LABORATORY MEASUREMENTS OF ELECTRICAL PROPERTIES OF ROCKS AND MINERALS

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Abstract. In this paper all important results on laboratory measurements of electrical properties of rocks and minerals for the last four years are presented. Although basic results from all over world are reviewed, East European and U.S.S.R. works are described more extensively. Only D.C. conductivity results are considered, however all principal conclusions hold in similar form for both D.C. and A.C. conductivities. At the end the most important areas of further study and measurement are depicted and the main problems of the future are outlined.

1. Introduction

Our present knowledge suggests that the crust and part of the upper mantle are dynamically the most active parts of the Earth. In this connection, the experimental investigation of the electrical properties under high temperatures and high pressures becomes important.

It is well known that the temperature dependence of electrical conductivity in virtually all minerals, with the exception of metals of course, is a thermally activated process. The charge carriers are ions, ion vacancies, electrons, or holes. The conductivity is the sum of the individual conduction mechanism $\sigma_i = \sigma_{0i} \exp\left(-E_i/kT\right)$. For an individual mineral, the most important variables in determining electrical conductivity are temperature, pressure, the partial pressure or fugacity of oxygen, the content of transition metal, and point defects.

In rocks at low temperatures, the important variables are the amount and shape of pore volume and the properties of the internal fluids like water solutions or partial melts. There are thus many factors which affect the electrical conductivity of rocks and minerals, and it is absolutely necessary to know the conditions of the experiment.

2. Electrical Conductivity of Rocks

Papers dealing with the study of electrical properties of various sets of rocks representing the most important building elements of the lower crust and upper mantle should find application in various interpretation models and geological projects.

The most extensive recent summary paper is that of Kariya and Shankland (1982) in which the authors have calculated the mean values of conductivity for rocks of two broad chemical compositions, granitic and mafic, in the temperature range of 500 to 1000 °C. They found statistically significant differences between the rock types; mafic rocks are better conductors than granites by about half an order of magnitude, and within the mafic group, fine-grained rocks have a higher conductivity than the coarse-grained.

As regards the Czechoslovak results (Laštovičková, 1982a; Laštovičková, in print; Laštovičková and Kropáček, 1980; Laštovičková and Kropáček, 1983), the temperature dependences of electrical conductivity for sets of volcanic rocks from Czechoslovakia are compared in Table I. It has been found that the alkaline volcanic rocks of the Bohemian Massif have the highest conductivity. The mean values of $\log \sigma$ for this most numerous group (72 localities) agree fairly well with the values published by Kariya and Shankland (1982).

As regards the effect of the modal composition on the basaltic rocks of the Bohemian Massif, analysis has shown that the conductivity decreases with increasing content of olivine and that the geometry and distribution of metallic minerals also has a considerable effect. As regards the influence of macro-chemical composition, the conductivity decreases with increasing contents of SiO₂ and MgO, and it increases with increasing content of alkali, TiO₂ and oxides of iron. It has also been shown that the effect of the individual components on the conductivity varies with temperature (Laštovičková and Parchomenko, 1978; Parchomenko and Laštovičková, 1978). The electrical conductivity of rocks of the teschenite formation, and trachyandesites of Moravia is lower over the whole range of temperatures than that of the volcanic rocks of the Bohemian Massif. The teschenites displayed dissociation of various carbonate minerals. As regards chemical composition, trachyandesites represent a link between the Bohemian Massif and the volcanic rocks of the Carpatian System (Laštovičková, 1982), which the conductivity values substantiate. The electrical conductivity of the Slovakian rocks is the lowest of the mentioned sets of rocks over the whole range of

TABLE I $Temperature \ dependence \ of \ electrical \ conductivity \ of \ volcanic \ rocks, \ measured \ in \ P_{O_3} \approx 10^{-1} \ Pa$

