Electrical Properties of Rocks

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INTRODUCTION

Electrical properties of rocks are used in induced polarization, resistivity, and electromagnetic methods of mineral exploration (Keller and Frischknecht, 1966; Ward, 1967; Madden and Cantwell, 1967; Von Voorhis *et al.*, 1973), in crustal sounding (Hermance, 1973), in lunar and planetary sounding (Banks, 1969; Brown, 1972; Dyal and Parkin, 1973; Simmons *et al.*, 1972), in glacier sounding (Rossiter *et al.*, 1973), and in other applications. Studies of electrical properties in rocks have been performed as functions of frequency, temperature, applied field, pressure, oxygen fugacity, water content, and other variables (Keller, 1966; Ward and Fraser, 1967; Parkhomenko, 1967; Brace and Orange, 1968; Fuller and Ward, 1970; Alvarez, 1973b; Dvorak, 1973; Hansen *et al.*, 1973; Katsube *et al.*, 1973; Waff, 1973; Gold *et al.*, 1973; Schwerer *et al.*, 1973; Marshall *et al.*, 1973; Olhoeft *et al.*, 1974*b*; Duba *et al.*, 1974; Hoekstra and Delaney, 1974; and others).

This will be a brief review of the behaviour of electrical properties of rocks for several of the above parameters, concentrating mainly upon frequency, temperature, and water content in the context of likely mechanisms. There are many experimental techniques available and a discussion of them will not be attempted here (see von Hippel, 1954; Collett, 1959; ASTM, 1970; Hill *et al.*, 1969; Suggett, 1972; and Collett and Katsube, 1973). For geological materials, the best procedure is usually to follow a combination of techniques involving the observation of electrical properties as functions of applied field (to test for voltage–current non-linearity) and of frequency, all for variations of relevant environmental parameters (temperature, water content, etc.).

ELECTRICAL PROPERTIES

Electrical properties are derived from the solution of Maxwell's equations. Such solutions (Stratton, 1941, or other standard textbooks) yield an electromagnetic wave with a propagation constant

FREQUENCY DEPENDENCE

All frequency dependent electrical properties are here considered to be described in the complex permittivity or the complex resistivity (see discussions in Fuller and Ward, 1970, or Collett and Katsube, 1973). The conductivity is considered to be the value at zero frequency only and independent of frequency. Note that this means that the conductivity is not the reciprocal of the resistivity except in the limit of $\omega \rightarrow 0$ or when $\sigma \gg \omega\varepsilon$.

The complex dielectric constant is the ratio of the permittivity of the material to the permittivity of free space

$$K' - jK'' = \varepsilon/\varepsilon_0$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m = free space permittivity

K' = real dielectric constant
K'' = imaginary dielectric constant

and the complex resistivity is

$$\rho' - \mathrm{j}\rho'' = \frac{1}{\omega\varepsilon_0 K'} \frac{(D - \mathrm{j})}{(1 + D^2)} \tag{2}$$

where D is the loss tangent

$$D = \tan\delta = \frac{K''}{K'} + \frac{\sigma}{\omega\varepsilon_0 K'} = \frac{\rho'}{\rho''} \tag{3}$$

representing the measure of the phase shift between the electric and magnetic field vectors in an electromagnetic wave (Olhoeft and Strangway, 1974b) and a measure of the energy dissipation.

The general behaviour of electrical properties observed as a function of frequency is shown in Figure 1 (discussed below), and may be modelled by a circuit such as Figure 2. The conductance G represents the DC conductivity path, the capacitances C_L and C_H determine the low frequency limit of the dielectric constant, the resistor-capacitor pair RC_L determines the time constant of relaxation (rate of relaxation of an energy dissipative process), and the capacitance C_H determines the high frequency limit of the dielectric constant. This circuit has a single time constant, but, in general, a distribution of time constants is observed (see Ghausi and Kelly, 1968; Shuey and Johnston, 1973; and others). The general form of a complex dielectric constant with a distribution of time constants is (Gevers, 1945)

$$K' - \mathrm{j}K'' = K_\infty + (K_0 - K_\infty)\int_0^\infty \frac{G(\tau)(1 - \mathrm{j}\omega\tau)\mathrm{d}\tau}{1 + \omega^2\tau^2} \tag{4}$$

where

$$K_0 = \lim_{\omega \rightarrow 0} K' = \text{low frequency dielectric constant}$$

