium ions on the electrical conductivity of muscovite has shown that, as in phlogopite, there is a rather regular tendency to reduction of the samples conductivity with an increment of the Na<sup>+</sup> cations content which is much more pronounced for the low-temperature region (Fig. 3). The dependence  $\lg \sigma = f(\text{Na}_2\text{O})$  at 200 °C is described by the expression  $\lg \sigma = 9.89 - 2.88 (\text{Na}_2\text{O})$  with a correlation coefficient  $R = -0.75$ .

Let's analyze the result. First, we take into account that the substitution of potassium for sodium gives related to muscovite mineral paragonite. Therefore, in the presence of sodium in the form of an isomorphous impurity, muscovite often contains significant admixture of paragonite depending on the physico-chemical conditions of their formation [15]. In dioctahedral mica, width of interlayer gap is determined mainly by the nature of the interlayer cations. The paragonite's layers are substantially close together compared with such in muscovite because of the small ionic radius of the sodium cations. That is, the interlayer cation  $\text{Na}^+$  being smaller in size than cation  $\text{K}^+$  creates around itself compact octahedral environment pulling oxygen atoms from tetrahedral grid [14]. Therefore, we can believe that the changes in the structural characteristics hinder movement of ions in the lattice, and this caused the decrease in electrical conductivity of muscovite due to an increment of the sodium content.

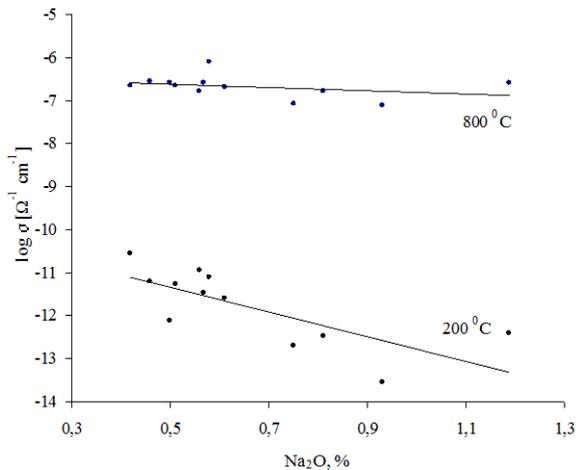


Fig.3. Dependence of  $\lg \sigma$  muscovites on the content of  $\text{Na}_2\text{O}$

At high temperatures ( $800^\circ\text{C}$ ) the dependence  $\lg \sigma = f(\text{Na}_2\text{O})$  in muscovite continues to show the tendency of electrical conductivity to drop with increment of the sodium content, as well as at  $200^\circ\text{C}$ , but the tilt angle of the averaging line, having the form:

$$\lg \sigma = -6.56 - 0.20 (\text{Na}_2\text{O}),$$

is significantly less than at  $200^\circ\text{C}$ . This reduction of the effect of sodium on the conductivity can be caused by the development of various kinds of thermal processes in muscovite under these conditions.

Investigation of the dependence  $\lg \sigma = f(\text{Na}_2\text{O})$  and interpretation of the proposed by us mechanism of the cations  $\text{Na}^+$  influence on muscovite conductivity are of interest in terms of development of methods to assess the physicochemical conditions of minerals formation reflecting changes in their structural features. This dramatic difference of K and Na influence on muscovite conductivity is additional confirmation of very limited K and Na isomorphism in muscovite, determined in [3] due to a sharp difference in structures of potassium and sodium varieties of mica.

#### IV. CONCLUSION

1. There is no clear effect of the potassium content on the increase in electrical conductivity of mica minerals. The significant potassium concentrations exceed the concentration of lattice defects providing the vacancy mechanism of ionic conductivity in the considered crystals. Therefore, only a small part of potassium ions contained in biotites is involved in charge transfer.

2. The reduction of electrical conductivity of phlogopite and muscovite with the sodium content increment is a peculiar response of the mineral lattice to the process of isomorphic replacement of potassium by sodium in the interlayer space. Such process takes place because of the compression of the crystal in the regions of sodium ions, due to their smaller ionic radius compared to potassium. This effect can serve as an indicator of the conditions under which the process of isomorphic replacement of potassium by sodium occurred.

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