ELECTRODE EFFECTS AND ELECTRICAL NON-LINEAR BEHAVIOR IN ROCKS

ROMAN ALVAREZ*

RESUMEN

Estudios previos en rocas saturadas con electrolitos han mostrado un comportamiento lineal hasta un cierto límite de densidad de corriente; por encima de dicho límite aparecen las no-linealidades. Se obtuvo evidencia de un comportamiento opuesto en algunas rocas resistivas secas en contacto con electrodos metálicos. Este comportamiento muestra la existencia de una región no-lineal seguida de una región lineal al aumentar el voltaje o la densidad de corriente.

La evidencia experimental de concentraciones de carga en la vecindad de los electrodos metálicos es relacionada a fenómenos no-lineales a bajos voltajes. Un modelo de conducción basado en respuestas transitorias de un sistema de arenisca hematítica – HgIn identifica dos grupos de portadores de carga. Un grupo está caracterizado por un mecanismo de relajamiento rápido que parece estar asociado a conducción superficial; el otro está asociado a portadores de baja movilidad aparentemente moviéndose a través de la matriz de la roca.

ABSTRACT

Previous studies on rocks saturated with electrolyte have shown electrical linear behavior up to a current density limit; above such a limit non-linearities appear. Evidence was obtained of the opposite behavior in some "dry" resistive rocks in contact with metallic electrodes. It shows the existence of a non-linear region followed by a linear one when the voltage, or current density, is increased.

Experimental evidence of charge concentrations in the metallic electrodes' vicinity is related to non-linear phenomena at low voltages. A conduction model based on transient responses of a hematitic sandstone-In Hg system identifies two groups of charge carriers. One group is characterized by a fast relaxation mechanism that appears to be associated with surface conduction, the other is associated with low-mobility carriers apparently moving through the rock matrix.

* *Instituto de Geofísica, Universidad Nacional Autónoma de México.*

INTRODUCTION

In the study of electrical properties of rocks the assumption of linear behavior is often made. In addition, it is admitted that rocks exhibit linearity up to a given current density value; above it non-linear effects appear. The existence of an upper limit in current density has been established in studies such as those of Madden and Marshall (1959) and Anderson and Keller (1964).

Information on the subject of non-linearity is scant and often incidental to other studies of electrical conduction in rocks. McEuen et al (1959) observed, for synthetic metalliferous ore, an impedance that was dependent on current density. Scott and West (1969) observed a decrease of resistivity with increasing current density in samples containing disseminated sulfides. Katsube et al (1973) have reported on electrical non-linearity using ac excitation. Possibly the only systematic approach to the problem has been that of Shaub (1965 and 1969; Shaub and Ivanov, 1971).

When sufficiently intense electric fields are applied to a material it will eventually undergo an irreversible change in electrical properties; before arriving at such a limit electrical non-linear phenomena will appear and, under some conditions, harmonic generation will occur (Shaub, 1965). However, intense electric fields are not the only possible cause of non-linearities. Non-linear behavior may also be observed at small applied electric fields in insulators and semiconductors in contact with metallic electrodes.

Contact effects have been discussed in relation to insulators and semiconductors by Mott and Gurney (1950), Frank and Simmons (1967) and others. Simmons (1971) has reviewed the three types of contacts that may arise in metal-insulator-metal and metal-semiconductor-metal systems: ohmic, blocking and neutral. Once an ohmic or blocking contact is established, linear and non-linear behavior may be obtained for the same metal-insulator-metal system depending on the voltage applied. Furthermore, a contact that in a given voltage region is ohmic may, at different voltages, become blocking and viceversa. A space charge is often found at the metal-insulator or a metal-semiconductor interface; it plays a central role in the contact properties. Consequently, the possibility exists of observing similar phenomena in the case of rock specimens, which are either semiconductors or insulators, in contact with metallic electrodes.

CHARGE CONCENTRATION AT ELECTRODES

The purpose of the experiment to be described next was to determine the effect of the metallic contacts on a resistive sample. If the properties of the metal-sample interface differ from those of the bulk of the sample, the voltage distribution in the electrode vicinity should manifest the difference.

Figure 1 shows the schematic arrangement used in the experiment; the rock sample was a hematitic sandstone and the measurements were made at room conditions. Indium-Mercury amalgam electrodes were used; one of them was constantly grounded while the other was either polarized to + 4.9 volts, floating, or short circuited to ground depending on the requirements of our observations. A micro-electrode with a platinum tip exposed five microns was used to determine the voltage with respect to ground at points (X, Y) on the sample surface. All measurements were performed at dc conditions when transients had disappeared. Readings were taken at separations of tenths of a millimeter when close to the electrodes and by a millimeter elsewhere. Y was kept constant while X-traverses were made between electrodes; after an X-traverse Y was incremented by a millimeter and the process repeated.

The sample average dimensions were X = 24 mm, Y = 19 mm, and Z = 14 mm; the measurements were performed on 8 lines (i.e. Y = 0 through 7) covering somewhat less than half the surface of the sample. Figures 2a, 2b, 2c, and 2d show the voltage values along four different lines; Y = 0 corresponds to the edge of the sample.

The effect of the electrode-sample interface is manifested, at the positive electrode, by a voltage drop of around 1.7 volts occurring within a tenth of a millimeter from the electrode for Y = 0 and Y = 1.0 mm, and a voltage drop of 0.3 volts and 0.7 volts within the same distance occurs for $Y = 4.0$ mm and $Y = 6.0$ mm respectively. At the grounded electrode a similar effect is observed; when going from the grounded electrode into the sample a "peak" is formed by a sharp increase followed by a decrease in voltage, subsequently the average voltage rises when X decreases

From the data in Figures 2a, 2b, 2c, and 2d and recalling that those voltages correspond to stationary flow of direct current (i.e. the displacement current was zero when the measurements were taken), one can use the relation

$$\nabla^2 V = -\rho/\epsilon = -\frac{(n_+ - n_-)\,e}{\epsilon} \tag{1}$$

to obtain information about the charge distribution in the sample. The concentrations (or charge densities) of positive and negative charge carriers at a given point are designated n_+ and $n-$; ϵ is the dielectric permittivity of the sample at the same point, e is the magnitude of the electron charge, and V is the electric potential. Although there is insufficient information to apply the above relation properly (i.e., we do not know ϵ locally) we can draw some general conclusions from it.

The large voltage drop close to the positive electrode corresponds to an accumulation of negative charge in its vicinity; that is $n- > n_+$ in this region, while close to the grounded electrode a concentration of positive charge (i.e., $n_+ > n-$) is observed. Along any line there is evidence of charge concentrations given by the increases and decreases in voltage over the average voltage slope. These reflect the inhomogeneous character of the sample; in order to have steady state conditions in an inhomogeneous sample it is necessary that charge accumulations occur at the interfaces between regions of different electrical properties (Alvarez, 1973a).

At stationary dc conditions the relation

$$J_X = -\sigma\, \partial V/\partial x = \text{const.} \tag{2}$$

indicates an inverse relationship between the slope of the voltage and the value of the conductivity within two points separated by a distance Δ x J_X is the current density in the X-direction, σ the conductivity and V the potential.

