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ELECTRICAL CONDUCTION IN ROCKS AND MINERALS: PARAMETERS FOR INTERPRETATION

T.J. SHANKLAND*

Department of Geological Sciences and Center for Earth and Planetary Physics, Harvard University, Cambridge, Mass. (U.S.A.)

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Recent studies of electrical properties have clarified the important parameters governing electrical conductivity in minerals – temperature, oxygen fugacity, stoichiometry, iron content – and in porous rocks – shape and interconnections of fluid-filled pore spaces. These parameters are discussed in terms of: (1) how they contribute to bulk conduction mechanisms within minerals; and (2) how they pertain to the conditions of rocks in situ.

1. Introduction

Most of the parameters governing electrical conduction in rocks and minerals have been known for some time, but it has usually been difficult to separate their different effects. Substantial compilations of electrical conduction in rocks and minerals are available (e.g., Keller, 1966, 1967; Keller and Frischknecht, 1966; Parkhomenko, 1967), but I believe 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. The purpose of this paper is to discuss some recent advances in order to clarify their application to field studies as well as to identify some remaining restrictions. This discussion considers only low-frequency (d.c. –1,000 Hz) conduction, the circumstance most common in terrestrial field work, although there are many instances in which high-frequency dielectric measurements can improve interpretations or be useful probes of extraterrestrial material.

Laboratory studies have two obvious applications. In common with all experimental work we must ask:

(1) Are the measurements made under conditions which are repeatable, where the important variables can be identified, and which lead to a physical model? Clearly a physical model of electrical conduction is necessary if we are to interpolate/extrapolate to pressure or temperature conditions apart from those that are measured. The second question is latent in laboratory studies of all physical properties, but is faced too rarely:

(2) Is there any assurance that electrical conduction in a laboratory sample duplicates conduction in rocks or minerals in situ? We can be less certain of this condition because electrical properties are so much more sensitive to trace impurities, grain boundaries, or the presence of water than are other properties such as thermal conductivity or elasticity. Again, a physical model is essential to evaluating this question.

For an individual mineral, the most important variables in determining electrical conduction are temperature T, the partial pressure or fugacity of oxygen, f_{O_2}, and the content of transition metal ions – which in practical terms means iron because of its greater abundance. Effects of orientation, twinning, order – disorder, have also been observed.

In rocks, one approach is the calculation of conductivity from conductivities of the composite minerals, e.g., using methods of Landauer (1952) or Waff (1974). However, we can take advantage of the high contrast between conducting interstitial fluids and relatively insulating mineral grains in rocks at low temperatures, in which case the important variables become the amount and shape of porous volume and the properties of the internal fluids like water solutions or partial melts.

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[*] Present address: Geosciences Group, Los Alamos Scientific Laboratory, Los Alamos, N.M. 87545, U.S.A.

With good control of experimental atmosphere another issue becomes investigation of the "natural" condition of minerals. For example, in pyroxenes there is appreciable evolution of water vapor from the sample on initial heating (Duba et al., 1973; Olhoeft et al., 1974) Monitoring conductivity during the initial heating period reveals a scattered trajectory on a $\sigma - T^{-1}$ plot, presumably evidence for irreversible removal of frozen-in defects and traps which may have been acquired since cooling as the result of strain release, creep, radiation damage, or exsolution lamellae. Reequilibration of lamellae acquired during geologic time is not possible in the laboratory so that the relatively small changes that occur when they are annealed out cannot be reversed. Samples such as surface lunar rocks which have acquired frozen-in radiation defects over a long time at low temperatures can present severe problems in interpretation of field data.

While it seems likely that annealed laboratory samples can achieve consistency and can represent the conductivity of high-temperature minerals in situ under similar conditions, these annealed samples that have irreversibly lost their out-of-equilibrium defects on heating should only rarely be representative of cold crustal minerals.

The question of oxygen fugacity in different regions of the mantle is still an uncertain one. Whether the relatively high oxidation state evidenced by electrical conduction in most terrestrial olivine and pyroxene compared to lunar material is a feature acquired near the earth's surface or is a property of at least the upper mantle is a matter for reasonable discussion. It can be seen from Fig. 1 that at constant conductivity a lower temperature would be inferred for an olivine under high f_{O_2} than for one under reducing conditions (Duba and Nicholls, 1973) – all within the olivine stability field of Fig. 2. Nitsan (1973b) argued that high fugacity in the upper mantle is consistent with the observed high oxidation state in olivines from peridotite bombs and other presumed samples of upper mantle and with relatively low temperatures which might be expected in a convecting mantle (Bott, 1967; Tozer, 1972). On the other hand, Boyd (1973) infers from the petrology of kimberlite pipes an upper mantle above 1,600°C in accord with the Duba and Nicholls' (1973) temperatures from olivine conductivity; but Boyd also suggests that kimberlite source regions may have unusually high local shear heating. For the moon, it is possible to make a strong case that highly reducing conditions prevail (Burns et al., 1972; Duba and Ringwood, 1973).

