LABORATORY ELECTRICAL CONDUCTIVITY
MEASUREMENTS ON MANTLE RELEVANT MINERALS

E. HINZE

Mineralogisch-Petrologisches Institut der Universität Bonn, Poppelsdorfer Schloss, 5300 Bonn 1, F.R.G.

Abstract. The influence of environmental conditions and the thermodynamic parameters which may determine the bulk electrical conductivity of, for instance, basaltic rocks are briefly discussed. At present it is not known to what extent these numerous variables determine the electrical conductivity of rocks quantitatively, since all too many laboratory measurements did not account for the required number of variables to define the system. Thus it is difficult to decide whether or not laboratory measurements on rocks have duplicated their in-situ electrical conductivity.

One approach is to calculate the bulk conductivity of rocks from conductivities of the constituent minerals, since it is much easier to define the thermodynamic equilibrium conditions for a single phase system. Therefore, laboratory data of the electrical conductivity of minerals, i.e. olivines and pyroxenes, are discussed to some extent particularly in the context of point-defect concentrations as a function of pO_2 and the chemical activities a_i of the binary components of the minerals.

The evaluation of a quantitative relationship requires a careful sample characterization. To find a basis for a reasonable interpretation of in-situ resistivity data, the test samples should be selected in regard to those conditions which are believed to exist in the appropriate layer of the earth.

1. Introduction

The past 20 yrs have documented an increasingly growing interest in the application of electrical properties of rocks in earth science, i.e. in induced polarization, resistivity and electromagnetic methods of mineral and geothermal energy exploration (Keller and Frischknecht, 1979; Parkhomenko, 1967; Olhoeft, 1976; Stegena, 1976; Hunt et al., 1979), in lunar and planetary sounding (Olhoeft et al., 1974; Dyal and Parkin, 1971), or in other applications. For the future, a frontier that still remains unexplored for earth scientists is to correlate electrical conductivity values measured in situ to geological formations or physical structures in the Earth's crust or mantle which they stand for (Schmucker, 1979; Beblo and Björnsson, 1978). In connection with problems appearing now, the electrical properties of rocks must be studied in the laboratory under those thermodynamic and environmental conditions which prevail in the geological systems of interest.

In many cases it is difficult to specify the thermodynamic conditions of the rock system, by which its electrical conductivity in situ is determined. The geoelectrical exploration methods, for instance, may require only laboratory data obtained at atmospheric pressure and ambient temperatures, but one has to take into consideration the porosity of rocks as environmental conditions, the content of pore fluid and its salinity etc. But since porosity decreases with depth other variables should dominate the electrical conductivity of rocks. If, for example, we are interested in the interpretation of geophysical field observations on the composition and state of matter deep in the Earth's

crust and mantle, we must conduct laboratory experiments at high pressure and tem-
perature up to about 2000 K and 150 kbar respectively. In addition, we have to take all
other thermodynamic variables into account which may significantly influence the
electrical conductivity of rocks deep in the earth's interior. Since we do not yet know the
real values of such thermodynamic variables as a function of depth, we are not absolutely
certain that electrical conduction in a laboratory sample duplicates conduction in rocks
or minerals in situ.

Although various studies on electrical properties in rocks have been performed as a
function of frequency, temperature, applied field, pressure, oxygen fugacity, grain shape
and size, porosity, permeability, pore water content and its salinity or even time etc,
there is no simple relationship available all along the line. But I would like to agree with
Shankland (1975): "that it is only recently that conduction theories and laboratory
measurements have advanced to the point that we can begin to satisfactorily isolate the
important parameters and to account for them separately and quantitatively".

Since it is not possible to review all the problems involved in the conduction of rocks
cited above in detail, further discussions will be restricted to two topics:

(i) Laboratory measurements on basalts, just to demonstrate the difficulties arising
from electrical conductivity measurements on rocks, and

(ii) on minerals relevant for the Earth's mantle.

2. Electrical Conductivity of Basalts

Basalt is the most widely distributed of volcanic rocks and therefore a significant constituent
of the earth's crust. In particular, the oceanic crust is built mostly of basalts. There is no
doubt that they are derived from the earth's mantle by partial melting (Green and Ring-
wood, 1967; Carmichael *et al.*, 1974; Wyllie, 1979). It thus provides a most direct contact
with the nature of the earth at depth and the processes that occur there.

A review of the results on basalts has already been given by Haak (1980), so I will
focus my discussion on distinct problems involved in conductivity measurements on
basalts, i.e. on the thermodynamic conditions which have to be fixed during the laboratory
measurements.

First of all we have to consider the chemical composition of basalts (Table I). Since
ferric and ferrous iron are components of rocks, these data at once show that the control
of pO_2 is essential during the measurement. Unfortunately we have no knowledge of the
intrinsic pO_2 values of erupted basalts. Most of them show an equilibrium of partial
pressure of oxygen near to the quartz-fayalite-magnetite (Q/Fa/M) buffer. However, a
submarine pillow lava was reported to have an intrinsic pO_2 close to the iron-wustite
(I/W) buffer (Arculus and Delano, 1980). Thus it could be possible that basalts deep in
the earth should have lower conductivity than predicted from laboratory measurements.
In addition, we have to take into account the water content of basalts, which is bonded
mostly in special minerals as amphibole, mica, serpentine, chlorite, zeolites etc. Due to
heating of specimens during conductivity measurements water might be released and as a

TABLE I

Average composition of the two main basalt
groups (Middlemost, 1975)

	Sub-alkalic basalts	Alkalic basalts
SiO_2	50.2	48.6
TiO_2	1.5	2.6
Al_2O_3	16.2	17.4
Fe_2O_3	2.6	4.0
FeO	7.1	6.0
MgO	7.7	5.0
CaO	11.4	8.4
Na_2O	2.8	4.7
K_2O	0.22	2.3
P_2O_5	0.13	0.84
MnO	0.18	0.17

result variation of conduction is observable. A thermochemical investigation of these minerals depicted in Figure 1 reveals that dehydration reactions of the various minerals occur at different temperatures. These investigations were performed in an open system comparable with some experimental devices for conductivity measurements. Thus water vapor is allowed to escape. But since the natural environment which we are interested to imitate in the laboratory might be closed, we have also to control the H_2O partial pressure during our measurements. From experimental work, however, it is obvious that the stability range of amphibole is shifted to higher temperature values at higher pH_2O values. (Allen and Boettcher, 1978). To my knowledge conductivity measurements at controlled pH_2O have never been performed and this, of course, might be difficult. Nevertheless it should be done, because water buffers pO_2 (Hamilton and Anderson, 1967).