Therefore, associated to the space charge concentrations there are decreases in conductivity. The total current in the steady state was 1.9×10^{-5} amp; the intensity of the electric field can be seen (Figure 2) to vary roughly from 1 volt/cm to 170 vots/cm. Consequently variations of two orders of magnitude are inferred between the average value of conductivity in the bulk of the sample and the regions close to the electrodes. In Figure 3 contours of the voltage are presented; the lines show equipotentials on the surface of the sample. The non-uniformity of the electric field is evident; contact effects are manifested by steep voltage gradients at the electrodes' vicinity.

Often, when the sample geometry corresponds to parallel faces of area A and thickness d, the relations $V/I = \rho\, d/A$ are used to obtain the resistivity ρ ; V and I are total voltage and curret in the sample. This operation results in deriving a point property, ρ (x, y, z), from the bulk properties of the sample (i.e., total I and total V). This way of proceeding will be valid only in special circumstances, since it implies uniformity of the electric field in the sample. In the present case, assuming uniformity of the electric field may lead to a gross simplification of the actual conditions; furthermore, essential information would be lost and explanation of phenomena such as the non-linearities would be unnecessarily complicated.

Incidentally, the type of resistivity values that would be obtained with a four-electrode system, having the same current electrodes and a separation of a few millimeters in the voltage electrodes can be inferred from Figure 3. The values of resistivity would evidently depend on position and would show scatter if various electrode separations were tried along the same line.

NON-LINEARITY CRITERION

When a metallic electrode is applied to an insulator or a semi-conductor charge is exchanged between them in such a way as to yield a continuous Fermi level across the interface (Simmons, 1971). In a two-electrode system, if the two electrode-sample interfaces are dissimilar, the charges exchanged at each interface will also be dissimilar and their difference will give rise to an intrinsic electric field within the sample. The presence of such a phenomenon will manifest itself as a "spontaneous" potential difference between the electrodes of the rock sample.

Persistent biases have been reported for dry rock samples studied with dc excitations (Alvarez, 1973b); the present report contains more such examples. The presence of a bias voltage has been commonly observed when determining rock responses in electrolytic systems. In metal-electrolyte systems the bias voltage is explained in terms of electrochemical reactions occurring at the interface (e.g., Koryta et al. 1970); this case has been extensively treated in the literature and we shall not deal with it directly. Scott and West (1969) report that when measuring at ac equilibrium conditions a bias remained in their potential measuring circuit. Anderson and Keller (1964) accounted for electrode biases at dc conditions in terms of overvoltage. The results of Katsube et al (1973) using dissimilar electrodes at .1 hertz on dry samples of serpentinite and asbestos tend to indicate that a bias was also present in their measurements, although it was not identify as such by the authors. These biases may indeed have different origins, but there is little doubt about its almost systematic presence in electrical determinations of rock properties.

A voltage existing between the sample terminals when non excitation is applied will produce a displacement from the origin of its I-V characteristic. In such a case the criterion commonly used to analyze linear behavior in rocks may yield misleading results. The criterion establishes that linear behavior occurs when the resistivity versus current density data of a sample plot in a straight, horizontal line. Departures from such a plot would correspond to non-liner behavior. The following discussion illustrates these statements

Figure 4a shows an idealized I-V characteristic displaced from the origin; the scales of current and voltage are multiplied by arbitrary factors. The characteristic will be used to model the behavior of a rock sample in contact with metallic electrodes. According to this I-V model, if the terminals of the sample were open-circuited they would show a voltage of + 1 unit; if they were short-circuited a curent of – 2 units would flow through the sample. The characteristic is linear, its only peculiarity being the displacement from the origin. Assuming that the geometry of the sample is that of a unit cube one can plot the corresponding ρ vs J curve (Figure 4b).

There are two resistivity branches in Figure 4b, the positive branch is denoted by ρ^+ and the negative branch by ρ^-. Since $\rho = k\ V/I$, where k is a geometric factor ($k = 1$ in the present case), the ratio V/I will be positive (ρ^+) for $V > 1$ and $V < 0$, and negative (ρ^-) for $0 < V < 1$. In materials obeying Ohms' law there is no displacement from the origin and, consequently, no negative branches appear.

There are two different values of voltage for the same absolute value of current density (Figure 4a); there are corespondingly, two different values of resistivity for one value of the current density modulus (Figure 4b). For large current density values (i.e., greater than $100\ J_0$, where J_0 is the current density flowing at short circuit) the resistivity tends to the actual resistivity (i.e., to the reciprocal slope of the I-V characteristic).

Therefore, a material with a linear I-V characteristic displaced from the origin gives rise to an *apparent* non-linear behavior when plotted as resistivity versus current density. The apparent non-linearities appear for values of the current density modulus $|J| < 100J_0$ whereas for $|J| < 100J_0$ the behavior will be linear.

In trying to determine non-linear behavior with dc excitations it is important to establish whether or not the I-V characteristic of the sample is displaced from the origin; otherwise non-linear behavoir may be inferred for samples with linear I-V responses. In conclusion, it will be more adequate to decide on the linearity of the rock response on the basis of I-V rather than $\rho - J$ plots.

NON-LINEARITIES: EXPERIMENTAL

Measurements were performed with samples exposed to room conditions and, consequently, subject to the effects of atmospheric moisture (Alvarez, 1973b) which ranged from 20 to 45 percent relative humidity. The samples can be divided into two groups: argillaceous sandstone, granite, limestone, and hematitic sandstone belong to the group hereafter called "resistive samples", and samples of massive galena and massive pyrite belong to the "conductive samples"

Total current and voltage were determined with two electrometers (Keithley, models 601 and 610B) of 10^{14} ohms imput impedance A two-electrode system was used throughout the experiments; electrodes were of Indium-Mercury amalgam, directly applied to the sample. DC excitations were applied with a dc regulated power supply (Princeton Applied Research, model TC 602 CR). Measurements were made after transients, which occur when establishing or discontinuing dc excitations, had disappeared.

(a) Limestone

Figure 5a shows data corresponding to a .74x.40 x 2.25 cm limestone sample. The voltage varies from $-$ 8.0 to + 7.0 volts; one electrode was constantly grounded while the other experienced variations from positive to negative voltages. The presence of a polarization within the electrode-rock-electrode system is manifested by a zero current flow at a voltage of .18 volts. A current of $-.3 \times 10^{-10}$ amp flows when the sample terminals are short-circuited.

The limestone - In Hg system shows a displacement from the origin plus an actual non-linear plot of the I-V characteristic, In Figure 5b the same data is presented in a ρ vs. J plot. As predicted from Figures 4a and 4b the data shows two resistivity branches; at the higher current densities the ρ^+ and ρ^- values, although coincident, show a non-zero slope which reflects the non-linear character of the I-V response at the higher voltages.

(b)Granite

Figure 6 shows the I-V characteristic coresponding to the granite - In Hg system. Sample dimensions are 3.18 x 2.14 x .70 cm. A linear region for $V > 3$ volts and a non-linear region for $V < 3$ volts were obtained. In the present case only positive voltages were used; approximately .1 volts were measured when the sample was open-circuited, indicating thus a displacement of the I-V characteristic from the origin. The main difference between the granite and limestone data is that the latter shows non-linear behavior throughout the voltage region analyzed, whereas the former presents linear behavior from 3 to 8 volts.