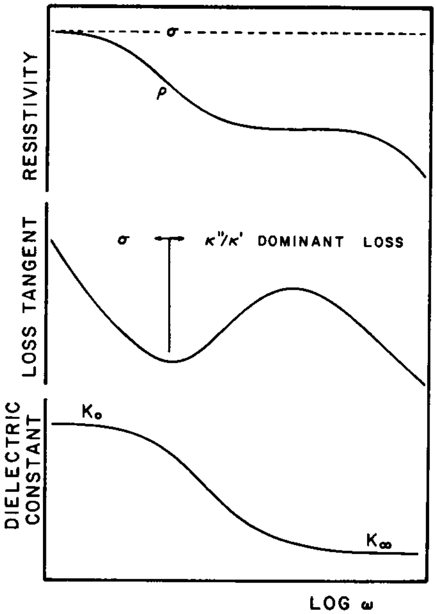

Figure 1. Schematic behaviour of the complex dielectric constant, loss tangent, and resistivity versus log frequency.

$$K_\infty = \lim_{\omega \to \infty} K' = \text{high frequency dielectric constant}$$

$$\tau = \text{time constant of relaxation}$$

and $G(\tau)$ is the time constant distribution function with the normalization

$$\int_0^\infty G(\tau)\mathrm{d}\tau = 1.$$

The high frequency dielectric constant is generally independent of temperature and water content, being mainly dependent upon density. In this context, the high frequency dielectric constant is valid for frequencies up to the optical where it becomes approximately equivalent to the square of the index of refraction (see von Hippel, 1954). The low frequency dielectric constant is primarily caused by the accumulation of charge at crystal boundaries and defects, and it will be further discussed below. The time constant distribution function may narrow with increasing temperature and generally tends to broaden with increasing water content, salinity, and defect structure.

Several specific distributions are found in the literature (Poole and Farach, 1971; de Batist, 1972; and others), one of the most useful being the Cole-Cole distribution (Cole and Cole, 1941)

$$K' - \mathrm{j}K'' = K_\infty + \frac{K_0 - K_\infty}{1 + (\mathrm{j}\omega\tau)^{1-\alpha}} \tag{5}$$

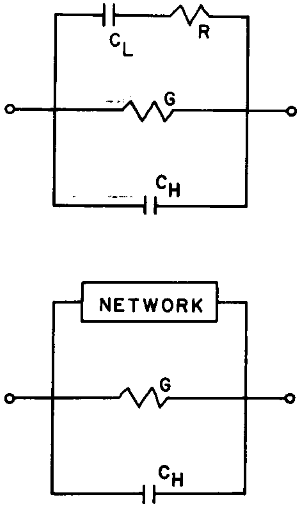

Figure 2. The equivalent circuit of a single relaxation with a DC conduction path (others are possible). A distribution of relaxation times substitutes a series of *RC* networks in place of RC_L.

where $1 - \alpha$ is the distribution breadth parameter with limits of $1 - \alpha = 1$ (a single relaxation) and $1 - \alpha = 0$ (an infinitely broad distribution). The slope of log loss tangent versus log frequency is equal to $1 - \alpha$ for $\omega\tau < 1$, and $-(1 - \alpha)$ for $\omega\tau > 1$. Examples of this distribution in rocks may be found in Saint-Amant and Strangway (1970), Alvarez (1973b), and Olhoeft *et al.* (1973, 1974a). The distribution parameter may be temperature dependent (Fuoss and Kirkwood, 1941; Olhoeft *et al.*, 1973, 1974a), tending to narrower distributions with increasing temperature. A common method of displaying data which fits the Cole–Cole type of distribution is the use of the Argand diagram which plots imaginary versus real dielectric constant. On this plot, the data form a semicircle with a depressed center. The amount of depression is a measure of $1 - \alpha$ (Poole and Farach, 1971; Alvarez, 1973b).