A further handicap for measuring electrical conductivities on rocks was made evident by Duba and Nicholls (1973), i.e. the time necessary to equilibrate the sample. He clearly demonstrated that σ might change with time due to disordering processes in plagioclase which is the most essential constituent of basalts. Unfortunately we are sure that equilibrium is never reached in feldspar, even in natural specimens. Thus it is questionable if laboratory measurements on basalts have imitated their conductance in situ.

As we know from point defect thermodynamics we have to take into consideration, besides those thermodynamic variables discussed to this point, further variables like the chemical activities of the components of the whole rock system. As components we may choose the binary oxides. From Table I we can accept that there are at least 11 in the case of basalts. Thus the number of variables increases to an extent which can no longer be handled in the laboratory. Of course, we do not know if these variables are important ones, but it should be investigated. This could be performed easier by the investigation of single phases, i.e. minerals. In addition, these data can be used to determine bulk electrical conductivity of rocks from a knowledge of individual phase conductivity by means of theoretical models (Meredith and Tobias, 1962; Waff, 1974; Shankland and Waff, 1977).
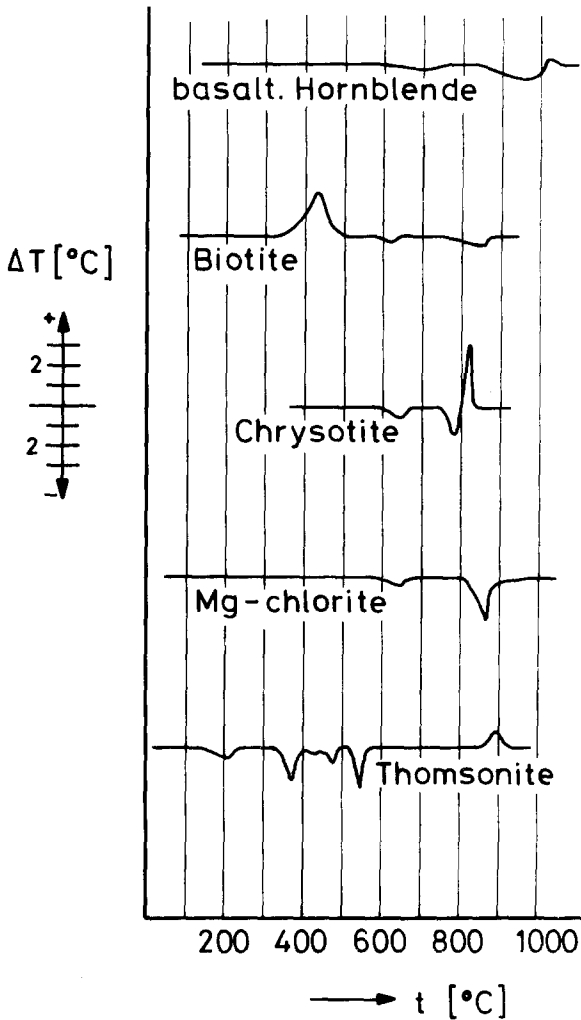
Fig. 1.   DTA curves of water bearing minerals in basalts (after Smykatz-Kloss, 1974).

3. Electrical Conductivity of Minerals

3.1. SOME THEORETICAL ASPECTS

Pertaining to the discussion on electrical conductivity of minerals, I would like to restrict myself to olivines and pyroxenes, which are the most prominent and most abundant minerals in the upper mantle. Electrical conductivity measurements on synthetic as well as on natural olivines and pyroxenes have been reported repeatedly, for ambient as well as for high pressure conditions (Bradley *et al.*, 1964; Akimoto and Fujisawa, 1965; Hamilton, 1965; Pluschkell and Engell, 1968; Schult and Schober, 1969; Mao and Bell, 1972;

Dvořák and Schloessin, 1973; Duba et al., 1973; Bradley et al., 1973; Sockel, 1974; Schock et al., 1977; Will et al., 1979; Voigt et al., 1979; Cemič et al., 1980; Hinze et al., 1979, 1981). Compilations have been given by Shankland (1975); Duba et al. (1976); Duba (1976); Schock et al., (1977); Haak (1980). However one notices appreciable variation in the results from one laboratory to another. The differences are mainly due to different compositions and histories of natural specimens, but also the lack in comensurability of the thermodynamic conditions under which the measurements were carried out (Shankland, 1975). In many cases these conditions are not clearly stated. For some cases Duba (1976) could evidently show that the experimentators did not spend sufficient time to equilibrate the sample with the surrounding atmosphere, thus obtaining higher conductivity values.

The fundamental expression describing the specific conductivity σ of silicates in a general form is given by

$$\sigma = \sum_j q_j \cdot n_j \cdot u_j$$

$$= e \cdot (e') \cdot u_{e'} + e \cdot (\overset{\cdot}{h}) \cdot u_{\overset{\cdot}{h}} + e \cdot (M_{\overset{\cdot}{M}}) \cdot u_{M_{\overset{\cdot}{M}}} + \sum_i q_i \cdot (i) \cdot u_i \tag{1}$$

n_j	=	point-defect concentration of the j-th kind,
$q_{i,j}$	=	charge for the point-defects with respect to the normal lattice charge,
$u_{i,j}$	=	mobility (velocity of charge carriers per unit potential gradient),
(e')	=	concentration of conduction-band electrons,
$(\overset{\cdot}{h})$	=	concentration of holes in the valence band,
$(M_{\overset{\cdot}{M}})$	=	concentration of transition metal ions having a different than normal valence,
(i)	=	concentration of ionic defects of kind i,
e	=	elementary charge.

As the concentration of point-defects is governed by the thermodynamic equilibrium conditions, the electrical conductivity will depend on temperature and pressure as well as on chemical activities of the components of the crystal. The choice for the independent activities is not always easy and has to be adapted to the problem under investigation.