Knowledge of fugacity also suggests that kinks such as that seen in Red Sea peridot near 1,500°C, Fig. 1 (Duba et al., 1974) arise when the crystal crosses a boundary into a different region of its stability field (Nitsan, 1974).

Despite its obvious importance in the mantle, pressure is not listed as a parameter here because large experimental discrepancies remain. Polycrystalline samples often show strong pressure effects (Bradley et al., 1964; Mao and Bell, 1972), particularly at the olivine–spinel phase change (Akimoto and Fujisawa, 1965). However, single-crystal measurements have pressure shifts comparable with temperature shifts caused by temperature uncertainties (Duba et al., 1974) or leakage current uncertainties (Hughes, 1955). Additional complications arise if heater parts, especially graphite, are close enough to alter the oxygen fugacity. Hence, pressure measurements remain a particularly thorny experimental problem and will benefit from still more-refined methods of temperature and fugacity control for single crystals at high pressure.

2.3. Effects of orientation and iron content

Even without the clarifications resulting from the use of controlled oxygen fugacity, there appears to be only a weak dependence of conduction upon crystal orientation. Thus, in olivine anisotropies are less than a factor of 2 (in unknown atmosphere, or air: Kobayashi and Maruyama, 1971; Duba, 1972) although there seems no agreement on which direction has the highest σ. Anisotropy is larger for pyroxene, by a factor of two to 10 between different directions (Dvorak and Schloessin, 1973). Duba et al. (1973) have the c-axis as the maximum-σ direction in a controlled atmosphere, whereas Hughes (1953 and given by Duba et al., 1973) gives the principal direction along the b-axis for measurements in air.

Iron content is considered below, but the main effect in olivine of increased Fe/(Mg + Fe) is an increase of σ_0 and of E at low temperatures (Hamilton, 1965) and mainly of σ_0 above 1,300°C (Kobayashi and Maruyama, 1971; Duba, 1972). Effects of varying iron content in single crystals under controlled f_{O_2} remain to be clarified.

2.4. Mechanisms of conduction in minerals

This section deals with application (1), understanding conduction in minerals. Knowledge of the conduction mechanism requires at least a knowledge of the identity of the carrier, the magnitude and sign of its charge q and preferably the number n of carriers per unit volume, and their mobility μ. Mobility is the drift velocity per unit applied field and has the traditional units cm^2 V^{-1} sec^{-1}. The conductivity is then:

$$\sigma_i = n_i q_i \mu_i \qquad (2)$$

for the i^{th} conduction mechanism. Because equations of the form of eq. 1 apply to charge transport by ions and vacancies or by electrons and holes, conductivity measurements by themselves are insufficient for unambiguous determination of carrier species. Despite the significant progress in understanding conduction processes in minerals, if we wish to discuss mechanisms in *single crystal* samples of minerals at known fugacity, we find that the needed measurements are yet to be accomplished:

(1) Nevertheless, some suggestions are present in existing data, and it is worthwhile to list the techniques in the hope that they will be used in the future.

The Hall effect (McKelvey, 1966, chapter 9) together with conductivity can provide the carrier sign and the Hall mobility μ_H which is usually comparable to or greater than the drift mobility μ in (2). Though unable to detect a Hall effect in synthetic single crystals of forsterite, Wilson (1965) and Shankland (1969) calculated upper limits of 10^{-2} cm^2 V^{-1} sec^{-1} at 293°K and 10 cm^2 V^{-1} sec^{-1}at 1,000°K respectively. Schober (1971) measured a negative Hall effect in the range 200–600°C in a hot-pressed polycrystalline olivine of 9% fayalite; his μ_H at 400° was 10^{-2} cm^2 V^{-1} sec^{-1} and rising with temperature. The fact that Schober obtained comparable conductivity in a single-crystal olivine of 12% fayalite tends to support this determination of a negative carrier. However, the magnitude of the conductivity (measured in a high-pressure apparatus) was greater by an order of magnitude than Duba and Nicholl's (1973) most-oxidized single crystal.

For a sample in a thermal gradient it is possible to measure a thermoelectric effect: the charge of the most mobile carrier is that of the voltage polarity of the lower-temperature electrode. The negative thermoelectric power obtained by Wilson (1965) in sintered synthetic forsterite, by Schober (1971) above 600°C in sintered olivine, and by Bradley et al. (1964) in sintered fayalite at 200–400°C are consistent with negative carriers. Wilson was not able to measure a thermo-emf in single-crystal forsterite, an observation that sustains doubts about the similarity of conduction mechanisms in sintered and single-crystal samples. The lack of f_{O_2} control during these measurements makes their redetermination a matter of greatest importance.