Type of rock	Mean log conductivity $\log \sigma [\Omega m]^{-1}$			Number	Chemically
	400 °C	600°C	800°C	of localities	analyzed in
alkaline volcanic rocks (alkaline basalts, nephelinites trachytes) of the Bohemian Massif	5.51 1 0.50	-3.00 + 0.63	-2.42 + 0.51	72	Laštovičková and Kropáček (1983)
teschenites trachyandesites of Moravia			-2.49 + 0.96 -3.37 + 1.08	41 10	Laštovičková (1982b)
alkaline basalts of Poland	-5.15 + 1.72	-3.75 + 0.72	-3.22 + 1.08	13	Jelenska <i>et al</i> . (1978)
calc-alkaline rocks of Slovakia (andesites, rhyolites dacites) and alkaline basaltic rocks of Slovakia	7.00	-4.47 + 0.80	-3.66 + 1.01	45	Laštovičková and Kropáček (1980 Laštovičková (in print)

temperatures and, according to Laštovičková and Kropáček (1980) and Laštovičková (in print), admixture elements have a pronounced effect on it.

As regards the problem of irreversibility of conductivity in basalts with multiple heating and cooling cycles, the conductivity during the re-heating cycles has been found to be higher than during the first heating (Gupta and Sharma, 1978; Laštovičková, 1978). This irreversibility in the conductivity of basalt specimens is explained by maghematization of titanomagnetite at 600-800° (Laštovičková, 1978). The different activation energies obtained by Reynoso et al. (1978) for the heating and cooling intervals appear to confirm textural changes in the specimen of volcanic rocks.

Olhoeft (1981) concludes that the conductivity of granites is mostly controlled by the water content and temperature up to melting, being relatively independent of hydrostatic and lithostatic pressure.

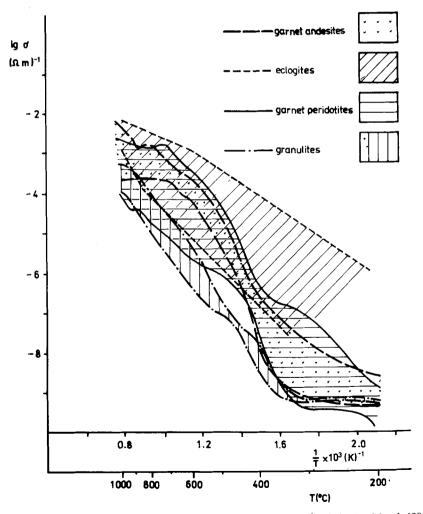


Fig. 1. Temperature dependence of conductivity of garnet rocks (P_{O₂} ≈ 10⁻¹ Pa), (Laštovičková, 1981).

Chelidze and Geladze (1978) claimed that, with a high probability, the pressure dependence of conductivity can be expressed as follows: $\sigma = \sigma_0 P^m$, where σ_0 corresponds to 1 atm and m is the power factor which varies from 0.15 to 0.45 in 75 % of the cases. This dependence was verified by the author on 72 data and results (Bondarenko, 1978; Lebedev and Shapel, 1980; Baranov et al., 1981) support this dependence.

The serpentinites and pyroxenites of the Ukrainian Shield may be devided into two groups with regard to the nature of the pressure dependence of σ . The specimens with electrical conductivity lower than $10^{-3}(\Omega m)^{-1}$ are characterized by decreasing conductivity with increasing pressure in contradiction to Chelidze and Geladze (1978). Pressure dependence of conductivity of moist and dry specimens is considerably different. The specimens with higher conductivities (over 10^{-3}) display conductivity increasing with pressure in agreement with Chelidze and Geladze (1978). The rate of increase of σ in moist and dry specimens is approximately the same in this group.

Most of the studies concerned with the properties of basalts contain almost no data for upper-mantle rocks such as peridotite, eclogite and related garnet-bearing rocks. The occurrence of garnet in rocks is an indicator of high temperatures and pressure at the time the rock originated (Hejtman, 1962). Figure 1 shows the range of conductivity values for granulites, garnet peridotites, and eclogites from the Bohemian Massif, and for garnet andesites from Central Slovakia (Laštovičková, 1981; Laštovičková et al., in press). The conductivity of the eclogites is higher than that of the other rocks. The