Ternary oxides like Mg_2SiO_4 (forsterite) and $MgSiO_3$ (enstatite) are thermodynamically defined with respect to their ionic defects if, and only if, the activities of the binary oxides can be fixed (Schmalzried, 1965; Schmalzried and Navrotsky, 1975; Cemič et al., 1980). If the concentration of the electronic point-defects in the crystal cannot be neglected, the oxygen partial pressure must also be controlled during the experiment (Greskovich and Schmalzried, 1970; Sockel, 1974; Cemič et al., 1980). Extended theoretical investigations of point-defect concentration in olivines and pyroxenes as a function of temperature and chemical activities of their constituents were undertaken by Smyth and Stocker (1975), Stocker and Smyth (1978) and Stocker (1978a, b, c).

Since the number of independent parameters defining the thermodynamic state of a crystalline solid increases with the number of constituents, it is even difficult to predict point-defect concentrations in minerals. This subject deserves further attention.

For olivines Smyth and Stocker (1975) have given an equation describing the relation between the molefraction of a specific defect concentration $[n]$, chemical activity of enstatite a_{En} and pO_2

$$[n] = (\prod_i K_i^{r_i}) \cdot [Fe_{Mg}^{2+}]^q \cdot a_{En}^s \cdot p_{O_2}^m \qquad (2)$$

$\prod_i K_i^{r_i}$ is the product of equilibrium constants. The values r_i, q, s, and m have been tabulated by Stocker and Smyth (1978).

Since the internal energies of formation are different for various point-defects, one type may overwhelm the other. One can therefore distinguish between majority and minority defects. Occasionally it is possible to neglect the minority defects in the balance equations. This is an advantage for the description of equilibrium.

The temperature dependence of electrical conductivity of minerals can be described by

$$\sigma = \sigma_0 \exp(-E_a / kT) \qquad (3)$$

σ = specific conductivity,
σ_0 = electrical conductivity at infinite temperature,
E_a = activation energy,
k = Boltzmann factor,
T = absolute temperature.

A $\log \sigma$ vs $1/T$ plot should lead therefore to a linear dependency. In general, the experiments on minerals yielded one or more linear sections, showing that the main conduction mechanism differs in different temperature regions. From the slopes, the activation energies represent the sums of the individual activation energies for generation of point-defects and/or for their movement.

3.2. COMPARISON OF RESULTS

Since the relationship between point-defect concentration and the thermodynamic equilibrium conditions in the cases of ternary oxides Mg_2SiO_4 (forsterite) and Fe_2SiO_4 (fayalite) is simpler than for natural olivines, I will compare at first some literature data of conductivity measurements on pure or almost pure (Fe^{2+}/Mg^{2+} maximum 0.3%) forsterite and pure fayalite. A compilation of selected data is depicted in Figure 2 for forsterite and Figure 3 for fayalite. The literature sources are given in the figure captions.

Forsterite: While lines 1–4, 6, 10–13 represent single crystal data, those of lines 5, 7, 8, 9, and 14 were taken from powder samples. It seems that powder data are shifted parallel to higher σ values due to grain boundary effects (lines 14, 7, 5, in relation to lines 1, 2, 6). But the picture does not look uniform if one compares for instance the data of lines 6 and 8. On the other hand it is likely that some experimental errors are included, i.e. line 3 (Parkin 1972) and line 6 (Shankland, 1969) depict results taken from samples of the same batch.

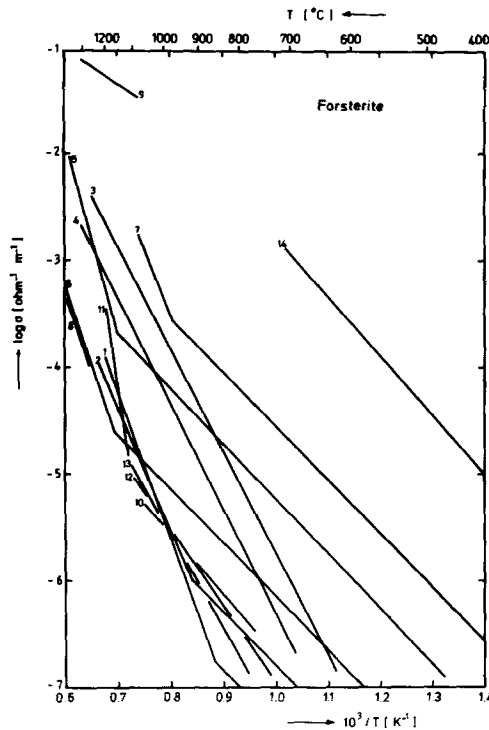No reasonable effect of pressure on the electrical conductivity of forsterite is to be

Fig. 2. Comparison of the measured electrical conductivity of forsterite. 1-5 Parkin (1972), 6 Shankland (1969), 7 Cemič et al. (1980), 8-9 Pluschkell and Engell (1968), 10-13 Duba (1972), 14 Bradley et al. (1964).

discovered from the data given in Figure 2 if one compares for instance the results which were taken at elevated pressures: line 14 (12 kbar), line 7 (10 kbar), lines 10 and 11 (2.5 kbar), line 12 (5 kbar), line 13 (7.5 kbar).

As a final point, we have to investigate the influence of the chemical activities of the binary components MgO or SiO_2 on the electrical conductivity of forsterite. The only investigators who have carried out experiments for this purpose are Pluschkell and Engell (1968) and Cemič et al. (1980). Their data are given by lines 8 and 9 and 7 respectively. If forsterite was equilibrated with MgO yielding stoichiometric crystals, Pluschkell and Engell (1968) obtained line 8 and Cemič et al. (1980) line 7. Since the activation energies are similar, the differences observed may be due to different amounts and/or kinds of impurities or to grain boundary effects. If the forsterite was equilibrated with SiO_2, the conductivity would increase by about 3 orders of magnitude yielding line 9. The reason for the increase of σ is due to additionally incorporated defects by the reaction (Pluschkell and Engell, 1968):

$$2 \, SiO_2 \rightleftharpoons 4 \, O_0 + Si_{Si} + Si_i^{4+} + 2 \, V_{Mg}^{2-} \, . \tag{4}$$
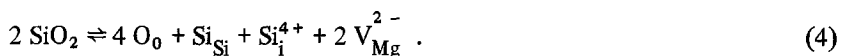
If these data are reasonable, the effect is strikingly high and must be taken into considera-

tion for discussing results on natural olivines, which are grown in equilibrium with enstaite as a more SiO_2 rich neighbour-phase in the system $MgO-SiO_2$.