Photoconductivity measurements using vacuum-ultraviolet light (Nitsan and Shankland, 1971; Nitsan, 1973a) showed a polarity consistent with electrons as carriers in forsterite and olivine, but these measurements were at room temperature and constrained to measure only electron/hole rather than ion-vacancy transport. Hence, the application to high-temperature measurements remains to be determined.

Von Pluschkell and Engell (1968) investigated conductivity in synthetic sintered forsterite of density 5–18% less than theoretical, and their results merit repeating with single crystals. Even though Parkin (1972) in his experiment found little similarity between sintered and single-crystal forsterite some observations of Von Pluschkell and Engell are worth recounting, because they illustrate a thorough approach. Their measurements were all in the high temperature regime, 1,000–1,600°C. First, by measuring the emf of a cell composed of MgO-rich forsterite against a cell of SiO_2-rich forsterite they established that Mg is more mobile than Si, at least for f_{O_2} greater than 10^{-4} atm. in their sintered samples. Further, they determined the emf of a forsterite cell having different oxygen pressures on opposite sides of the sample and obtained a result consistent with ionic conduction in the high temperature range regardless of whether the stoichiometry was Mg- or Si-rich. Another significant observation is a jump in conductivity of more than two orders of magnitude when the Mg/Si ratio decreases below 2, the stoichiometric value. They found this result to agree with high solubility of SiO_2 in Mg_2SiO_4 where Si is in tetrahedral interstitial positions in which it tends to link together the isolated silicate tetrahedra of Mg_2SiO_4 into a configuration similar to that in $MgSiO_3$. Their suggested reaction is:

$$2SiO_2 \rightleftharpoons Mg_2SiO_4 + 2V''_{Mg} + Si_I^{\bullet\bullet\bullet\bullet} \quad (3)$$

in which Mg vacancies V''_{Mg} are the carriers at high T and high f_{O_2}. In this notation, $^{\bullet}$ implies a positive charge with respect to the normal charge of the ion in the lattice and $'$ implies a negative charge.

At this point there is enough evidence to show in Table I some possible parameters, not including pressure, that are important in conduction in single crystals of olivine and pyroxene divided into regions of high and low magnitude. The boundaries are somewhat arbitrary and not independent; for instance, the high/low temperature boundary tends to rise with increasing iron content; there may be more than 2 regions of Fe-effects; and the f_{O_2} boundary differs in olivine and pyroxene. In practice the boundaries are interpreted as changes of conduction mechanism. Since there are 2^4 possible combinations, it is not surprising that no single experimenter has covered them all; in particular, insufficient information about f_{O_2} and Mg/Si stoichiometry may be to blame for the relatively rare occurrence of agreement between different experiments. Enough statements have been made during more than two decades of electrical measurements that some of them have to be correct, but the experimental evidence must remain sketchy until more, admittedly difficult, transport measurements can be obtained on single crystals at known fugacity. However, with the knowledge of these parameters that is emerging the subject of electrical conduction in minerals is moving toward firmer ground, and some old uncertainties will be resolved.

(2) If we examine the explicit dependence upon f_{O_2} at constant temperature as shown in Fig. 3 for pyroxene, some consistent results appear. First, in the low f_{O_2} range, the decrease of σ with f_{O_2} is also shown in the single crystal silicates as well as Von Pluschkell and Engell's (1968) SiO_2-rich synthetic specimens and in MgO (Osburn and Vest, 1971; Parkin, 1972). Doubly ionized oxygen vacancies are expected to yield $\sigma \propto (f_{O_2})^{-1/6}$ (Osburn and Vest, 1971; Parkin, 1972; Smyth and Stocker, 1975). At low f_{O_2} Parkin's data seem closest to providing a slope of $-\frac{1}{6}$ in forsterite; while for pyroxene (Fig. 3) the low f_{O_2} points mostly have a shallower depth that this. Second, Parkin's samples of iron fraction less than 0.1% are independent of f_{O_2} in the *high* fugacity region, consonant with an intrinsic mechanism such as formation of a Mg interstitial and vacancy from Mg at a lattice site:

$$Mg_M \rightleftharpoons Mg_I^{\bullet\bullet} + V''_{Mg} \quad (4)$$

(Smyth and Stocker, 1975); whereas his samples containing more than 0.1% Fe in the high-T, high f_{O_2} range show slopes of log σ on the order of $\frac{1}{6}$–$\frac{1}{4}$. These increases are consistent with oxidation of ferrous to ferric iron in a reaction such as:

$$2Fe \rightleftharpoons 2Fe^{\bullet} + V''_{Mg} \quad (5)$$

Smyth and Stocker (1975) have elaborated the changes

TABLE I
Parameters in mineral conductivity

low T	1,000–1,300°C	high T
low f_{O_2}	10^{-10}–10^{-5} atm	high f_{O_2}
low Mg/Si	2	high Mg/Si
low Fe/(Mg + Fe)	0.1%–30%	high Fe/(Mg + Fe)