(c)Argillaceous Sandstone and Muscovite Schist

Figure 7 shows the I-V characteristic of the argillaceous sandstone - In Hg system. Sample dimensions are 1.24 x 2.16 x 2.59 cm. The characteristic is linear and it appears not to be displaced from the origin.

Figure 8 shows the I-V characteristic of the muscovite schist - In Hg system. Sample dimensions were .89 x 1.19 x 2.57 cm. The characteristic is linear; however, it presents a displacement from the origin of approximately -.05 volts contrasting with the positive displacements observed in limestone and granite.

(d) Galena and Pyrite

Figure 9 shows resistance versus voltage plots of galena -In Hg and pyrite - In Hg systems. In the present case it is immaterial to present the data as R - V, ρ -J, or I-V plots since both systems show a definite linear behavior with no displacements from the origin. Experiments were not carried to higher voltages owing to the low resistance of the samples which demanded larger than available currents; in any event the region of interest was around zero volts.

(e) Hematitic Sandstone

Figure 10 shows the I-V characteristic of a hematitic sandstone -In Hg system. Non-linearity is observed below three volts; above 3 volts the behavior is linear. The I-V characteristic shows a displacement of + 1 volt from the origin. When the sample was not subjected to voltage excitations for several weeks the displacement was observed to decrease to + .5 volts. Observation periods ranging from a few minutes to half an hour were necessary to establish steady-state conditions in the sample. Periods of approximately one hour to attain equilibrium conditions have also been reported in ac measurements (Scott and West, 1969).

TRANSIENT RESPONSES

Transient responses of electrical systems often help to identify physical phenomena occurring in them. In order to learn more about the non-linear behavior of rocks in contact with metallic electrodes a discussion will be made on a set of such responses.

Figure 11a shows the typical voltage response versus time of many resistive samples in contact with metallic electrodes. The three parameters shown: V_O, V_F, and V_R require definitions, V_O is the total dc voltage applied to the sample for a given time (i.e., the excitation voltage); when the excitation voltage is disconnected there is a "fast" voltage decay of magnitude V_F, followed by a "slow" decay resembling an exponential function which attains a small value (i.e. with respect to the magnitude of the applied excitation) within a few seconds. The final value of this voltage seldom attains a zero value, even after several hours of observation; for this reason it shall be labeled *residual voltage* (V_R).

Data in Figures 11b and 11c correspond to the hematitic sandstone specimen described in the previous section and in Figure 10. Along with measurements of total current (I) and total applied voltage (V_O) (i.e., the data in Figure 10), transient responses of the sample were recorded so that V_F and V_R values could be determined for each value of the excitation voltage V_O.

With total current I and voltages V_O and V_F one can obtain the total resistance of the sample $R_T = V_O/I$ and define the resistance associated with the fast decay voltage $R_F = V_F/I$. Figure 11b shows a plot of R_F versus V_O and Figure 11c shows a plot of R_T versus V_O. The R_T plot differs only by a constant factor from a resistivity plot.

The plot of R_T versus V_O suggests non-linear behavior up to the maximum voltage used (i.e., $V_O = 9$ volts), contrasting with the linearity range, from 3 to 9 volts, shown by the R_F versus V_O plot. There is an excellent correlation of the linear region in the I-V characteristic (Figure 10) and the linear region associated with the fast voltage decay (Figure 11b); both start at 3 volts and continue to the maximum applied voltage.

These observations suggest that the overall electrical response of the sample can be represented by two superimposed components: a linear response dominating above 3 volts and a non-linear one domi nating below 3 volts. The total resistance of the sample (Figure 11c) clearly shows the tendency to attain a constant value at the higher voltages (i.e., the region dominated by the linear response), while the low-voltage region shows large variations of the V_O/I ratio (i.e. the region dominated by the non-linear behavior).

Notice that in the non-linear region there are currents flowing in the opposite direction of the applied voltage for voltages of less than 1 volt; the negative value of $V_O/I = -8.33 \times 10^5$ ohms (Figure 11c) is one such example. The negative value of R_F (Figure 11b) corresponds to a negative value of V_F; that is, instead of the fast voltage decay there was a fast voltage raise, after which the normal decay took place.

A CONDUCTION MODEL

A discussion of a schematic model of conduction in resistive samples shall be made in relation to the results of Figure 10 and Figures 11a, 11b, and 11c. The two decay regions in the voltage response of a resistive sample in contact with metallic electrodes (Figure 11a) may be attributed to two different relaxation mechanisms. Each one would be associated to a different set of charge carriers and they would have a marked difference in relaxation times The fast decay is similar to that of samples in which electronic conduction predominates, whereas the slow decay resembles ionic diffusion characterized by low mobilities.

Information reported elsewhere (Alvarez, 1973b) shows that the magnitude of the fast voltage decay (V_F) tends to zero when the atmospheric moisture content is reduced in the sample; eventually, in vacuums of around 10^{-7} torr, V_F becomes zero and the magnitude of the slow voltage decay (V_R) equals the magnitude of the applied voltage (V_O) at the time of discontinuing the excitation.

The above observation implies that the fast relaxation mechanism was effectively supressed in the sample by evacuation, leaving only the low-mobility charge carriers to conduct current through it. The low-mobility charge carriers cannot be moving in an aqueous medium (i.e., an aqueous electrolyte) since water in the sample was lost upon evacuation. Consequently, these ions must be moving through the solid matrix of the sample (i.e., through the minerals forming the rock) One may therefore conclude that the slow relaxation mechanism is controlled by the rock forming minerals and its interaction with the metallic electrodes.

If the evacuated sample is exposed again to atmospheric moisture, the fast voltage decay (V_F) reappears in the rock response. According to observations previously made (Alvarez, 1973b), atmospheric moisture induces an electronic-type conduction in the sample surfaces Thus, the fast relaxation voltage (V_F) appears to be associated with electronic-type conduction on the sample's surfaces.

Summarizing the discussion on this conduction model of resistive samples we have: (1) a fast relaxation mechanism that appears to be associated with an electronic type conduction taking place on the sample surfaces and induced by atmospheric moisture; such a mechanism gives rise to linear responses, (2) a slow relaxation mecanism that appears to be associated with conduction through the rock matrix, influenced by the metallic electrode contacts, and giving rise to non-linear responses at small voltages.

CONCLUSIONS

Observations made elsewhere on metal insulator-metal or metal-semiconductor-metal systems have shown that space charge accumulations play an important role in the contact properties and give rise to non-linearities. Evidence of space charge accumulations at the interfaces of a hematitic sandstone-In Hg system were presented; the I-V characteristic of a similar hematitic sandstone sample showed (Figure 10) non-linear behavior for voltages of less than 3 volts.

Displacement of the I-V characteristic from the origin in the cases of limestone and granite coincide with non-linear behavior at low voltages; in the case of the muscovite schist, however, a linear characteristic was obtained notwithstanding a small negative displacement from the origin. For argillaceous sandstone, galena, and pyrite no displacement of the I-V characteristic from the origin could be detected; the response was linear for all measured voltages.