Fayalite: All data depicted in Figure 3 are taken from powder samples. To my knowledge no single crystal data are available in the literature.

In the case of fayalite the situation differs immensely from forsterite. Because of the easy change in the valence state from Fe^{2+} to Fe^{3+}, vacancies and defect electrons are expected to be majority defects in fayalite. Since the mobility of electron holes is several orders of magnitude larger than that of the ions (Sockel, 1974) we have to look for the relationship between concentration of electron holes and the thermodynamic variables. These are the chemical activities of FeO or SiO_2 (a_{FeO}, a_{SiO_2}) and pO_2.

During the conductivity measurements Cemič *et al.* (1980) have embedded their sample in quartz, thus fixing the SiO_2 activity. In addition they controlled pO_2 via buffer mixtures, i.e. fayalite/quartz/magnetite (Fa/Q/M) line 7 and fayalite/quartz/iron (Fa/Q/I) line 6, thus carrying out their experiments at the heterogeneous oxidation and heterogeneous reduction boundaries of the fayalite stability field respectively (Nitsan, 1974). These results are in agreement with results of Akimoto and Fujisawa (1965) (line 3) and Sockel (1974) (lines 4 and 5) but not with the data of Bradley *et al.* (1964) (lines 1 and 2). The conductivity curve from Bradley *et al.* (1964) intersects the others. This may be due to the uncontrolled pO_2-conditions resulting in oxidation of iron in their fayalite phase during measurements. Cemič *et al.* (1980) derived a maximum of 0.066 wt % Fe^{3+} in their oxidized fayalite, while the samples used by Bradley *et al.* (1964) contained more than 0.066 wt % Fe^{3+}, probably in the form of magnetite exsolution.

Synthetic olivine mixed crystals: Cemič *et al.* (1980) have systematically investigated the influence of iron content on the electrical conductivity of synthetic olivines. They controlled the pO_2 via the buffer mixtures I/W (iron/wustite) or Fa/Q/I (fayalite, quartz,
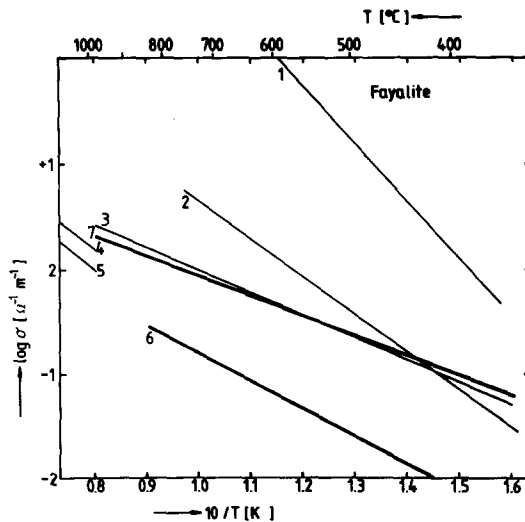

Fig. 3. Comparison of the measured electrical conductivity of fayalite. 1-2 Bradley *et al.* (1964), 3 Akimoto and Fujisawa (1965), 4-5 Sockel (1974), 6-7 Will *et al.* (1979).

iron), respectively. Again, their data have been taken on powder samples. The results are depicted in Figure 4. The synthetic olivines were prepared with a fixed (Mg, Fe)/Si ratio of 2:1. Thus the SiO_2 activity could be included as a constant in Equation (2). In these crystals, iron vacancies and defect electrons are to be expected as the majority defects. Since the mobility of defect electrons is 10^3 times larger than the mobility of Fe-vacancies (Sockel, 1974) one can neglect the vacancies. According to the concentration of defect electrons $[h^{\cdot}] = K' \cdot pO_2{}^{1/6}$ (Buening and Buseck, 1973; Sockel, 1974; Cemič et al., 1980) the conductivity of these olivines depends on $pO_2{}^{1/6}$. As a proof, Cemič et al. (1980) have made calculations to determine the pO_2 for the Fa/Q/M-buffer from their conductivity data at 900 °C and $p = 10$ kbar. As a basis they have used the well established values for the equilibrium I/W and Fa/Q/I. In the case of pure fayalite they have derived (pO_2 in bar) log pO_2 (Fa/Q/M) = −13.33, for the mixed crystals with 20 mole % Fa log pO_2 (Fa/Q/M) = −13.12 and for those of 10 mole % Fa log pO_2 (Fa/Q/M) = −13.19. Schwab and Söhnlein (1977) have estimated log pO_2 (Fa/Q/M) = −13.16 for the same buffer after correction to 10 kbar, while Wones and Gilbert (1969) estimated a somewhat higher value: log pO_2 = −12.14. Thus these data appear very reasonable.

Natural olivines: As already mentioned, a great number of electrical conductivity measurements have been performed on olivines with a composition of about 90 mole % forsterite and 10 mole % fayalite, which is believed to be the composition of olivines in the mantle. However, most of the data obtained are partly or wholly inconsistent. The differences are mainly due to histories of natural specimens, but also to the lack of commensurability of the thermodynamic conditions under which the measurements were
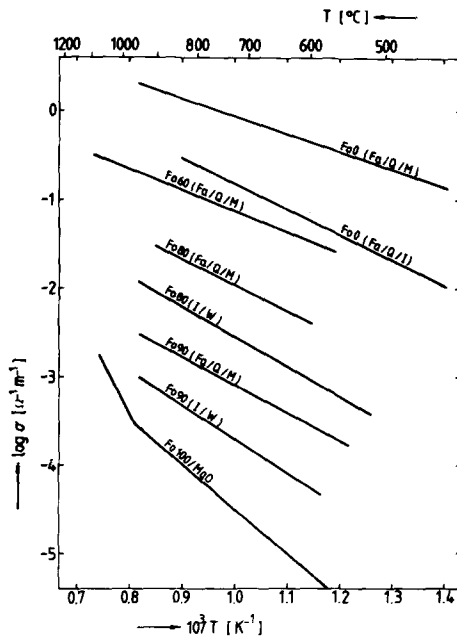

Fig. 4. Electrical conductivity of forsterite-fayalite mixed crystals, pO_2 control and composition are indicated by (Fa/Q/M) or (Fa/Q/I) or (I/W) and Fo 0 to Fo 100 respectively (Cemič et al. 1980).

carried out. This problem has already been noted earlier by Shankland (1975), Smyth and Stocker (1975), Duba (1976), and by Stocker (1978). In his review, Duba (1976) discussed methods to reduce the spread. I do not, therefore, feel the necessity to repeat the entire discussion. On the contrary I will take the liberty to emphasize certain problems. For this purpose I have selected only a few data taken from powder samples (lines 4—6) as well as single crystal experiments (lines 3, 7, 8), which are placed together in Figure 5. The measurements were performed in high pressure gas vessels as well as in a solid state apparatus. The sources are given in the figure caption. For the purpose of comparison I have included lines 1 and 2, which represent the conductivities of synthetic olivines (Fo 90, Fa 10) under oxidizing (Fa/Q/M-buffer) or reducing conditions (W/I-buffer) respectively. These data may provide a demonstration for the effect of Fe^{3+} on σ of olivine under equilibrium conditions.