TEMPERATURE DEPENDENCE

As there are distributions of time constants describing the frequency dependence of electrical properties, so there are distributions of activation energies describing the temperature dependence. Both the time constants in the above distribution and the DC conductivity follow a generalized Boltzmann temperature dependence of the form

$$\tau = \sum_i \tau_i e^{E_i/kT} \qquad (6)$$

where

τ_i = infinite temperature time constant (conductivity)
E_i = activation energy (positive for time constants, negative for conductivity, and possibly temperature dependent, see Olhoeft *et al.*, 1973)

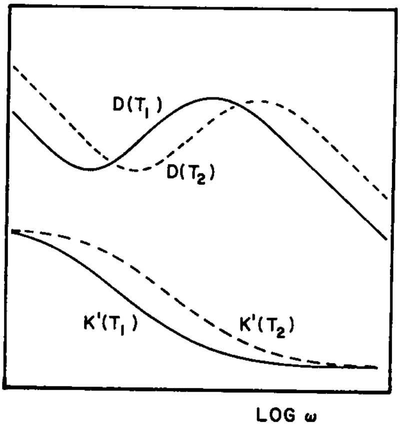

Figure 3. Schematic behaviour of the dielectric constant and loss tangent versus frequency for a distribution of time constants and a single thermal activation energy for two temperatures, T_2 greater than T_1.

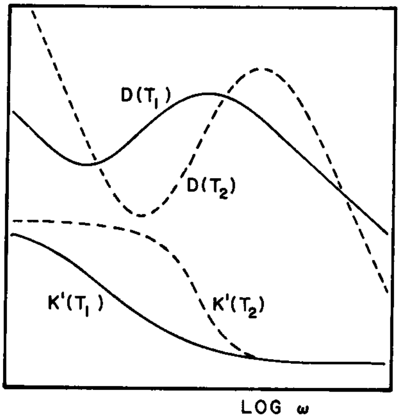

Figure 4. Schematic behaviour of the dielectric constant and loss tangent versus frequency for a distribution of time constants and a distribution of activation energies for two temperatures, T_2 greater than T_1.

k = Boltzmann's constant = 8.6176×10^{-5} eV/K
T = temperature (Kelvin).

The behaviour of a single term expression such as (6) with the Cole–Cole distribution (5) is shown in Figure 3. Increasing the temperature, increases the frequency of relaxation. More generally however, there may be a different expression (6) for each time constant in the distribution (4) thus generating behaviour as in Figure 4. Both the frequency of relaxation and the shape of the time constant distribution alter with increasing temperature. In equation (5) this would appear as a temperature variation in $1 - \alpha$.

VOLTAGE–CURRENT DEPENDENCE

The usual method of measuring electrical conductivity utilizes an application of voltage across a sample of known dimensions. The resultant current flow through the linear *VI* (voltage–current) relation of Ohm's law yields

$$\sigma = AI/V \tag{7}$$

where I is current, V is voltage, and A is a constant determined by geometry. Not all materials obey linear *VI* relations however. The best example of one which does not is a semiconductor diode with a *VI* relation of the form

$$I = I_s(e^{qV/kT} - 1) \tag{8}$$

where kT is as in (6), q is the electronic charge, and I_s is the saturation current (see Gray *et al.*, 1964, for details). This behaviour is not only nonlinear, but it is asymmetrical (positive and negative voltages produce different magnitudes of current). This latter type of nonlinearity is caused by accumulations of charge at regions where the material electrical properties change abruptly, such as from *p*-type to *n*-type semiconductor material in the diode above. Such regions (space charge layers, SCL) also occur at the edges of crystal lattices, at cracks and other defects, and at other abrupt changes in material energy.

As well as the cause of *VI* nonlinearity, these space charge layers are the cause of contact potentials and the Maxwell–Wagner frequency response of heterogeneous materials (Alvarez, 1973b), and of the complex interfacial effects between electrodes and samples (Covington, 1970, 1973; Baker and Buckle, 1968; Buck, 1969; Hampson, 1972, 1973; Hever, 1972; and others). The electrical properties within a space charge layer determine the rate of relaxation of the charge distribution. Thus, a heterogeneous material will have space charge layers in many different materials resulting in many time constants and a distribution of time constants as discussed above. Space charge layers are also the mechanism behind the low frequency dielectric constant, and the effects on low frequency properties are particularly pronounced in wet materials where the water forms the electrochemical double layer (space charge layer in a liquid; see Delahay, 1965; Schiffrin, 1970, 1972, 1973; Payne, 1973). In wet materials, the differentiation between the electrode-sample low frequency response and the response inherent in the interfacial properties of the sample is a particularly difficult problem in experiment design and data analysis.

Though *VI* nonlinearity in rocks is a well known and accepted phenomenon, it has not been subjected to any great scrutiny. Scott and West (1969) and Katsube *et al.* (1973) have observed *VI* nonlinearities in laboratory experiments using conductive minerals. Schwerer *et al.* (1973) and Olhoeft *et al.* (1974*b*) have reported nonlinear VI phenomena in very low conductivity lunar samples. Halverson *et al.* (1973) have reported nonlinear induced polarization responses in field surveys. These phenomenon have all been observed below 1000 Hz.