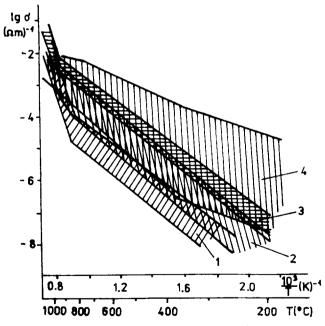


Fig. 2. Intervals of conductivity values of various types of eclogites (Parchomenko and Laštovičková, 1978); the eclogites are arranged in order of increasing content of the almandine component: (1) mantle eclogites of Siberia; (2) ophiolitic eclogites of the South Urals (in air); (3) crustal eclogites of Kazakhstan; (4) crustal eclogites of the Bohemian Massif ($P_{O_2} \approx 10^{-1} \text{ Pa}$).

granulites originated at $T \approx 800$ – 1000° and $P \approx 0.5$ –0.6 GPa, the eclogites at $T \approx 800^\circ$ and $P \approx 0.6$ GPa. These conditions of origin were determined on the basis of the scale of methamorphic facies (Hejtman, 1962). As regards garnet andesites $T \approx 950$ – 980° and $P \approx 1.5$ GPa; the garnet peridotites were determined to be upper-mantle rocks with the highest $T \approx 1300^\circ$ and highest $P \approx 1.5$ –2.0 GPa). For the latter two groups of garnet rocks, the origination temperature and pressures were calculated on the basis of the corresponding geothermometers and geobarometers (Akella, 1976; Pertchuk and Rjabtchikov, 1976; Fiala, 1966). An increase is observed in the activation energy with increasing P–T garnet rock origin (Figure 1).

The comparison of the temperature dependence of conductivity of a wide range of eclogites from the U.S.S.R. and C.S.S.R. is shown in Figure 2. The eclogites are arranged in order of increasing content of almandine component. It leads to the conclusion (Parchomenko and Laštovičková, 1978) that the electrical conductivity of eclogites increases as one proceeds from the mantle to the crust as a result of the growth of the almandine component and of secondary transitions. The conductivity increases with increasing content of iron oxides, CaO and TiO2, but decreases with increasing content of Al₂O₃, SiO₂, and MgO. Under conditions of quasi-hydrostatic pressure of up to 2.0 GPa at 600 °C and of isothermal regime, the conductivity of eclogites increases only very little, by 10-20%. In oliving pyroxenites, dunites and peridotites of the Urals (Baranov et al., 1981), the effect of temperature exceeds that of pressure by 2-3 orders of magnitude in the interval 200-1200 °C and up to 0.2 GPa. Under hydrostatic pressure exceeding 0.5 GPa, the conductivity no longer changes, of which even more distinct proof is given in (Laštovičková and Parchomenko, 1976) where the principal change in the conductivity of eclogites occurs up to 0.4 GPa due to their high density and low porosity. The metabasic rocks of the ophiolitic formation of the Lesser Caucasus (Bajuk et al., 1978) with different degrees of serpentinization (serpentinites, serpentinized peridotites, pyroxenites) display conductivities between 10^{-9} to $10^{-4} (\Omega \text{m})^{-1}$ in the temperature interval 200-1000 °C which does not exceed the conductivity interval in Figure 1.

Manghani and Rai (1978) studied the electrical conductivity of garnet-bearing peridotites and an eclogite up to 1550° . They found the conductivity of spinel lherzolite and garnet peridotite increase with the degree of partial melting. A melt fraction of about 15% is required for the conductivity to increase by ≈ 1 order of magnitude. According to Sluckij et al. (1981), at high pressures of up to 2.8 GPa the partial melting (up to 10%) of garnet-bearing peridotite is responsible for the conductivity increasing by 1.5 orders of magnitude. In basalts, an approximately equal change of conductivity could only be observed when they were completely melted under high pressures.