Line 3 represents the electrical conductivity temperature variation of the (001) direction of San Carlos olivine measured by Duba and Nicholls (1973) under different conditions. In forsterite the electrical conductivity values parallel c-axes are found to plot between those of the a- and b-directions (Morin *et al.*, 1979). Section 3a was measured in air ($pO_2 - 10^{-7}$ bar). Due to oxidation of Fe^{2+} to Fe^{3+} the authors observed an increasing slope of the curve above approximately 600 °C. Therefore they reduced pO_2 to $<10^{-12}$ bar within the furnace (close to Fa/Q/M-buffer). Under these conditions they determined line 3b. On heating above approximately 950 °C at pO_2 close to the W/M-buffer (wustite-magnetite) conductivity rapidly decreases as temperature increases. This path is indicated schematically by arrows. For half an hour they kept the temperature at approximately 1335 °C and then further measurements began along a pO_2-T path close to the W/I buffer yielding line 3c. The data depicted on line 3b demonstrate that oxidation of
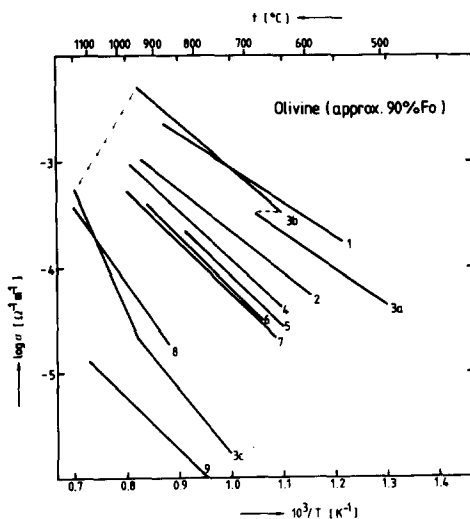

Fig. 5. Comparison of the measured electrical conductivity of olivines (Fo/Fa ca. 90/10 mole %), 1-2 Cemič *et al.* (1980), 3 Duba and Nicholls (1973), 4-6 Hinze *et al.* (1979, 1981), 7 Manko *et al.* (1980), 8 Duba *et al.* (1974), 9 lowest values for forsterite, taken from Figure 2.

olivines would increase their σ values by several orders of magnitude above values taken from olivines in their stability field, i.e. lines 3c and 7. This effect is due to magnetite exsolution. If one is not aware of these oxidizing processes such data could misslead to the assumption that σ could change, say, by three orders of magnitude for natural olivines under the same temperature conditions, however variable pO_2, or more dramatical temperature differences of more than 600 °C may be estimated from a distinct value. Under such circumstances it would be difficult to estimate the temperature profile of the earth if we don't possess any knowledge of the pO_2-depth distribution in the mantle. But for natural environments in the mantle we may conclude that pO_2 values are not higher than given by the Q/Fa/M-buffer. Fortunately under these conditions the influence of pO_2 on σ is much lower as, for instance, has been estimated by Cemič et al. (1980) and is indicated by lines 1 and 2.

Hinze et al. (1979, 1981) have carried out conductivity measurements on powdered olivines from Dreiser Weiher, Germany, at 10 kbar and at different oxygen fugacities fO_2, namely with Fa/Q/M; W/I and at fO_2 of the natural parageneses. The observed σ values were reproducible for up and down cycles within each buffer system. Line 7 is a plot of single crystal data along (100), the most conductive direction in forsterite (Morin et al., 1979) taken by Manko et al. (1980) from San Carlos olivine at 10 kbar and an oxygen fugacity given by the Fa/Q/M-buffer. In relation to our synthetic sample (lines 1 and 2) the conductivity values of these natural olivines are half an order of magnitude lower and the activation energies are higher than those for the synthetic ones. The influence of fO_2 on σ seems to be still more lowered and decreases in relation to synthetic samples. There remains the spread between individual samples and measuring devices.

It is, however, difficult to decide which data are better. Duba and Nicholls (1973) have a good argument on hand for their data (line 3c), which fits Red Sea data (line 8) very well and which is known to have no Fe^{3+} content. In addition, line 3c does not remain under line 9, which represents the lowest σ values of forsterite to be found in the literature (Figure 2).

Unfortunately till now Manko et al. (1980) have not performed measurements on San Carlos olivines at the reducing boundary (W/I-buffer) and along the same direction as Duba and Nicholls (1973) have done. It would be interesting of they could fit into Duba and Nicholl's data line 3c. Such measurements would offer the possibility to decide if both experimental techniques would yield equivalent results.

The strongest arguments on behalf of Cemič et al. (1980) is, firstly, the fact that they were able to recalculate reliable pO_2-values from their σ measurements, and secondly, from their electrical conductivity measurements they calculated the maximum concentration (Fa/Q/M-buffer) of 0.0066 wt % Fe^{3+} in fayalite. This value is in agreement with that of Sockel (1980), which he has estimated by thermogravimetric measurements (personal communication). The reason why the absolute value of σ for synthetic olivines is higher than those for Dreiser Weiher olivines may be due to different trace impurities like hydrogen, which increases the conduction as Morin et al. (1979) have shown. The hydrogen might be incorporated into the synthetic samples by Aerosil (SiO_2-gel) although it was fired before the synthesis of olivines. Another explanation might be found in grain

sizes, which in the case of the synthetic olivines was estimated to be 10 μm, the Dreiser Weiher olivines occured with grain sizes of mm region and San Carlos olivines were available as single crystals. The differences are not due to a_{En} according to Equation (2) since the natural and synthetic samples were equilibrated with enstatite. In any case it is difficult to compare the electrical conductivity values of different samples quantitatively, since the ionic transport in olivine can depend on a subtle balance between different trace impurities as Morin *et al.* (1979) have already stated.