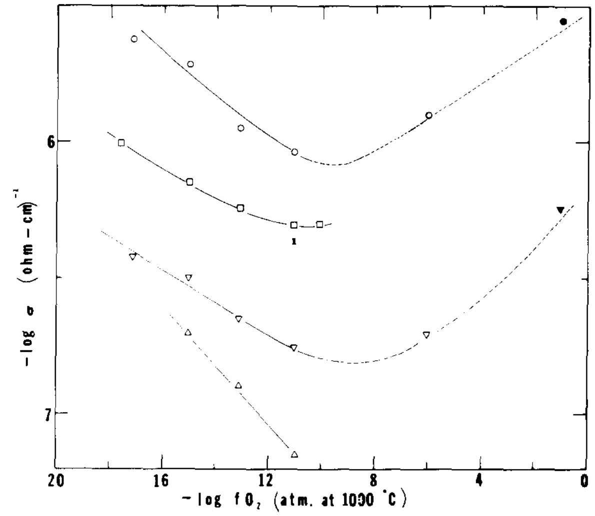


Fig. 3. Log-log plot of σ vs. f_{O_2} at 1,000°C in pyroxenes of various orientations: × = (010); ○ = (001); □ = (100); ∇ = (010); Δ = unoriented. The two upper curves and point × are for a sample having Fe/(Mg + Fe) ≃ 14%; the two lower curves are for samples of about 8% Fe/(Mg + Fe). Lines are dashed for $f_{O_2} \gtrsim 10^{-10}$ due to lack of data and uncertainty of exact fugacity in the air measurement, indicated by the solid symbols (Duba et al., 1973).

in the olivine lattice which are necessary to produce this reaction and show that the number of Mg-site vacancies is proportional to $f_{O_2}{}^{1/6}$, a result also obtained from a simpler consideration of reaction 5 (e.g., Buening and Buseck, 1973). In some of his measurements at high f_{O_2}, Parkin (1972) obtained slopes closer to $\frac{1}{4}$, a suggestion of singly ionized defects or of defect association (Fig. 4).

Most of the discussion so far is concerned with conduction mechanisms at high temperature. It is a frequent interpretation of the low temperature region, below 900–1,000°C, that the carriers are electronic (e.g., Bradley et al., 1964, 1973; or Mao and Bell, 1972 for fayalite). Parkin (1972) has discussed this conduction mechanism arising from ionized defects and Nitsan (1973a) has related the association of electronic carriers with Fe^{3+}, that is $Fe^{\bullet}$, to the optical properties of minerals. Nitsan discussed the arguments for conduction by a small polaron, i.e., an electron or hole tightly bound to a defect such as $Fe^{\bullet}$ and indicated that an electron ionized from an $(Fe^{\bullet})_2V''_{Mg}$ complex could have a conductivity increasing as $f_{O_2}{}^{1/6}$. The polaron "hops" by thermal excitation within a narrow band of d electrons and its strong association with a defect accounts for the difficulty in observing photoconductivity with ultraviolet light (Wilson, 1965; Hughes, 1953). The subject of hopping conduction in narrow bands in ordered and disordered materials is a topic of some interest and debate in materials sciences (e.g., Austin and Mott, 1970; Adler and Feinleib, 1970; Mott and Davis, 1971) and it should find application to minerals.

If electrons or holes can move in the broad conduction or valence bands, respectively, then they are likely to have high mobilities. Recent optical measurements have delineated the separation of these bands in a range of possible mantle phases (Nitsan, 1973a; Nitsan and Shankland, in preparation); the separation between the bonding oxygen 2p orbitals and the antibonding cation 3s or 4s orbitals is roughly given by a sharp reflectivity peak. Table II gives the energies of these peaks and it is seen that neither phase transitions nor chemical substitution can lower the separation between these bands much below 8 eV in mantle silicates. Nitsan (1973a) has demonstrated that intrinsic semiconduction by electron and holes in these bands requires impossibly high mobilities to account for existing silicate conductivities. If this mode of conduction is not permitted under mantle conductions (Shankland, 1968) and if ionic conductivity is squeezed out by pressure (Tozer, 1959), the mechanism of electron-hole hopping in narrow d bands becomes a process to be considered especially seriously for the deep mantle.

(3) The possibility of hopping conductivity by electrons or holes is relevant to discussing the last parameter in Table I, the effect of transition metal concentration, represented mainly by iron. If conduction proceeds by such an exchange in the reaction:

$$Fe^{\bullet}_{M} + e' \rightleftharpoons Fe_{M} \qquad (6)$$

as it probably does in iron-rich minerals known to have both ferrous and ferric ions such as magnetite and fayalite, then one might expect to have a threshold effect with a sharp drop in σ when the Fe ions become sufficiently dispersed that there are no longer continuous connections of next-nearest neighbor Fe