The evidence presented suggests that displacement of the I-V characteristic is usually associated with non-linear behavior at low voltages, the only exception in these observations being the muscovite schist response; no formal explanation can be given to it. Further experiments on this type of material should help explain why it does not conform to the rule established by the other six samples analyzed.

In summary, an interrelation has been shown to exist between contact effects, non-linear phenomena, and shifting of the I-V characteristic in metal-rock-metal systems.

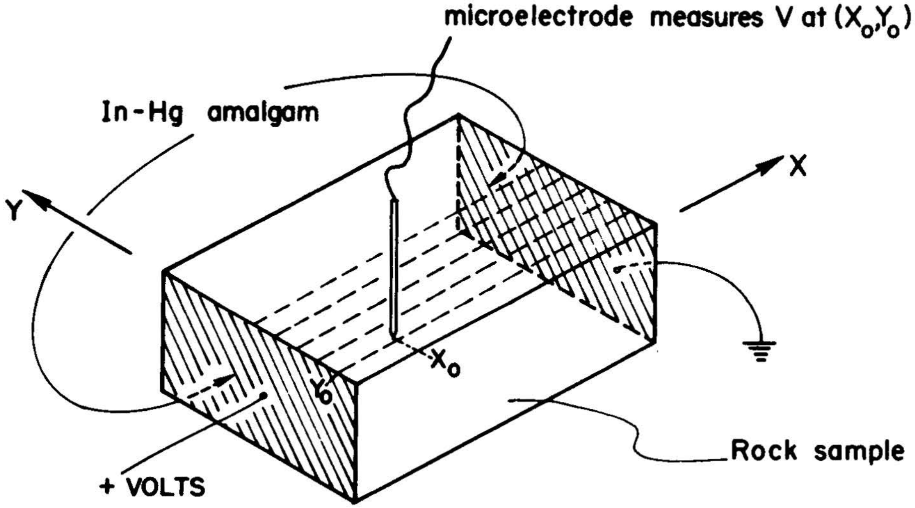


Figure 1. Schematic set-up for the determination of the voltage distribution in the surface of a sample. The micro-electrode traverses the lines taking voltage readings at points (X, Y) when a constant current is flowing.

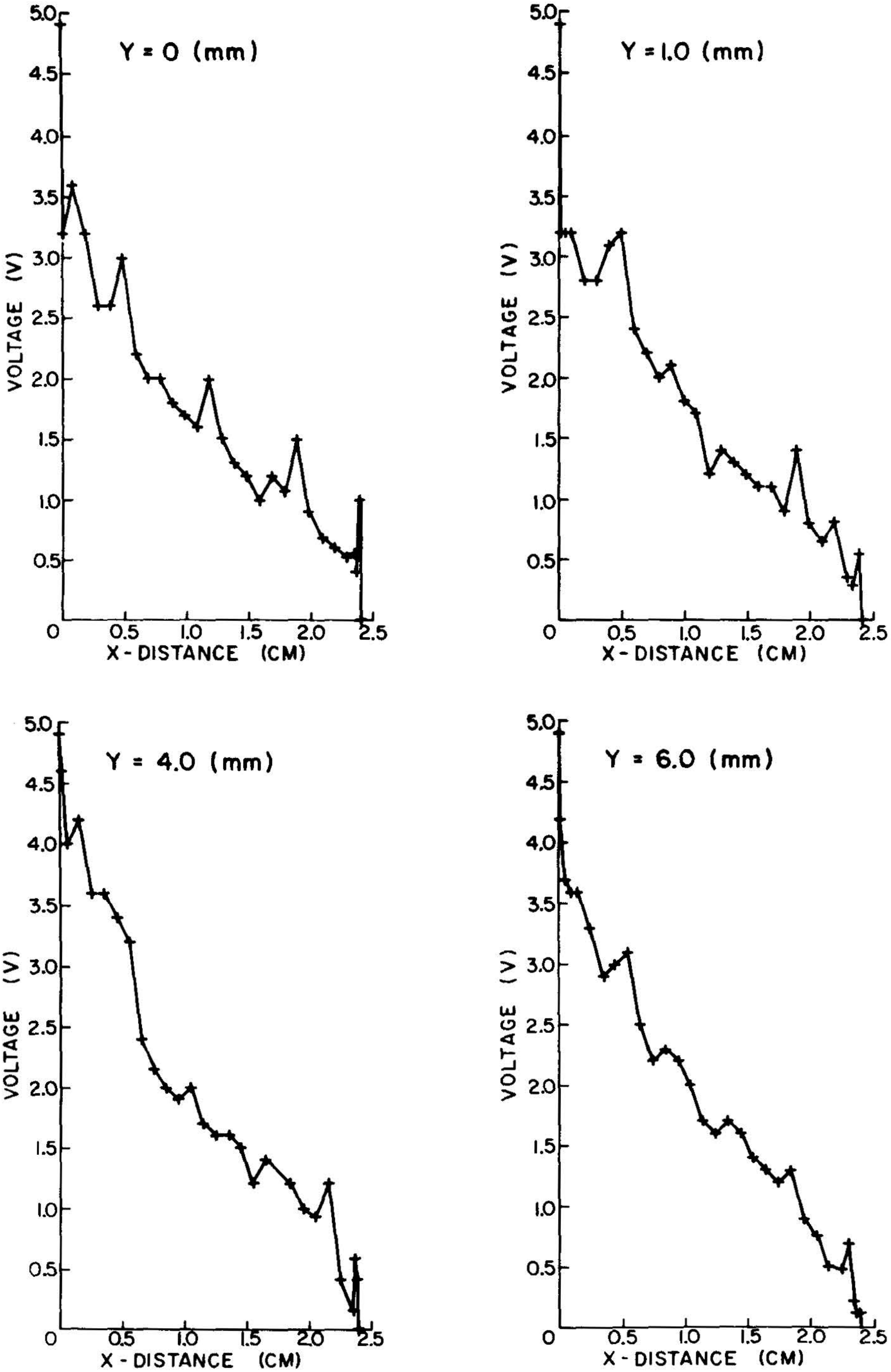


Figure 2. Voltage values as a function of distance X for a hematitic sandstone sample showing larg gradients at the electrodes' vicinity. (a) Y = 0, (b) Y = 1 mm, (c) Y = 4 mm, and (d) Y = 6mm.