3. Electrical Conductivity of Minerals

It is quite evident that we must study the electrical properties of the separate rockforming minerals, if we wish to understand the mechanism of electrical conductivity of rocks in more detail. It is generally accepted that the major phase in the Earth's upper 206 m. laštovičková

mantle is olivine. A large number of authors have already studied olivine in detail. I do not intend to repeat the exhaustive reviews (e.g. Duba, 1976; Shankland, 1979, 1981; Schock *et al.*, in print) in which the problems of olivine have been discussed in detail, but I would like to add the values of measuring olivine (Fa: Fo = 1:3), separated from the basaltic rocks of the Bohemian Massif and given in Table I: conductivity at $200 \,^{\circ}\text{C} \approx 7 \times 10^{-8} \, (\Omega \text{m})^{-1}$, at $800 \,^{\circ}\text{C} \approx 8 \times 10^{-4} \, (\Omega \text{m})^{-1}$ under pressure $P_{O_2} \approx 10^{-1} \, \text{Pa}$ (Laštovičková, 1978), and the values of the electrical conductivity of the olivine from the Urals whose conductivity at $1600 \,^{\circ}\text{C} \approx 10^{-1} \, (\Omega \text{m})^{-1}$ and at $2000 \,^{\circ}\text{C} \approx 5 \times 10^2 \, (\Omega \text{m})^{-1}$ under a pressure of 20 MPa in an Ar-atmosphere (Alekseev and Sokolovskij, 1981). The conductivity values of melted olivine under high temperatures show a tendency towards saturation, the level of which increases with increasing pressure and approaches the limit characteristic for liquid semiconductors.

The second group of minerals which plays an important role in the composition of the upper mantle, consist of pyroxenes and amphiboles. This group of minerals represents a good example of the role cations play in forming the conductivity. Figure 3 shows the dependence of conductivity on the cation parameters of pyroxenes. The variation in cation composition, which consist in the replacement of the bivalent cations Mg^{2+} , Ca^{2+} by the univalent cations Li^+ , Na^+ , and in the growth of Fe

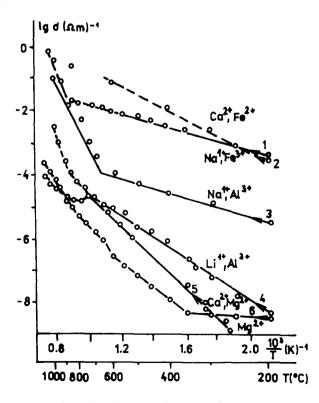


Fig. 3. Temperature dependence of conductivity of pyroxenes (in air) (Parchomenko, 1979): (1) aegirine; (2) hedenbergite; (3) jadeite; (4) spodumene; (5) diopside; (6) enstatite.

cations, is responsible for the wide range of conductivity values. The data on the pressure dependence of conductivity up to 6.0 GPa for some materials containing Na⁺ and K⁺ cations support this theory (Parchomenko *et al.*, 1979; Parchomenko, 1979, 1981).

Three natural orthopyroxene single crystals measured by Heubner *et al.* (1979) have an electrical conductivity higher by more than 1/2 an order of magnitude than crystals measured previously. The small concentrations of Al_2O_3 and Cr_2O_3 present in these crystals may be responsible for their relatively high conductivity.

One of the processes which may cause phase changes in minerals which is accompanied by a change in volume, density and physical properties is volatility, in principle due to chemically bound H_2O , CO_2 , and SO_2 . Laboratory investigations of the conductivity of rocks and of some minerals containing chemically bound water under high P and T, indicate that, when the water is separated, the conductivity increased by 1–2 orders of magnitude over a narrow range of temperatures (Parchomenko *et al.*, 1978; Mrktchian, 1978; Parchomenko *et al.*, 1979).

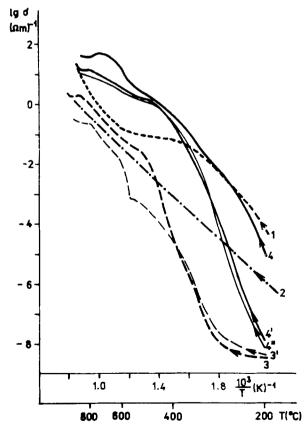


Fig. 4. Temperature dependence of conductivity of Fe-Ti-O minerals ($P_{O_2} \approx 10^{-1}$ Pa), Laštovičková and Kropáček, 1979): (1) natural FeTiO₃; (2) natural Fe₃O₄; (3) synthetic TiO₂; (3) natural TiO₂; (4) synthetic $\alpha - \text{Fe}_2\text{O}_3$; (4') natural $\alpha - \text{Fe}_2\text{O}_3$ (1st specimen); (4") natural $\alpha - \text{Fe}_2\text{O}_3$ (2nd specimen).