TABLE II

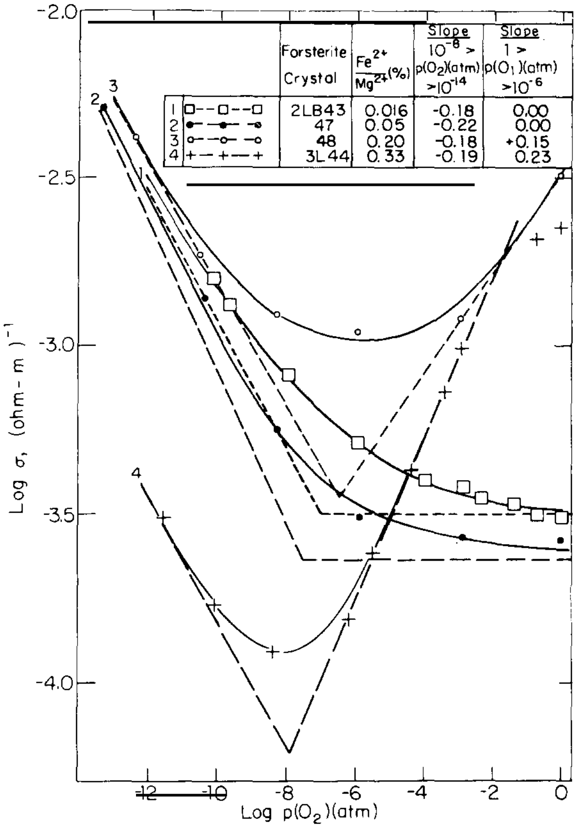
Band gap energies (eV). Chemical charge varies from the left to the right, structural charge varies from the top to the bottom

Oxides:							
SiO_2	10.5	}→	{$MgSiO_3$	8.7	→	Fe_2SiO_4	7.8
MgO	7.8		Mg_2SiO_4	8.6		↓	
Al_2O_3	9.3	}→	$MgAl_2O_4$	8.2	→	$SiFe_2O_4$	7.5
CaO	6.8						
FeO	6.6		$(Mg_{0.46}Fe_{0.43}Ca_{0.11})_3Al_2Si_3O_{12}$				8.8
SiO_2 (quartz, 4-fold)	10.5						
↓							
SiO_2 (stishovite, 6-fold)	~9.2						

From Nitsan and Shankland (in preparation).

ions in the crystal. Percolation theory (Kirkpatrick, 1973) predicts just such a concentration threshold, above which there is an abrupt rise in the probability of continuity across a cluster of conducting elements; Tolland and Strens (1972) infer such a transition between 20 and 50% fayalite in the forsterite–fayalite series at low temperatures. Also, Shankland (1969) noted the existence of qualitative changes in conduction mechanism in sintered FeO–MgO mixes as observed by Hansen and Cutler (1966) between 14 and 18% Fe/(Mg + Fe) – percolation theory (Shante and Kirkpatrick, 1973) predicts a critical fraction of 20% for the face-centered-cubic cation sublattice – and between 0–1% fayalite in the sintered measurements of Bradley et al. (1964). However, all these measurements are on sintered samples and the conclusions must be verified for single crystals, a reservation that applies to most of the interpretations presented so far.

The only single-crystal measurements which indicate qualitative changes with composition at controlled oxygen fugacity are those of Parkin (1972) in the high temperature regime, whose forsterite conductivities have different f_{O_2} dependences between 0.05% and 0.20% fayalite content (Fig. 4).



		Forsterite Crystal	$\frac{Fe^{2+}}{Mg^{2+}}$(%)	Slope $10^{-8} >$ p(O_2)(atm) $>10^{-14}$	Slope 1 > p(O_1)(atm) $>10^{-6}$
1	□--□--□	2LB43	0.016	-0.18	0.00
2	●—●— ●	47	0.05	-0.22	0.00
3	○—○— ○	48	0.20	-0.18	+0.15
4	+—+—+	3L44	0.33	-0.19	0.23

Fig. 4. Dependence of conductivity upon f_{O_2} in forsterite at 1,422°C. Despite the low overall Fe-content, the relatively Fe-rich samples behave differently at higher f_{O_2} than the lowest Fe-containing samples. From Parkin (1972).

2.5. Parameters determining electrical conduction in rocks

In a recent review, Brace (1971) discussed laboratory measurements of conductivity in fluid-saturated and dry rocks and illustrated the effects of porosity, pressure, temperature, and pore fluid on resistivity models of three continental regions. In this section I would like to discuss some models of fluid-saturated rock in order to isolate some of the variables which define porosity.