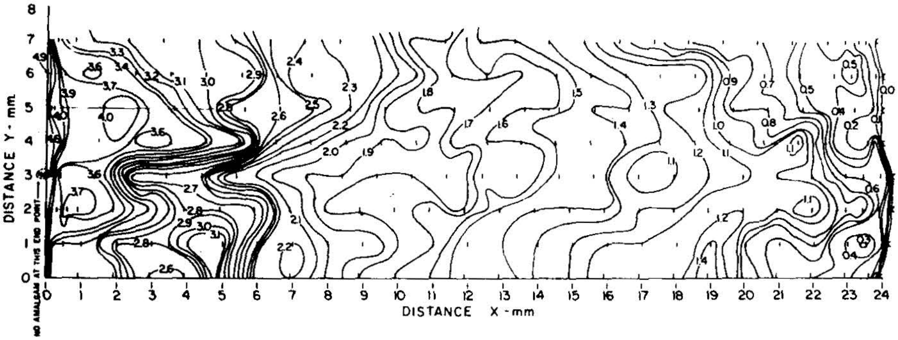
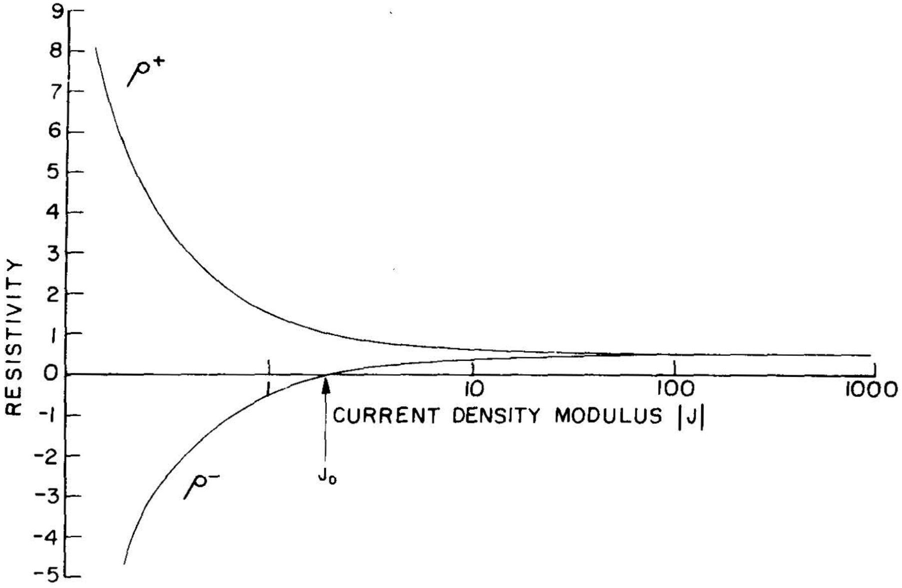
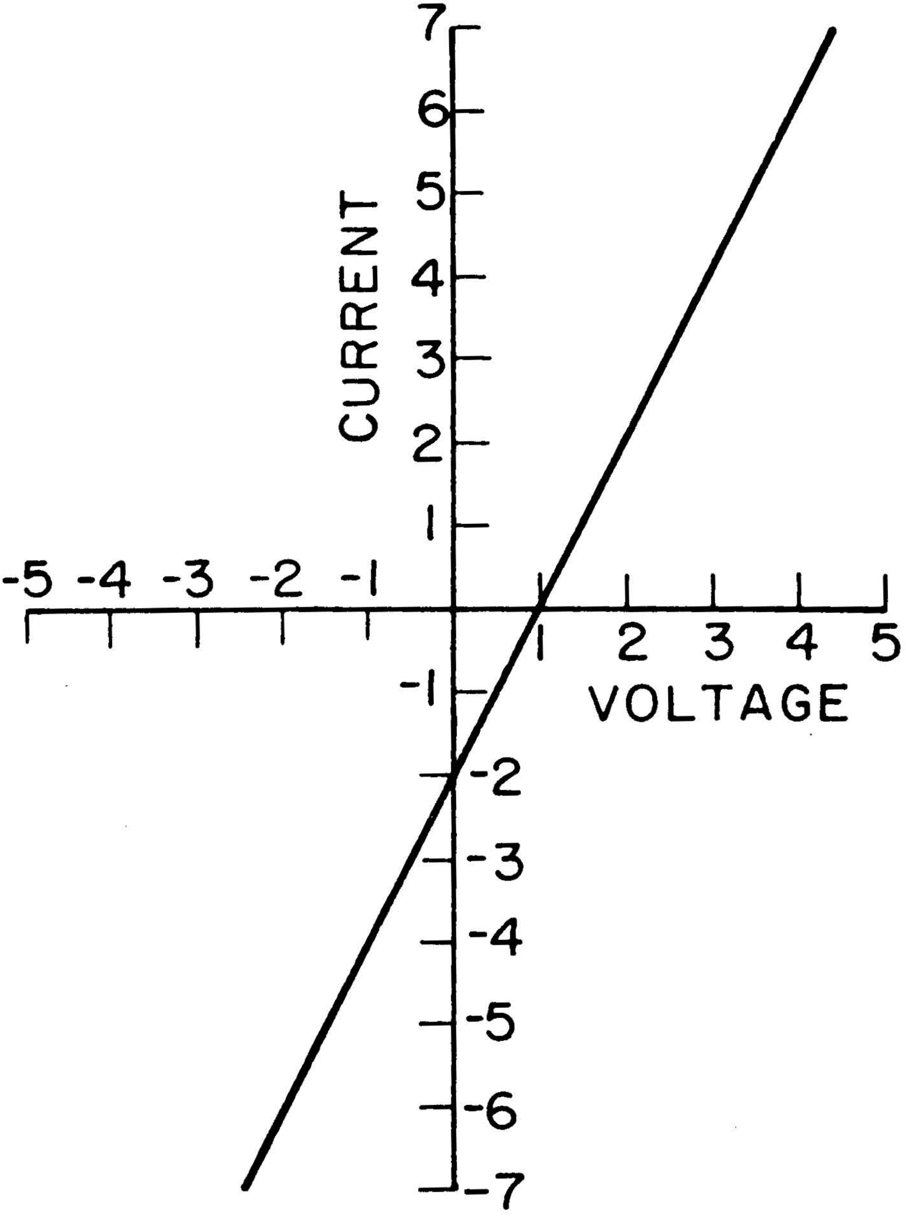
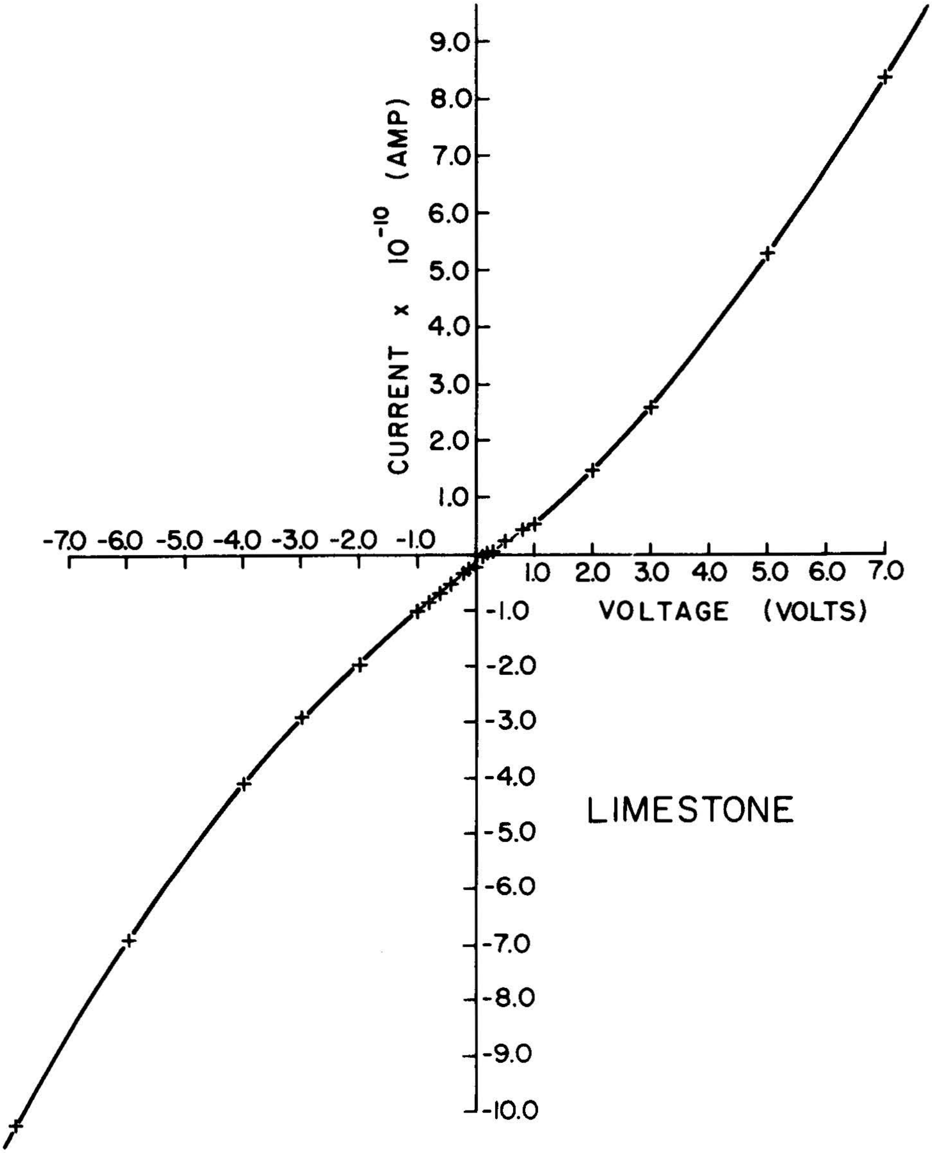