Very recently Arculus and Delano (1980) have estimated the intrinsic oxygen fugacities of spinels selected from Dreiser Weiher peridotites yielding fO_2-values just above the W/I-buffer. As these spinels were grown in equilibrium with their parageneses (olivine, pyroxene) it should show the same oxygen fugacities. Just that was performed in my measurements on the olivines from Dreiser Weiher buffered with their own parageneses (line 5 in relation to lines 6 and 4).

For a second series of spinels separated from peridotites from Mt. Poorndon (Victoria, Australia) Arculus and Delano (1980) estimated an intrinsic oxygen fugacity even below the W/I-buffer. These results indicate that the upper mantle, in the spinel peridotite facies at least, might be heterogeneous with respect to oxidation state or there might be a continuously decreasing pO_2—depth relationship. Since these results are very important in view of the electrical conduction profile in the mantle, further experiments must be performed:

(i) The intrinsic oxygen fugacity—T relationship of further peridotites should be measured to estimate the variability of fO_2 in the mantle, although most basalts show fO_2 values close to the Q/Fa/M-buffer.

(ii) The equilibration temperatures and pressures of those peridotites must be ascertained, to determine the depth of their sources, and

(iii) the electrical conductivity of olivines from such peridotites should be measured in equilibrium with their natural parageneses.

With the aid of these data it should be possible to decide whether the in-situ almost constant resistivity in the mantle down to 800 km (Schmucker 1974) is due to a low temperature gradient or is on the other hand a result of changing pO_2 conditions or other chemical variations.

I guess, in this manner, laboratory electrical conductivity measurements on olivines are still very important. But besides these experiments we need further information to find a basis for a reasonable interpretation of in-situ resistivity data.

Enstatite: The electrical conductivities of single-crystal ortho-pyroxenes were measured by Duba *et al.* (1973), by Olhoeft *et al.* (1974) in vacuum, by Duba *et al.* (1976) and by Huebner *et al.* (1979) at different fO_2. These samples display only slight anisotropy in contrast to the almost-pure forsterite. Conductivities of powdered synthetic pyroxenes are reported by Voigt *et al.* (1979) and on natural pyroxenes from Dreiser Weiher (Eifel/Germany) by Hinze *et al.* (1981). The pyroxenes studied by Huebner *et al.* (1979) and Hinze *et al.* (1981) are notable for their high content of trivalent impurities Al^{3+} and Cr^{3+}; their conductivity is higher than ordinary pyroxene and virtually independent of fO_2. Compilations of most of these data are given by Haak (1981). An interpretation and

discussion of these data would run along the same lines as for olivines. But since our data on synthetic samples are not as extensive as for the olivines, I will not go into further detail.

4. Conclusion

The interpretation of the resistivity distribution in-situ in relation to a temperature distribution in the earth requires knowledge of composition and the oxygen fugacity of the respective layers. In addition we have to estimate the resistivity of rocks and relevant minerals as a function of all thermodynamic variables, which define the respective system. At present it seems that pressure has no significant influence on conductivities except where phase transformations are involved. Temperature, pO_2 and chemical activities of the components are the most important variables. Unfortunately their influences are not very well established in detail. However, experimentalists have started to isolate satisfactorily the important parameters and to account for them separately and to some extent quantitatively. The results are encouraging the further development of conduction theories and laboratory techniques.

Some problems still arise from the nature and concentration of aliovalent ions like Al^{3+}, Fe^{3+}, Mn^{3+}, Mn^{4+}, or especially protons, since their influence on the absolute values of the transport phenomena are sensitive. However, there are now laboratory techniques available for the detection of such trace impurities. Therefore we can hope to evaluate their influence on the electrical conductivity too.

Nevertheless we need further developments in the experimental techniques for conductivity measurements under higher pressures and temperatures than we can perform up to now, i.e. the gas vessels have to be operated at higher pressures and for solid media devices the available temperature region must be increased. The developments should be done in parallel, since both techniques have their own advantages, but there are also limitations for both: the solid-media cell allows the measurement of electrical conductivities of minerals as a function of p, T, pO_2 and a_i of the components of the minerals. But during one measuring cycle the pO_2 is defined by the solid state buffer mixture as a function of p and T, and thus cannot be changed at will. One has, therefore, to perform several independent measurements with different buffers in order to scan and evaluate a functional relationship between σ and pO_2.

For gas vessels this handicap can be droped, since it is possible to adjust to any pO_2 value at will. On the other hand it would be difficult to define the chemical activities a_i in the sample during conductivity measurements in a gas apparatus, which, without doubt, can be performed easily in a solid media cell.

But up to now the application of laboratory results for a particular set of samples to the interpretation of geophysical data should be done with care. It is my suggestion that it would be better for such purposes to study natural minerals under the environmental conditions. But in that case it is necessary to evaluate these conditions independently.

Acknowledgement

References

Akimoto, S. I. and Fujisawa, H.: 1965, 'Demonstration of the Electrical Conductivity Jump Produced by the Olivine-Spinel Transition', *J. Geophys. Res.* **70**, 443–449.

Allen, J. C. and Boettcher, A. L.: 1978, 'Amphiboles in Andesite and Basalt: II. Stability as a Function of p-T-fH_2O-fO_2', *Amer. Mineral.* **63**, 1074–1087.

Arculus, R. J. and Delano, J. W.: 1980, 'Intrinsic Oxygen Fugacities of the Earth's Mantle: A New Approach and Results for Spinel Peridotites', in *Lunar and Planetary Science XI*, 28–30.

Beblo, M. and Björnsson, A.: 1978, 'Magnetotelluric Investigation of the Lower Crust and Upper Mantle Beneath Iceland', *J. Geophys.* **45**, 1–16.

Bradley, R. S., Jamil, A. K., and Munro, D. C.: 1964, 'The Electrical Conductivity of Olivine at High Temperatures and Pressures', *Geochim. Cosmochim. Acta* **28**, 1669–1678.

Bradley, R. S., Milnes, G. J., and Munro, D. C.: 1973, 'The Electrical Conductivities at Elevated Temperatures and Pressures of Polycrystalline Manganese, Cobalt, and Nickel Orthosilicates', *Geochim. Cosmochim. Acta* **37**, 2379–2394.