As an example, consider the modeling of conduction through a network of interconnected cracks and pores *saturated* with a highly conducting fluid such as water or partial melt and imbedded in a matrix of insulating mineral grains. The conductivity of such a mixture is usually described by Archie's law:

$$\sigma/\sigma_0 = \eta^r \qquad (7)$$

where σ_0 is the conductivity of the pore fluid, η the porosity, and r an exponent commonly of order 1–2 (Keller, 1967). Because the interconnections between conducting elements are visible and variable, resistor arrays have often been used to model conduction in porous and/or cracked rocks containing a conducting fluid (Fatt, 1956; Greenberg and Brace, 1969). Fig. 5 depicts results from an array of 2,340 resistors from which the branches or bonds were removed at random to simulate changes of porosity; the fraction $p = p_b$ of remaining branches is analogous to certain kinds of porosity. Kirkpatrick (1971, 1973) has established the correspondence between p_b of an array and the fraction η of conducting volume in an insulator–conductor composite as calculated by effective medium theory (Landauer, 1952). Two interesting features of the array are apparent: one is the linear slope of the conductance G, normalized to G_0 ($p_b = 1$); and the other is the existence of the threshold or critical fraction p_{cb} of branches, two separate effects which can

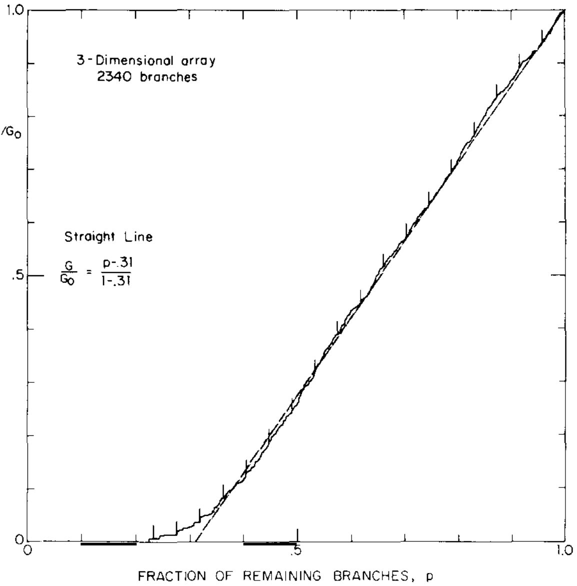


Fig. 5. Normalized conductance of a resistor array showing threshold effect and linear slope (Shankland and Waff, 1974).

be isolated in arrays. A critical fraction exists in both cases, and the conductance is given by:

$$G/G_0 = [(p - p_0)/(1 - p_0)]^r \qquad (8)$$

Here p_0 is determined by the straight-line intercept 0.31 in Fig. 5; p_0 is above $p_{cb} = 0.25$ for the simple cubic array.

A correspondence between p and η tells us two things. First, in cases where $r = 1$ such as saturated dilatant rocks below the yield point or in fractured rock (Brace and Orange, 1968; Brace, 1971) the *measured* η is a measure of the crack porosity η_k. Second, it is quite significant that critical porosity η_c does not usually appear in rocks; p_c or η_c reflects poor interconnectivity between conducting elements as is the case when the conductors are treated as spheres that do not contact each other at low porosity (Landauer, 1952). Shante and Kirkpatrick (1973) give an empirical relation for p_{cb}:

$$tp_{cb} = D/(D - 1) \qquad (9)$$

where t is the number of branches per node and D is the dimensionality of the array, either 2 or 3. The absence or very low value of p_c in rocks tells us that t must be a very large number; hence, the conducting volume elements must have a large number of intersections, as can be the case of intersecting surfaces or of partial melts which wet the adjacent grain boundaries (Waff, 1974).

It is possible to obtain an exponent $r \doteq 2$ in eq. 8 when $p = p_s$, the fraction of remaining sites or nodes of the array (Kirkpatrick, 1973), in which case there is a highly correlated removal of bonds from the region of each removed site. Brace et al. (1965) obtained Archie's law (eq. 7) with $r = 2$ under special circumstances, namely, by selecting different rocks of varying initial porosity and measuring conductivity at 4 kbar pressure where the porosity η_k of the interconnected cracks was mostly removed. The analogy with arrays from which sites (nodes) are removed then suggests that most of the residual porosity η_r is indeed pore porosity η_p in rounded pores, and that p_s corresponds to η_p. Thus:

$$\eta_r = \eta_k + \eta_p \simeq \eta_p \qquad (10)$$

and

$$\eta_k \ll \eta_p \qquad (11)$$

Selecting samples of lower porosity corresponds to eliminating rounded pore volume from sample to sample together with the flattened cracks interconnecting them. However, could we measure η_k of the cracks, the previous result would still imply that $\sigma \sim \eta_k$.

In short, comparison of eq. 8 for arrays with Archie's law (eq. 7) separates two parameters of conduction in porous rocks. The apparent absence of a critical porosity η_c in analogy with p_c implies that the conducting elements in a rock remain interconnected down to quite low porosities. The exponent r in eq. 7 reveals something about the shapes of *measured* porosity; $r \doteq 1$ for most of the porosity in interconnected cracks and $r \doteq 2$ for most of the porosity in rounded "storage" pores (Keller and Frischknecht, 1966; Katsube and Collett, 1973). As a further note, Madden (1974a,b) has pointed out that the use of arrays containing a single value of resistor is an oversimplification. He finds that $r = 2$ can be obtained when G is the geometric mean of a distribution of conductances and the width of the distribution varies appropriately.