Figure 3. Equipotentials on the surface of a hematitic sandstone sample showing the non-uniformity of the electric field when a constant current flows.

Figure 4. (a) An I-V characteristic displaced from the origin is used to model the behavior of a rock sample in contact with metallic electrodes. The current and voltage scales are multiplied by arbitrary factors. (b) Assuming that the rock is made in a unit cube one can obtain its resistivity vs current density modulus plot. Non-linear behavior is shown for current density values smaller than $\sim 100 J_0$, while for large values a linear region is obtained. J_0 is the current flowing in the sample when its terminals are short circuited.




CURRENT
VOLTAGE
7
6
5
4
3
2
1
-1
-2
-3
-4
-5
-6
-7
-5 -4 -3 -2 -1
1 2 3 4 5


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
CURRENT x 10^-10 (AMP)
-7.0 -6.0 -5.0 -4.0 -3.0 -2.0 -1.0
1.0 2.0 3.0 4.0 5.0 6.0 7.0
VOLTAGE (VOLTS)
LIMESTONE

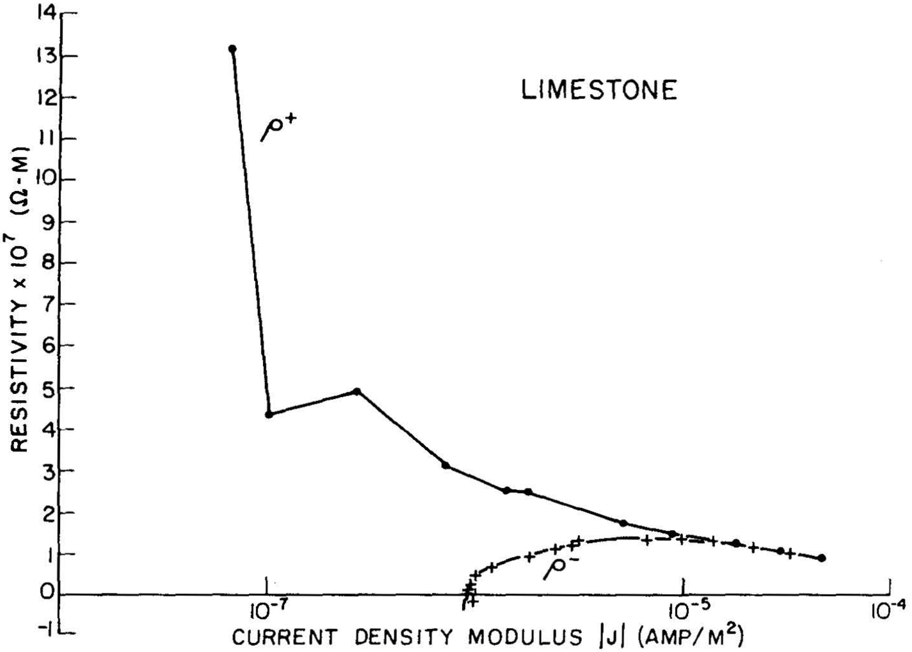


Figure 5. (a) I-V characteristic of a limestone sample. One electrode was constantly grounded while the other underwent positive and negative voltage variations. The non-linear region extends throughout hte voltage region analyzed. Notice the displacement of the I-V characteristic from the orign. (b) The data in figure (a) is plotted as resistivity vs currunt density modelus.

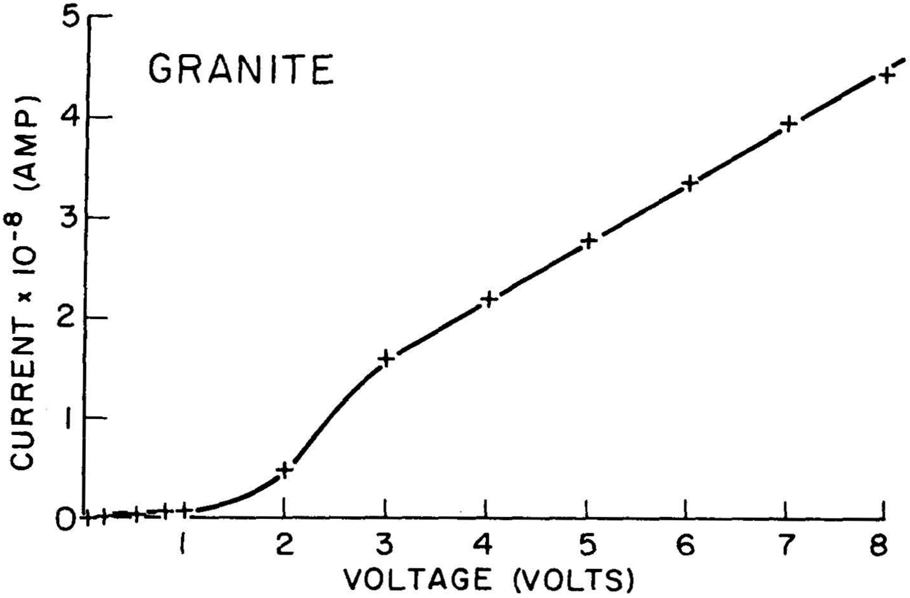


Figure. 6. I-V characteristic of a granite sample. The non-linear region appears below 3 volts, above this voltage the behavior is linear.