The electrical conductivity of Fe-Ti-O minerals, the main rock-forming minerals of basaltic rocks, was investigated (Laštovičková and Kropáček, 1979; Kropáček and Laštovičková, 1980). Generally, the electrical conductivity was found to decrease with increasing degree of oxidation. Some samples are in Figure 4. It was proved that a uniform type of electrical conductivity exists only in magnetite. With hematite and rutile there exist two types of electrical conductivity: The first in the interval up to 500° and the second above. These two types of conductivity can also be observed in ilmenite but at temperatures over 600° ilmenite oxidized. X-ray measurements have shown that rutile, hematite and pseudobrookite are generated in the process of oxidation of ilmenite.

The electrical conductivity of hematite was measured under shock compression in the range of 24 to 76 GPa (Kondo et al., 1980). The behaviour during transit into the

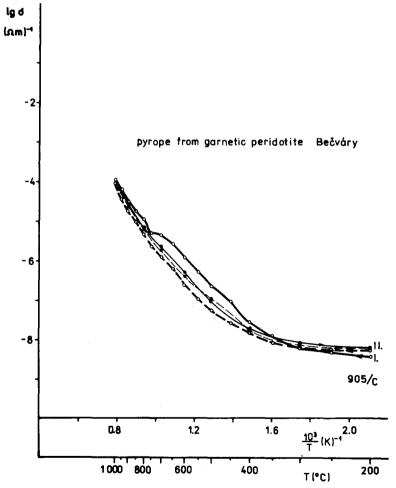


Fig. 5. Temperature dependence of conductivity of pyrope separated from Bečváry garnet paridotite (Laštovičková *et al.*, in print): (I) full line: the 1st temperature treatment; (II) dashed line: 2nd temperature treatment; $P_{O_2} \approx 10^{-1} Pa$.

high-conductivity state depends on the crystallographic axis of shock propagation.

In order to study the main rock-forming minerals of garnet-bearing rocks, (Laštovičková, 1981; Laštovičková et al., in print; Laštovičková, 1982) we separated various types of garnets (almandines, spesartines, pyropes, andradites, grossularites) from the garnet-bearing rocks shown in Figure 1; this enabled us to compare the conductivities of natural garnets of various types with the conductivities of the rock containing these garnets. Depending on the behaviour of the conductivity, the characteristic types of garnet could be devided into two groups. The first group – pyropes, an example is shown in Figure 5, displays conductivity curves similar during the first and second temperature treatment, and the values of conductivity and activation energy do not differ much. The lattice constant of the pyropes (a = 1.1521 nm) is the same at the initial stage and after heating up to 1000° , that means

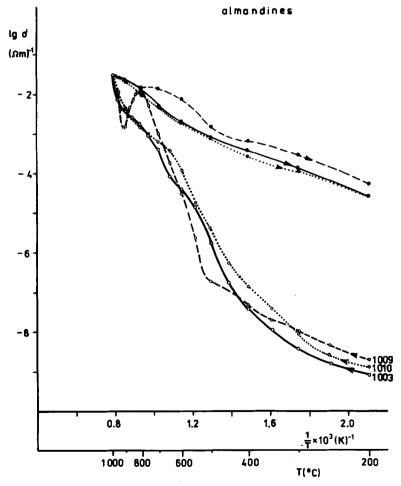


Fig. 6. Temperature dependence of conductivity for 3 almandines from different localities of the Bohemian Massif ($P_{O_2} \approx 10^{-1} \text{ Pa}$) (Laštovičková, 1981).

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the garnet structure is preserved throughout the whole cycle of conductivity measurements. Practically the same character of conductivity was observed in 10 other pyropes separated from peridotites and eclogites, and also in the series of andradites and grossularites.