Another example is the determination of the effect of a possible partial-melt fraction in the upper mantle on electrical conductivity. Melting can produce contrasts of 2–4 orders of magnitude (Presnall et al., 1972; Waff, 1974; Waff et al., in preparation) in conductivity. It is very helpful that Waff et al. have demonstrated conductivity in their silicate melts to be virtually independent of oxygen fugacity. Hence, in a zone containing partial melt, the parameter f_{O_2} can be neglected, while the melt fraction η and the interconnectedness of the melt become important. The latter depends on the extent of wetting by the melt pockets of their surrounding mineral grains. Waff (1974) has modeled electrical conduction in a partial melt using a self-consistent modeling theory. In the case of good wetting and a high degree of interconnection of the melt, so that $p_0 = 0$, he obtains a result similar to eq. 8, $\sigma/\sigma_0 \doteq \frac{2}{3}\eta$ at low melt fractions. If only 70% of the melt is in liquid bridges and $t = 4$ (branches), Waff finds that the conductivity results of Hermance and Grillot (1970) can be obtained with a 3.5% melt fraction at 1,200°C under Iceland.

The picture which comes from modeling the porosity of a rock with resistor arrays is still oversimplified. Many problems have been ignored, e.g., partially "healed" cracks or electrolytic conduction on the generally messy interfaces between grains (Madden, 1974b). Weathering or serpentinization (Stesky and Brace, 1973) present problems of another order of complexity.

Because we now understand that conductivity is determined by several parameters and that they can be traded against each other, e.g., either a high T or high f_{O_2} can produce a high σ, it becomes even more important to use supplementary information such as petrologic studies of ultramafic xenoliths or of regional crustal rocks to constrain the number of variables. In this connection it is somewhat easier to interpret conductivities rather than the resistivities that customarily emergy from field studies because of the fact that conduction mechanisms like eq. 1 acting in parallel are simply additive in conductivity, whereas the summing of reciprocal resistivities can mask possibly simple relations.

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References

Adler, D. and Feinleib, J., 1970. Phys. Rev. B, 2: 3112–3134.

Akimoto, S.-I. and Fujisawa, H., 1965. J. Geophys. Res., 70: 443–449.

Aronson, J.R., Bellotti, L.H., Eckroad, S.W., Emalie, A.G., McConnell, R.K. and Von Thüna, P.C., 1970. J. Geophys. Res., 75: 3443–3456.

Austin, I.G. and Mott, N.F., 1970. Science, 168: 71–77.

Bott, M.H.P., 1967. Geophys. J.R. Astron. Soc., 14: 413–428.

Boyd, F.R., 1973. Geochim. Cosmochim. Acta, 37: 2533–2546.

Brace, W.F., 1971. In: J.G. Heacock (Editor), The Structure and Physical Properties of the Earth's Crust, American Geophysical Union, Monograph 14, pp. 243–255.

Brace, W.F. and Orange, A.S., 1968. J. Geophys. Res., 73: 1433–1445.

Brace, W.F., Orange, A.S. and Madden, T.R., 1965. J. Geophys. Res., 70: 5669–5678.

Bradley, R.S., Jamil, A.K. and Munro, D.C., 1964. Geochim. Cosmochim. Acta, 28: 1669–1678.

Bradley, R.S., Milnes, G.J. and Munro, D.C., 1973. Geochim. Cosmochim. Acta, 37: 2379–2394.

Buening, D.K. and Buseck, P.R., 1973. J. Geophys. Res., 78: 6852–6862.

Burns, R.G., Huggins, F.E. and Abu-Eid, R.M., 1972. Moon, 4: 93–102.

Duba, A., 1972. J. Geophys. Res., 77: 2483–2495.

Duba, A.G. and Nicholls, I.A., 1973. Earth Planet. Sci. Lett., 18: 59–64.

Duba, A. and Ringwood, A.E., 1973. Moon, 7: 356–376.

Duba, A., Boland, J.N. and Ringwood, A.E., 1973. J. Geol., 81: 727–735.

Duba, A., Heard, H.C. and Schock, R.N., 1974. J. Geophys. Res., 79: 1667–1673.

Dvorak, Z. and Schloessin, H.H., 1973. Geophysics, 38: 25–36.

Fatt, I., 1956. Am. Inst. Min. Metall. Pet. Eng., Pet. Trans., 207: 144–181.

Greenberg, R.J. and Brace, W.F., 1969. J. Geophys. Res., 74: 2099–2102.

Hamilton, R.M., 1965. J. Geophys. Res., 70: 5679–5692.

Hansen, K.W. and Cutler, I.B., 1966. J. Am. Ceram. Soc., 49: 100–102.

Hermance, J.F. and Grillot, L.R., 1970. J. Geophys. Res., 75: 6582–6591.