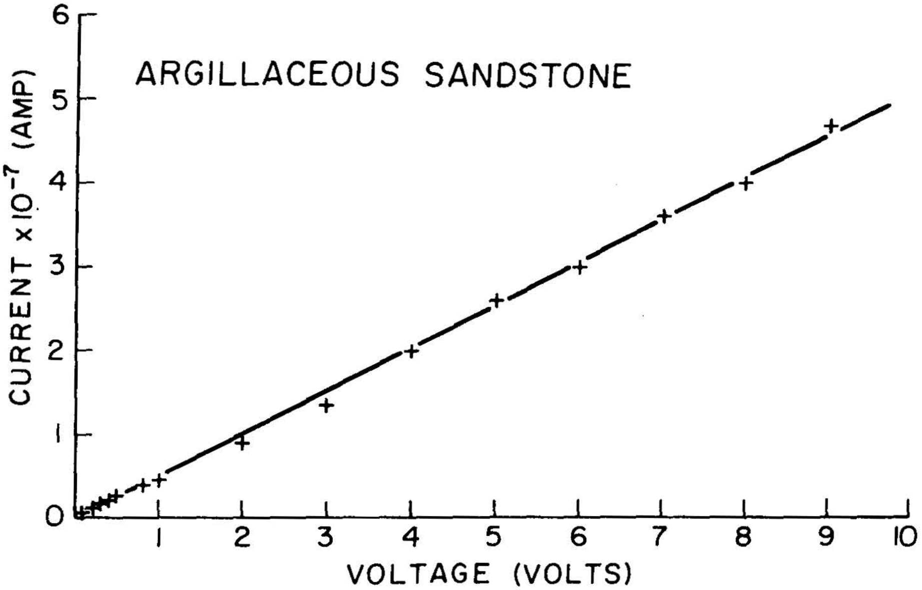


Figure 7. I-V plot of an argillaceous sandstone showing linear behavior; it is not displaced from the origin.

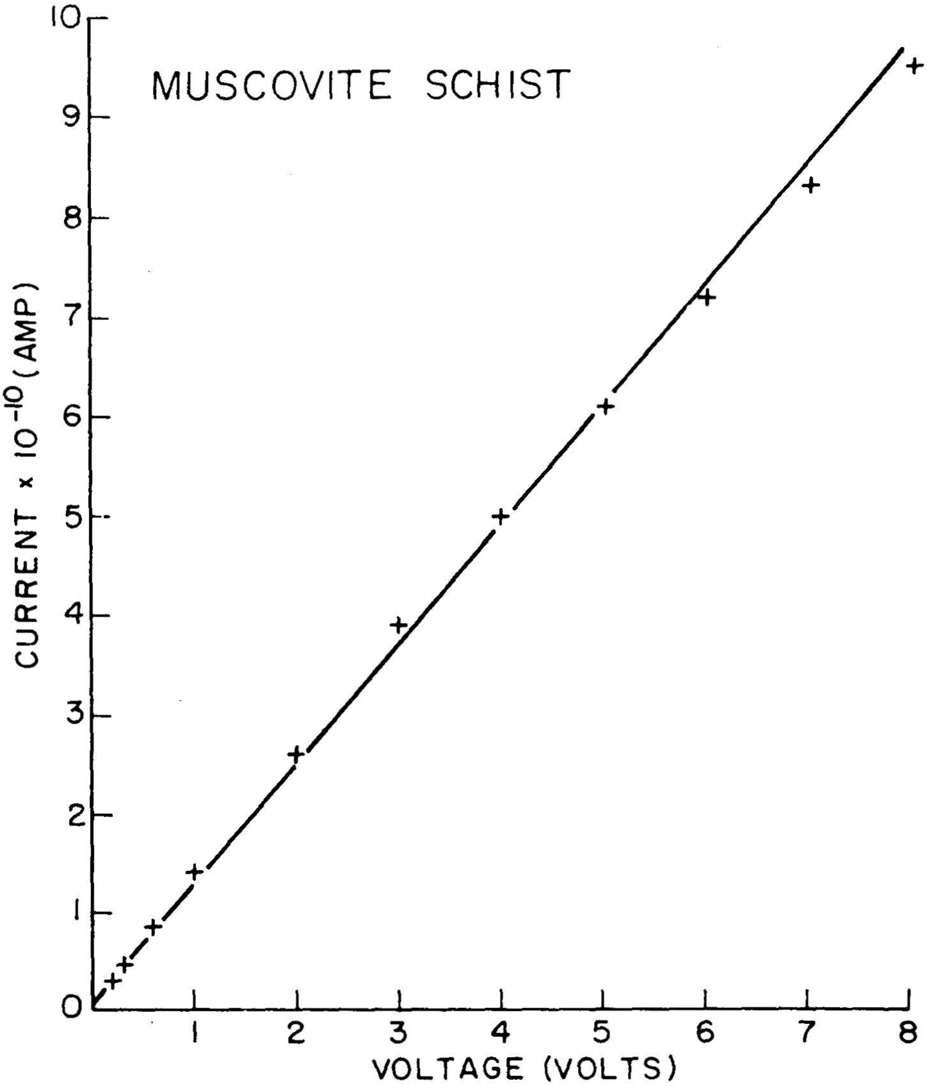


Figure 8. I-V plot of a muscovite schist sample showing linear behavior; a negative displacement from the orign is inferred.