MOISTURE DEPENDENCE

Baldwin (1958), Von Ebert and Langhammer (1961), and McCafferty and Zettlemoyer (1971) have observed that a monolayer of water adsorbed onto a dielectric surfaces does not alter the dielectric constant of the bulk material from that in the dry state. Successively adsorbed layers drastically increase the low frequency dielectric constant, increase the frequency of relaxation, increase the time constant activation energy, and tend to broaden the width of the time constant distribution. Beyond about seven layers, free pore water begins to form and pore fluid conduction dominates the electrical properties. Adding alteration products and electrolytes to the water further increases the low frequency dielectric constant and the breadth of the time constant distribution. In addition, monolayers and successive layers increase the DC conductivity by several orders of magnitude. Examples of the above have been discussed by Saint–Amant and Strangway (1970), Strangway *et al.* (1972), Hoekstra and Doyle (1971), Alvarez (1973a), and others.

The process or mechanism of the modification of electrical properties by water is the formation of the electrochemical double layer. The monolayer is the strongly bonded Stern layer (on the order of 10 angstroms thick), and successively adsorbed layers become the Gouy–Chapman layer. The changes of electrical properties due to the addition of water are primarily within the space charge layer of the Gouy-Chapman layer (which may influence general physical properties to 1000 angstroms from the solid-liquid interface). These are further discussed and reviewed by Clark (1970), Schiffrin (1970, 1972, 1973), Sing (1973), and Payne (1973).

The additional problems caused by geometries in porous systems have been discussed by Davies and Rideal (1963), Rangarajan (1969), and Everett and Haynes (1973). Marshall *et al.* (1973) have remarked on anomalous dielectric properties attributed to fine parallel capillaries in rocks. The particular problem of connectivity with regard to electrical conductivity in porous media has been discussed by Shankland and Waff (1973) and Madden (1974) in the geological context.

A general discussion of electrolytes in aqueous solution may be found in Hasted (1972), Rao and Premaswarup (1969), and Pottel (1973). In such solutions, chemical reactions and Faradaic mass transport processes must also be considered in addition to the double layer (see Ott and Rys, 1973a, b; Schmidt, 1973a, b, c; DeVevlie and Pospisil, 1969; Reinmuth, 1972a, b, c; Armstrong and Firman, 1973a, b).

The effects of temperature and water content on electrical properties have been investigated by Baldwin (1958), Von Ebert and Langhammer (1961), Dransfeld *et al.* (1962), McCafferty and Zettlemoyer (1971). Hoekstra and

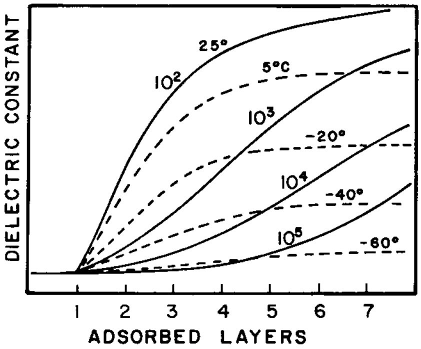

Figure 5. Schematic behaviour of the dielectric constant versus water content for various frequencies at room temperature (solid lines) and for various temperatures at 100 Hz (dashed lines).

Doyle (1971), and Hoekstra and Delaney (1974). The effects of temperature for a monolayer or less of water is the same as for a dry rock. For larger quantities of water, as the temperature is lowered to and through 0 °C, the relative alteration in electrical properties between wet and dry states becomes smaller. Below about – 60 °C, the effect of water in any quantity becomes extremely small and electrical properties are virtually indistinguishable from the dry state. The implications of these results are further discussed by McCafferty and Zettlemoyer (1971), Hoekstra and Doyle (1974), and Olhoeft and Strangway (1974a). Figure 5 quickly summarizes these findings.

The effects of temperature, water content, and pressure have been investigated by several groups with ambiguous results. Dvorak (1973), Dvorak and Schloessin (1973), Duba *et al.* (1974), Akimoto and Fujisawa (1965), and others have investigated the pressure effects in dry rocks, generally finding little or no change in electrical conductivity below 8 kilobars, but sometimes large and irreversible changes (possibly correlated with chemical changes) above 8 kb.