Buening, D. K. and Busek, P. R.: 1973, 'Fe-Mg Lattice Diffusion in Olivine', *J. Geophys. Res.* **78**, 6852–6862.

Carmichael, J. S. E., Turner, F. J., and Verhoogen, J.: 1974, *Igneous Petrology*, New York, McGraw Hill Book Company.

Cemič, L., Will, G., and Hinze, E.: 1980, 'Electrical Conductivity Measurements on Olivines Mg_2SiO_4-Fe_2SiO_4 Under Defined Thermodynamic Conditions', *Phys. Chem. Minerals* **6**, 95–107.

Duba, A.: 1972, 'Electrical Conductivity of Olivine'. *J. Geophys. Res.* **77**, 2483–2495.

Duba, A.: 1976, 'Are Laboratory Electrical Conductivity Data Relevant to the Earth?' *Acta Geodaet., Geophys. et Montanist. Acad. Sci. Hung.* **11**, 485–495.

Duba, A. and Nicholls, I. A.: 1973, 'The Influence of Oxidation State on the Electrical Conductivity of Olivine', *Earth and Planet. Sci. Lett.* **18**, 59–64.

Duba, A., Boland, J. N., and Ringwood, A. E.: 1973, 'Electrical Conductivity of Pyroxenes', *J. Geol.* **81**, 727–735.

Duba, A., Ito, J., and Jamieson, J. C.: 1973, 'The Effect of Ferric Iron on the Electrical Conductivity of Olivine', *Earth and Planet. Sci. Lett.* **18**, 279–284.

Duba, A., Heard, H. C., and Schock, R. N.: 1974, 'Electrical Conductivity of Olivine at High Pressure Under Controlled Oxygen Fugacity', *J. Geophys. Res.* **79**, 1667–1673.

Duba, A., Piwinskii, A. J., Heard, H. C., and Schock, R. N.: 1976, 'The Electrical Conductivity of Forsterite, Enstatite, and Albite', in Strens, R. G. J. (ed.), *The Physics and Chemistry of Minerals and Rocks*, London, Wiley and Sons, 249–260.

Dvořák, Z. and Schloessin, H. H.: 1973, 'On the Anisotropic Electrical Conductivity of Enstatite as a Function of Pressure and Temperature', *Geophys.* **38**, 25–36.

Dyal, P. and Parkin, G. W.: 1971, 'The Apollo 12 Magnetometer Experiment: Internal Lunar Properties from Transient and Steady Magnetic Field Measurements', in Levinson, A. A. (ed.), *Proceedings of the Second Lunar Science Conf.*, MIT Press, 3, 2391–2413.

Green, D. H. and Ringwood, A. E.: 1967, 'The Genesis of Basaltic Magmas', *Contr. Mineral. Petrol.* **15**, 103–190.

Greskovitch, C. and Schmalzried, H.: 1970, 'Nonstoichiometry and Electronic Defects in Co_2SiO_4 and in $CoAl_2O_4$-$MgAl_2O_4$ Crystalline Solutions', *J. Phys. Chem. Solids* **31**, 639–646.

Haak, V.: 1980, 'Relations Between Electrical Conductivity and Petrological Parameters of the Crust and Upper Mantle', *Geophys. Surveys* **4**, 57–69.

Haak, V.: 1981, 'Electrical Conductivity of Minerals and Rocks at High Temperatures and Pressures', *Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaft und Technik* (in preparation).

Hamilton, R.M.: 1965, 'Temperature Variation at Constant Pressures of the Electrical Conductivity of Periclase and Olivine', *J. Geophys. Res.* **70**, 5679–5692.

Hamilton, D. L. and Anderson, G. M.: 1967, 'Effects of Water and Oxygen Pressures on the Crystallization of Basaltic Magmas', in Hess, H. H. and Poldervaart (eds.), *Basalts, the Poldervaart Treatise on Rocks of Basaltic Composition* New York, J. Wiley and Sons, **1**, 445–482.

Hinze, E., Will, G., and Cemič, L.: 1979, 'Electrical Conductivity Measurements on Synthetic Olivines and on Olivine, Enstatite, and Diopside from Dreiser Weiher Eifel/Germany Under Defined Thermodynamic Activities as a Function of Temperature and Pressure', A paper, presented at the XVII General Assembly of IUGG, Canberra.

Hinze, E., Will, G., and Cemič, L.: 1981, 'Electrical Conductivity Measurements on Synthetic Olivines and on Olivine, Enstatite, and Diopside from Dreiser Weiher, Eifel/Germany Under Defined Thermodynamic Activities as a Function of Temperature and Pressure', *Phys. Earth Planet. Interiors* **25**, 245–254.

Huebner, J. S., Duba, A., and Wiggins, L. B.: 1979, 'Electrical Conductivity of Pyroxene Which Contains Trivalent Cations: Laboratory Measurements and the Lunar Temperature Profile', *J. Geophys. Res.* **84B**, 4652–4656.

Hunt, G. R., Johnson, G. R., Olhoeft, G. R., Watson, D. E., and Watson, K.: 1979, 'Initial Report of the Petrophysics Laboratory', Geol. Survey Circular 789, Denver, Colorado.

Keller, G. V., and Frischknecht, F. C.: 1979, 'Electrical Methods in Geophysical Prospecting', *International Series in Electromagnetic Waves* **10**, Oxford, Pergamon Press.

Manko, M., Hinze, E., and Will, G.: 1980, 'Die elektrische Leitfähigkeit und ihre Frequenzabhängigkeit, gemessen an synthetischen und natürlichen Olivinen', in Haak, V. and Homilius, J. (eds.), *Protokoll über das Kolloquium 'Elektromagnetische Tiefenforschung'*, Berlin, Niedersächsisches Landesamt für Bodenforschung, Hannover, 103–110.

Mao, H. K., and Bell, P. M.: 1972, 'Electrical Conductivity and the Red Shift of Absorption in Olivine and Spinel at High Pressure', *Science* **176**, 403–406.

Meredith, R. E., and Tobias, Ch. W.: 1962, 'Conduction in Heterogeneous Systems', in: Tobias, Ch. W. (ed.), *Advances in Electrochemistry and Electrochemical Engineering*, New York, Interscience, **2**, 15–47.

Middlemost, E. A. K.: 1975, 'The Basalt Clan', *Earth-Science Rev.* **11**, 337–364.