Housley, R.M., Morin, F.J. and Oliver, J.R., 1975. Earth Planet. Sci. Lett. (in press).

Hughes, H., 1953. The Electrical Conductivity of the Earth's Interior. Thesis, University of Cambridge, Cambridge, 130 pp.

Hughes, H., 1955. J. Geophys. Res., 60: 187–191.

Hutson, A.R., 1959. In: N.B. Hannay (Editor), Semiconductors. Reinhold, New York, N.Y.

Katsube, T.J. and Collett, L.S., 1973. Geochim. Cosmochim. Acta, Suppl. 4, 3: 3111–3131.

Keller, G.V., 1966. In: S.P. Clark (Editor), Handbook of Physical Constants, Geological Society of America, Memoir 97, pp. 553–577.

Keller, G.V., 1967. In: E.I. Parkhomenko (Editor), Electrical Properties of Rocks. Plenum, New York, N.Y., pp. 265–308.

Keller, G.V. and Frischknecht, F.C., 1966. Electrical Methods in Geophysical Prospecting. Pergamon, London.

Kirkpatrick, S., 1971. Phys. Rev. Lett., 27: 1722–1728.

Kirkpatrick, S., 1973. Rev. Mod. Phys., 45: 574–588.

Kobayashi, Y. and Maruyama, H., 1971. Earth Planet. Sci. Lett., 11: 415–419.

Landauer, R., 1952. J. Appl. Phys., 23: 779–784.

Madden, T.R., 1974a. EOS (Trans. Am. Geophys. Union), 55: 415.

Madden, T.R., 1974b. Near Surface Electrical Properties of Rocks as a Guide to Mechanical Properties. Air Force Cambridge Research Laboratories, Rep. AFCRL-TR-75-0179, 65 pp.

Mao, H.K. and Bell, P.M., 1972. Science, 176: 403–405.

McKelvey, J.P., 1966. Solid-State and Semiconductor Physics. Harper and Row, New York, N.Y., 512 pp.

Mott, N.F. and Davis, E.A., 1971. Electronic Processes in Non-Crystalline Materials. Oxford University Press, Oxford, 437 pp.

Nitsan, U., 1973a. Electronic Structure and Transport Properties of Dense Silicates. Thesis, Harvard University, Cambridge, Mass., 311 pp.

Nitsan, U., 1973b. EOS (Trans. Am. Geophys. Union), 54: 1207.

Nitsan, U., 1974. J. Geophys. Res., 79: 706–711.

Nitsan, U. and Shankland, T.J., 1971. EOS (Trans. Am. Geophys. Union), 52: 926.

Nitsan, U. and Shankland, T.J., in preparation. Optical properties and electronic structure of mantle silicates.

Olhoeft, G.R., Frisillo, A.L., Strangway, D.W. and Sharpe, H., 1974. Moon, 9: 79–87.

Osburn, C.M. and Vest, R.W., 1971. J. Am. Ceram. Soc., 54: 428–435.

Parkhomenko, E.I., 1967. Electrical Properties of Rocks. Plenum, New York, N.Y., 314 pp.

Parkin, T., 1972. The Electrical Conductivity of Synthetic Forsterite and Periclase. Thesis, School of Physics, The University of Newcastle, Newcastle upon Tyne.

Presnall, D.C., Simmons, C.L. and Porath, H., 1972. J. Geophys. Res., 77: 5665–5672.

Schober, M., 1971. Z. Geophys., 37: 283–292.

Shankland, T.J., 1968. Science, 161: 51–53.

Shankland, T.J., 1969. In: S.K. Runcorn (Editor), The Application of Modern Physics to the Earth and Planetary Interiors. Wiley-Interscience, New York, N.Y., pp. 175–190.

Shankland, T.J. and Waff, H., 1974. J. Geophys. Res., 79: 4863–4868.

Shante, V.K.S. and Kirkpatrick, S., 1973. Adv. Phys., 20: 325–357.

Smyth, D.M. and Stocker, R.L., 1975. Phys. Earth Planet. Inter., 10: 183–192.

Stesky, R.M. and Brace, W.F., 1973. J. Geophys. Res., 78: 7614–7621.

Tolland, H.G. and Strens, R.G.J., 1972. Phys. Earth Planet. Inter., 5: 380–386.

Tozer, D.C., 1959. In: L.M. Ahrens, K. Kalervo, F. Press and S.K. Runcorn (Editors), Physics and Chemistry of the Earth, 3. Pergamon, London.

Tozer, D.C., 1972. Phys. Earth Planet. Inter., 6: 182–197.

Von Pluschkell, W. and Engell, H.J., 1968. Ber. Dtsch. Keram. Ges., 45: 388–394.

Waff, H., 1974. J. Geophys. Res., 79: 4003–4010.

Wilson, J., 1965. The Optical and Electrical Properties of Synthetic Olivine Crystals. Thesis, University of Newcastle, Newcastle upon Tyne.