Brace *et al.* (1965), Brace and Orange (1968), and Stesky and Brace (1973) have observed large variation in electrical conductivity in wet samples with pressure to only 6 kbars. This alteration may be attributable to changes in pore volume and crack connectivity with pressure, but much more work has yet to be done (particularly with the additional complication of temperature as a variable). Holzapfel (1969) has observed that water under high pressure and high temperature becomes very conductive (more than 0.01 mho/m at 200 °C and 10 kbar), in some cases becoming more conductive than many rocks under similar conditions of temperature and pressure.

Frisillo *et al.* (1975) have observed the effects of temperature and pressure on the dielectric constant and loss tangent of soils in vacuum. After allowing for density changes, they found no change in loss tangent with pressure, though large changes were observed in the dielectric constant with only 30 bars pressure.

EXAMPLES

The variation of electrical properties with temperature has been discussed above. This is further illustrated in Figures 6 through 8 for a dry (outgassed in vacuum better than 10^{-7} torr), terrestrial pyroxene (salite) which has been partially discussed by Olhoeft *et al.* (1974b). The composition is shown in Table 1. The DC conductivity and the low frequency dielectric constant were tested and found to be linear in voltage–current from 123 to 5000 volt/cm of applied field.

The temperature and frequency response of the dielectric constant and loss tangent are shown in Figures 6 and 7 in vacuum as well as in air at room temperature. The complex resistivity and DC conductivity are shown in Figures 8 and 9. Also illustrated in Figure 9 are the equivalent AC conductivities calculated from Figures 6 and 7 by

$$\sigma_{AC} = \sigma_{DC} + \omega\varepsilon_0 K' \tan\delta$$

This data is parameterized by $K_\infty = 6.4$, a temperature dependent K_0 varying from 90 below 163 °C to 100 at 415 °C, and both a distribution of time constants and a distribution of activation energies. The distribution of time constants may be characterized by a temperature dependent Cole–Cole breadth para-

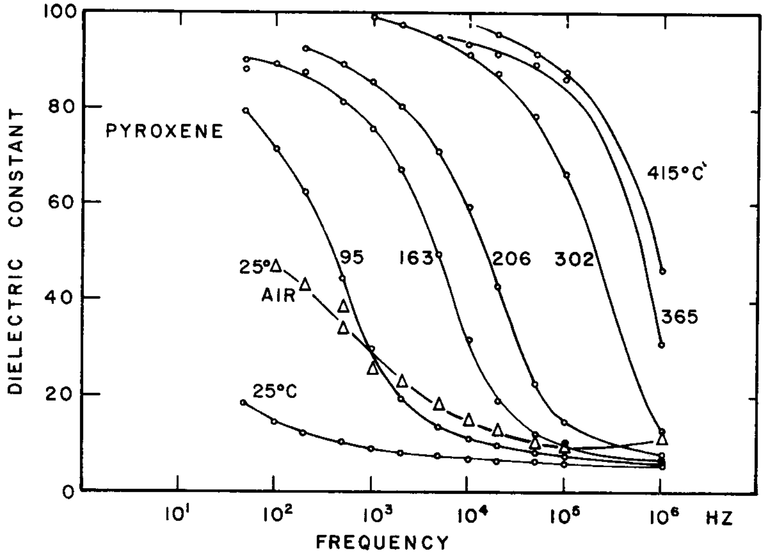

Figure 6. The dielectric constant versus frequency for a dry pyroxene in vacuum at various temperatures and in air at room temperature.