Morin, F. J., Oliver, J. R., and Housley, R. M.: 1979, 'Electrical Properties of Forsterite, Mg_2SiO_4, II', *Phys. Rev. B.* **19**, 2886–2894.

Nitsan, U.: 1974, 'Stability Field of Olivine With Respect to Oxidation and Reduction', *J. Geophys. Res.* **79**, 706–711.

Olhoeft, G. R.: 1976, 'Electrical Properties of Rocks', in Strens, R. G. S. (ed.), *The Physics and Chemistry of Minerals and Rocks*, London, John Wiley and Sons, 261–278.

Olhoeft, G. R., Frisillo, A. L., Strangway, D. W., and Sharpe, H.: 1974, 'Temperature Dependence of Electrical Conductivity and Lunar Temperatures', *The Moon* **9**, 79–87.

Parkhomenko, E. I., 1967, *Electrical Properties of Rocks*, Plenum Press, New York.

Parkin, T.: 1972, 'The Electrical Conductivity of Synthetic Forsterite and Periclase', Thesis, University of Newcastle upon Tyne.

Pluschkell, W., and Engell, H. J.: 1968, 'Ionen- und Elektronenleitung im Magnesiumorthosilikat', *Ber. Dtsch. Keram. Ges.* **45**, 388–394.

Schmalzried, H.: 1965, 'Point Defects in Ternary Ionic Crystals', in Reiss, H. (ed.), *Progress in Solid State Chemistry* **2**, Oxford, Pergamon Press, 265–303.

Schmalzried, H., and Navrotsky, A.: 1975, *Festkörperthermodynamik, Chemie des Festen Zustandes*, Weinheim, Verlag Chemie GmbH.

Schmucker, U.: 1979, 'Erdmagnetische Variationen und die elektrische Leitfähigkeit in tiefen Schichten der Erde', in K. H. Olsen (ed.), *Sitzungsberichte und Mitteilungen der Braunschweigischen Wissenschaftlichen Gesellschaft*, Verlag Erich Goltze GmbH und Co, Göttingen, 45–102.

Schock, R. N., Duba, A., Heard, H. C., and Stromberg, H. D.: 1977, 'The Electrical Conductivity of Polycrystalline Olivine and Pyroxene Under Pressure', in Murli H. Manghnani and Syun-Iti Akimoto

(ed.), *High Pressure Research, Applications in Geophysics*, New York, Academic Press, Inc., 39–51.

Schult, A., and Schober, M.: 1969, 'Measurements of Electrical Conductivity of Natural Olivines at Temperatures up to 950 °C and Pressures up to 42 kbar', *Z. Geophysik* 35, 105–112.

Schwab, R. G. and Söhnlein, G.: 1977, 'Homogene und heterogene Redoxgleichgewichte des Fayalits', *N. Jb. Miner. Abh.* 129, 15–31.

Shankland, T. J.: 1969, 'Transport Properties of Olivines', in Runcorn, S. K. (ed.), *The Application of Modern Physics to the Earth and Planetary Interiors*, Wiley-Interscience, New York, 175–190.

Shankland, T. J.: 1975, 'Electrical Conduction in Rocks and Minerals: Parameters for Interpretation', *Phys. Earth and Planet. Interiors* 10, 209–219.

Shankland, T. J. and Waff, H. S.: 1977, 'Partial Melting and Electrical Conductivity Anomalies in the Upper Mantle', *J. Geophys. Res.* 82, 5409–5417.

Smykatz-Kloss, W.: 1974, 'Differential Thermal Analysis, Application and Results in Mineralogy', Springer Verlag, Heidelberg.

Smyth, D. M. and Stocker, R. L.: 1975, 'Point Defects and Nonstoichiometry in Forsterite', *Phys. Earth Planet. Interiors* 10, 183–192.

Sockel, H. G.: 1974, 'Defect Structure and Electrical Conductivity of Crystalline Ferroussilicate', in Schmelzer, M. S., Jaffe, R. J. (eds.), *Defects and Transport in Oxides*, New York, Plenum Press, 341–355.

Sockel, H. G.: 1980, Private communication.

Stegena, L.: 1976, 'Electrical Conductivity Structure and Geothermal Reservoirs', *Acta Geodaet. Geophys. et Montanist. Acad. Sci. Hung.* 11, 377–397.

Stocker, R. L.: 1978a, 'Point-Defect Formation Parameters in Olivine', *Phys. Earth Planet. Interiors* 17, 108–117.

Stocker, R. L.: 1978b, 'Influence of Oxygen Pressure on Defect Concentrations in Olivine With a Fixed Cationic Ratio', *Phys. Earth Planet. Interiors* 17, 118–129.

Stocker, R. L.: 1978c, 'Variation of Electrical Conductivity in Enstatite With Oxygen Partial Pressure: Comparison of Observed and Predicted Behavior', *Phys. Earth. Planet. Interiors* 17, P34-P40.

Stocker, R. L. and Smyth, D. M.: 1978, 'Effect on Enstatite Activity and Oxygen Partial Pressure on the Point-Defect Chemistry of Olivine', *Phys. Earth Planet. Interiors* 16, 145–156.

Voigt, R., Seifert, K. -F., and Will, G.: 1979, 'Die elektrische Leitfähigkeit von Pyroxenen der Reihe $MgSiO_3$-$FeSiO_3$ bei 10 und 20 kbar unter definierten thermodynamischen Bedingungen', *N. Jb. Mineral. Mh. Jg.* 1979, 296–308.

Waff, H. S.: 1974, 'Theoretical Consideration of Electrical Conductivity in a Partially Molten Mantle and Implications for Geothermetry', *J. Geophys. Res.* 79, 4003–4010.

Will, G., Cemič, L., Hinze, E., Seifert, K. -F., and Voigt, R.: 1979, 'Electrical Conductivity Measurements of Olivines and Pyroxenes Under Defined Thermodynamic Activities as a Function of Temperature and Pressure', *Phys. Chem. Mineral.* 4, 189–197.

Wones, D. R., and Gilbert, M. C.: 1969, 'The Fayalite-Magnetite-Quartz Assemblage Between 600° and 800 °C, *Amer. J. Sci.* 267A, 480–488.

Wyllie, P. J.: 1979, 'Magmas and Volatile Components', *Amer. Mineral.* 64, 469–500.