The second group, represented by the almandines in Figure 6, on the contrary shows large differences in the values of conductivity and activation energy under heating and cooling. Also the lattice constant increased $(1.5030 \rightarrow 1.547 \, \text{nm})$ after heating. The same behaviour was observed with the spessartines. The comparison of Figures 5 and 6, as well as the comparison of the conductivity of almandine with that of other types of garnets shows that almandine is the most conducting of the garnets for higher metamorphic facies. Thus, the decisive effect of the almandine component in garnet on the electrical conductivity, discussed above for garnet-bearing rocks, is proved.

Figure 7 shows the pressure dependence. In spessartine (21% almandine) the $\sigma_{0.1\,\mathrm{GPa}}$ -value is considerably lower than the $\sigma_{2.5\,\mathrm{GPa}}$. On the other hand, grossularite (0% almandine) showed no pronounced change between $\sigma_{0.1\,\mathrm{GPa}}$ and $\sigma_{2.5\,\mathrm{GPa}}$. The main reason for the different conductivity values in the garnet group is apparently the different number of cations Fe and Mn, in particular one must find the possible transitions between Fe²⁺ and Fe³⁺ (Parchomenko and Mamedov, 1978); Laštovičková, 1982).

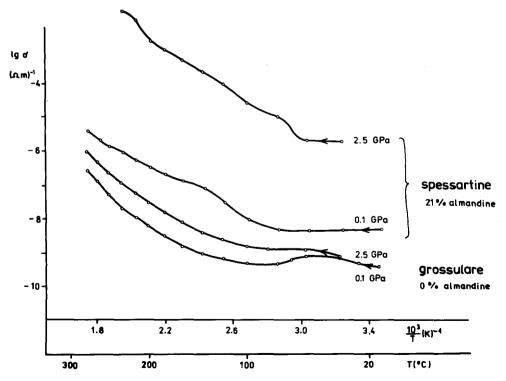


Fig. 7. Temperature dependence of conductivity of spessartine and grossularite at 0.1 GPa and 2.5 GPa in air (Laštovičková, 1981).

4. Concluding Remarks

Without drawing a conclusion, I should like to make a few concluding remarks. To achieve sufficient accuracy of measurements and geophysical applicability of their results, it is also necessary to devote attention to oxygen fugacity, to questions of reversibility of measurements and to the problems of time dependence of electrical conductivity. For some substances, for example harzburgite and olivine (Geladze, 1978), the change of the partial pressure of oxygen is responsible for a change in conductivity amounting to as much as several orders of magnitude, on the other hand, the conductivities of eclogites depend weakly on oxygen fugacity. The reversibility of laboratory measurements of electrical conductivity depends on whether irreversible changes occured in the specimen during temperature treatment. Irreversibility applies to basalts, reversibility to eclogites (Laštovičková, 1978). It has recently been found that the effect of the time factor on electrical conductivity must not be neglected (Duba, 1976; Duba et al., 1978; Mamedov and Parchomenko, 1979; Laštovičková, 1982b). Indeed, if we are measuring at a temperature at which long-term physical or chemical changes occur in the specimen, we arrive at a stable value of the electrical conductivity which is only geophysically applicable after a long time.

As regards minerals, in my opinion it is necessary to use the conductivity data of minerals directly separated from these rocks for analysis. The conductivity of these minerals does in fact differ slightly from the conductivity of synthetic minerals (Laštovičková and Kropáček, 1979).

Laboratory measurements of electrical conductivity of rocks and minerals under high pressures and temperatures are exploited in two ways: In magnetotellurics and in studying the physical properties of rocks. As regards the former, refer, e.g. to recent review papers (Shankland and Waff, 1977; Haag, 1978, Chelidze, 1979; Drury, 1979; Shankland et al., 1981). As regards the latter, either the simultaneous study of various physical properties of a given rock is involved to provide a comprehensive understanding, or some other parameters have to be determined from the measured electrical conductivity. Estimation of the Curie point (Laštovičková and Kropáček, 1976; Chelidze and Geladze, 1979) or determining the temperatures, under which various physical and chemical changes take place in rocks and minerals are two examples.

I should like to express my hope that the laboratory measurements of electrical conductivity of rocks and minerales will continue to develop successfully.

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