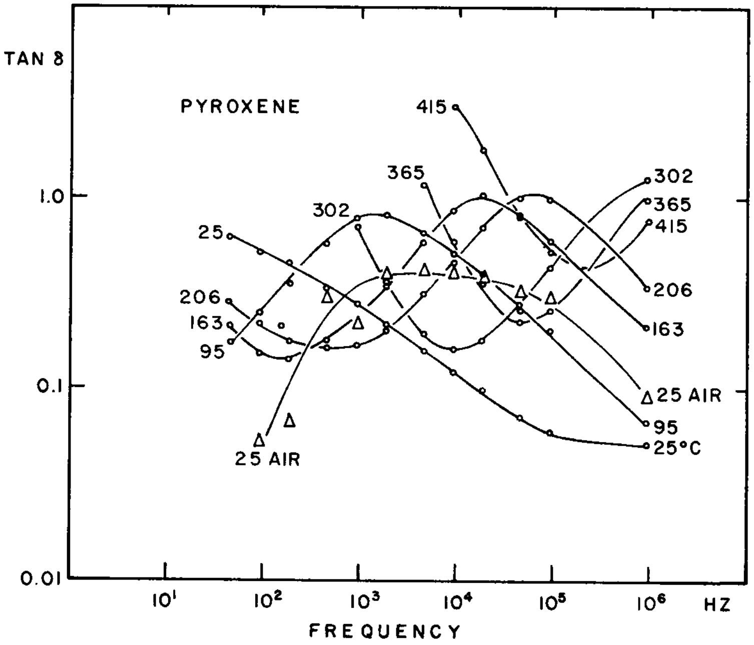

Figure 7. The loss tangent of a dry pyroxene in vacuum for various temperatures and in air at room temperature.

meter (indicative of the distribution of activation energies) $1-\alpha$ equal to 0.32 at 25 °C, 0.47 at 95 °C, and 0.63 above 302 °C. The activation energy of the apparent peak in the time constant distribution is constant at 0.60 eV, but the infinite temperature time constant at that point varies from 2.4×10^{-12} seconds at 95 °C to 4.1×10^{-12} seconds at 365 °C. This latter variation is indicative of a slight distribution of activation energies (as is also the variation in $1-\alpha$). The infinite temperature DC conductivity is 1.4 mho/m with an activation energy of − 0.54 eV.

The electrical properties in Figure 8 clearly show the three regions where different terms dominate the solutions of Maxwell's equations. At 197 °C, the DC value of the resistivity (reciprocal of the DC conductivity) is asymptotically approached by the real part of the complex resistivity at frequencies below 100 Hz. Below 100 Hz in this sample is thus the region of electromagnetic induction where the permittivity may be safely neglected.

Continuing to higher frequencies, the loss tangent decreases in value and passes through a relative minimum near 4 kHz. Below 3 kHz, the DC conductivity is the dominant loss, and between 100 Hz and 3 kHz both the conductivity and permittivity are important to solutions of Maxwell's equations. Above 3 kHz, the DC conductivity may be safely neglected in the region of electromagnetic propagation (where dielectric mechanisms cause the dominant loss). The critical frequency separating the inductive region from the inter-

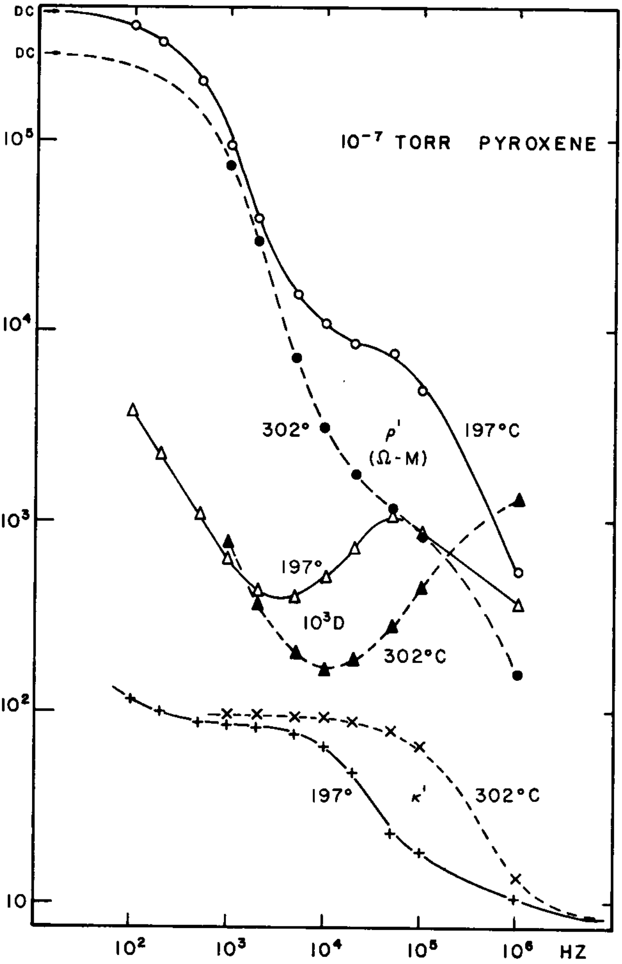

Figure 8. The dielectric constant, loss tangent, and real resistivity versus frequency at two temperatures to illustrate the critical frequencies (see text).

Table 1. Pyroxene Analysis (data from A. M. Reid, private communication)

SiO_2	52.67
TiO_2	0.05
Al_2O_3	0.94
FeO	9.62
MgO	12.04
CaO	23.94
Total	99.26

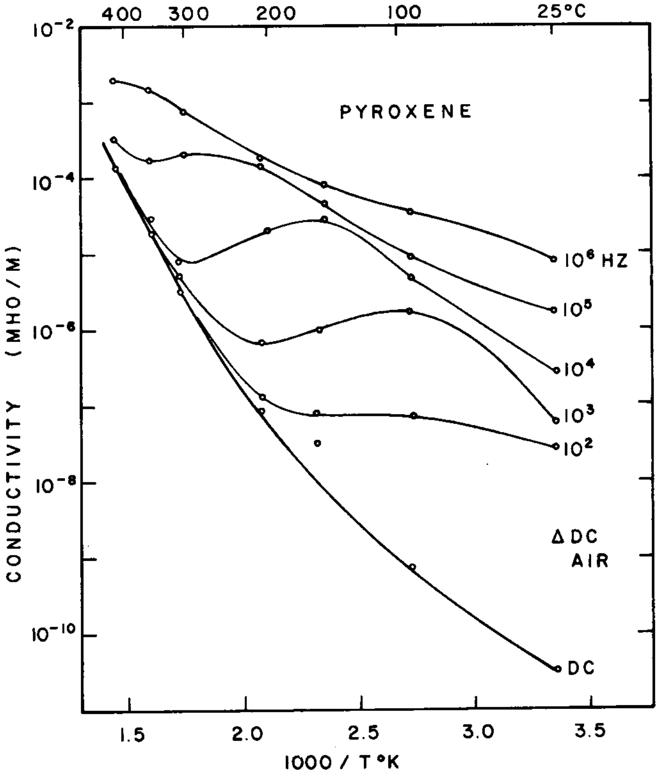

Figure 9. The AC and DC conductivities versus reciprocal temperature (see text).

mediate region occurs at $\omega = \sigma/\varepsilon_0 K'$, and the critical frequency separating the intermediate region from the propagation region occurs at $\omega = \sigma/\varepsilon_0 K''$.

Increasing temperature, increases the critical frequencies separating the regions, and the DC conductivity becomes relatively more important. This latter point may be seen in a slightly different manner in Figure 9 where the equivalent AC conductivities asymptotically approach the DC conductivity with increasing temperature or decreasing frequency.

Figures 10 and 11 show the dielectric constant and loss tangent of a granite at room temperature in solid and powder form (after Strangway *et al.*, 1972) in vacuum after outgassing at 200 °C and in 30 per cent atmospheric humidity. The difference between the solid and powder vacuum dielectric constants is directly attributable to the change in density. This may be calculated by using a formula of geometric mean between the dielectric constant of vacuum (equal to 1.0 at a density of 0.0) and the dielectric constant of the solid at the density of the solid by (Lichteneiker's formula, von Hippel, 1954)

$$K_p = K_s^{p/G} \tag{9}$$

where K_p and K_s are the dielectric constant of the powder and solid at densities

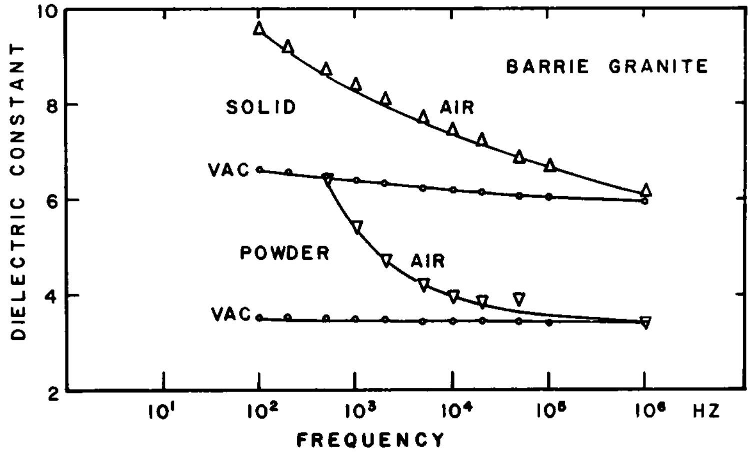

Figure 10. The dielectric constant of a solid and powder granite in vacuum and in air at room temperature.

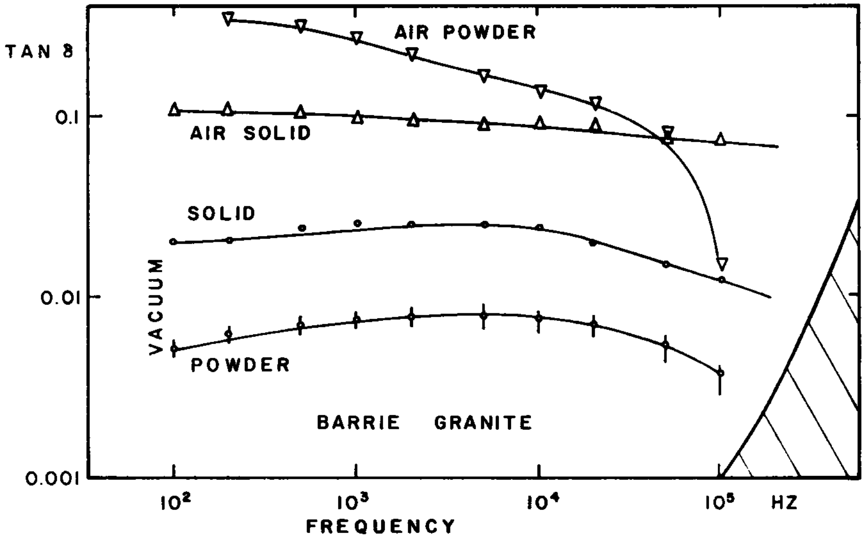

Figure 11. The loss tangent of a solid and powder granite in vacuum and in air at room temperature.

of p and G respectively. Allowing a complex dielectric constant, this formula yields a loss tangent of the form

$$\tan \delta_p = \tan (\delta_s p/G) \qquad (10)$$

where $\tan\delta_p$ and $\tan \delta_s$ are the loss tangents of the powder and solid at densities of p and G respectively. The behaviour for the vacuum data in the dielectric constant of Figure 10 is consistent with formula (9), but the loss tangent then predicted through (10) for the transformation from solid to powder predicts a slightly higher powder loss tangent than is actually measured. As Olhoeft and Strangway (1975) have observed consistent fits by regression analysis to 91 lunar sample data points for both solids and soils in both formulas (9) and (10), this latter discrepancy in the granite powder loss tangent of Figure 11 may be attributable to the grinding process which produced the powder. This is under further investigation. The DC conductivity in vacuum reduced from 5.3×10^{-14} mho/m in solid form to 6.2×10^{-15} mho/m in powder form and may be attributable to both the change in density and the reduced grain contacts (connectivity) in the powder form.

As air of 30 per cent relative humidity enters into the sample chamber, all of the electrical properties change. The DC conductivity rises by several orders of magnitude, the dielectric constant increases at low frequencies, and the loss tangent increases. Of particular importance though is the change in shape of the frequency response and of the different changes observed in the solid and powder forms. Note that in both the dielectric constant and the loss tangent in vacuum that the solid and powder forms have similar frequency responses (remember that the slope of log frequency versus log loss tangent is proportional to the breadth of the time constant distribution). As water is added in the humid air, the frequency response of the dielectric constant and loss tangent in the solid is no longer similar to that of the powder. The powder response is now characteristic of a narrower distribution of time constants. In addition, the powder loss tangent increases in relative magnitude between vacuum and air (dry and wet) much more than the increase in the solid loss tangent. These latter effects may be attributable to the changed geometry of water adsorption (in pores for the solid and onto particulate grains in the powder) as well as the increased surface area in the powder over that available in the solid.

SUMMARY

This has been a brief introduction and review of some areas of current interest in the electrical properties of rocks. The different types of electrical properties and ways of presenting and parameterizing them have been discussed; the concepts of distributions of time constants and distributions of activation energies have been illustrated.

The transition from the inductive limit in the solution to Maxwell's equations where permittivity may be neglected to the region of propagation where the DC conductivity may be neglected has been shown by way of an experimental example, as have the specific effects of temperature on electrical properties. The effects of water on electrical properties have been reviewed with particular regard for the mechanism of the electrochemical double layer. The effects of pressure, electrolyte solutions, and voltage-current nonlinearity have been briefly mentioned, and it is hoped that a later paper may go into these and other similar phenomena in greater detail.

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