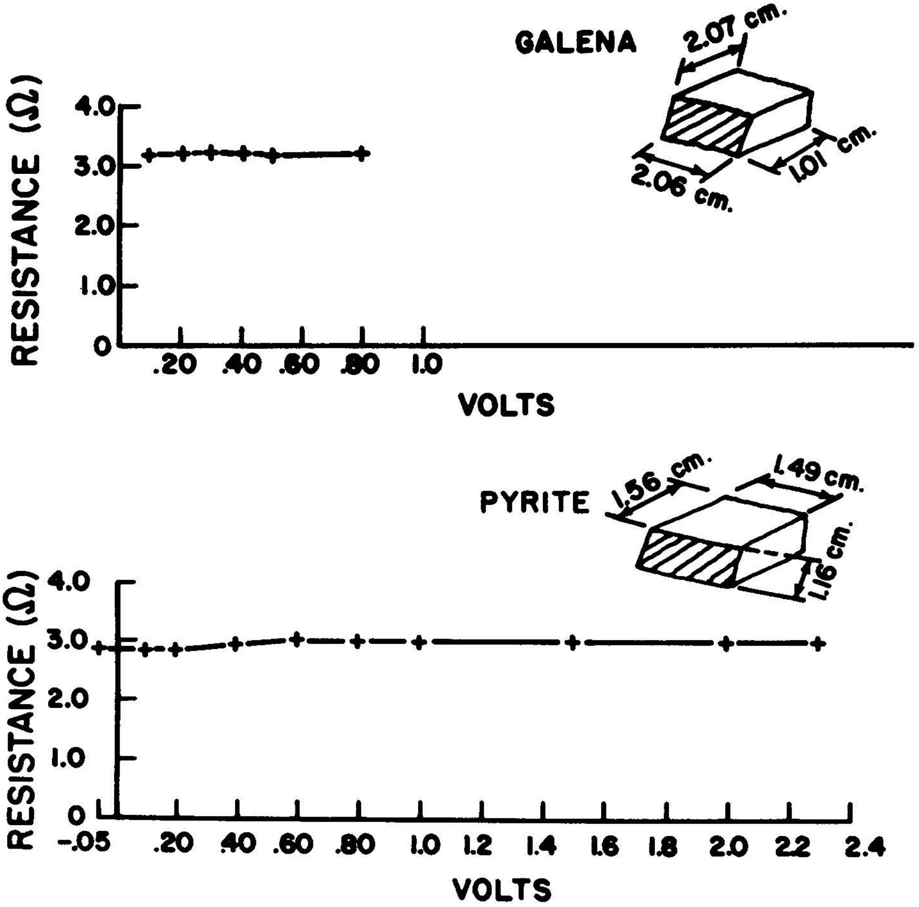


Figure 9. R-V responses of galena and pyrite. Both show linear behavior.

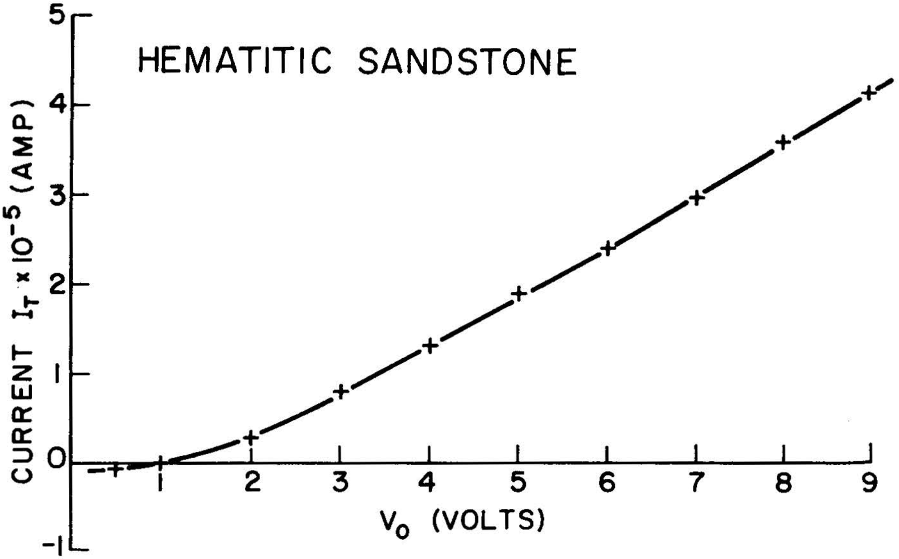


Figure 10. I-V characteristic of a hematitic sandstone sample showing a displacement of +1.0 volt from the origin. Non-linear behavior is shown below 3 volts, above this voltage the characteristic is linear.

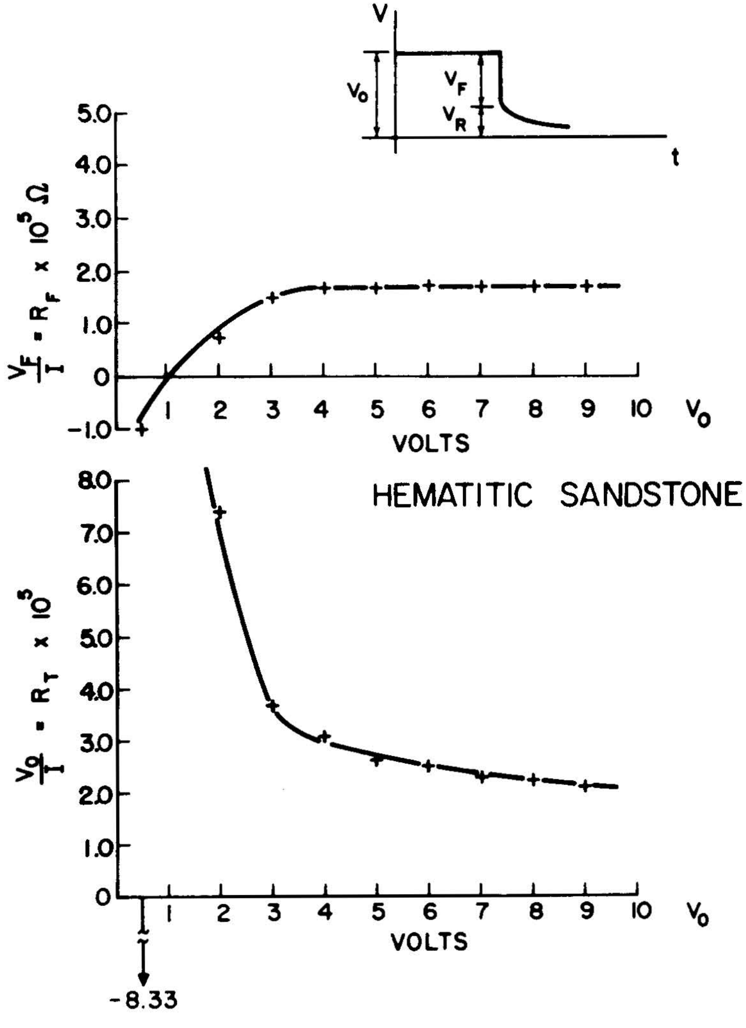


Figure 11a. Response of a resistive-type rock sample upon interruption of an externally applied voltage V_O; V_F and V_R are the magnitudes of the "fast" and "slow" decays. (b) Ratio of V_F to the total current in the hematitic sandstone sample of Figure 10, (c) Ratio of the total voltage to the total current in the same sample.

ACKNOWLEDGMENTS

The author acknowledges H. F. Morrison for criticisms and comments. Most of this work was carried out at the University of California, Berkeley.

BIBLIOGRAPHY

ALVAREZ, R., 1973a. Complex dielectric permittivity in rocks: a method for its measurement and analysis, *Geophysics,* No. 5, Vol. 38, 920.

ALVAREZ, R., 1973b. Effects of atmospheric moisture on rock resistivity, *Jour. Geophys. Res.,* No. 11, Vol. 78, 1979.

ANDERSON, L. A. and G. V. KELLER, 1964. A study in induced polarization, *Geophysics,* No. 5, Vol. 29, 848.

FRANK, R. I. and J. G. SIMMONS, 1967. Space-charge effects on emission-limited current flow in insulators, *Jours. Appl. Phys.,* No. 2, Vol. 38, 832.

KATSUBE, T J., R. H. AHRENS, and L. S. COLLET, 1973. Electrical nonlinear phenomena in rocks, *Geophysics,* No. 1, Vol. 38, 106.

KORYTA, J., J. DVORAK, and V. BOHACKOVA, 1970. *Electrochemistry,* Methuen, London. 350 pp.

MADDEN, T. R. and D. J. MARSHALL, 1959. Electrode and membrane polarization, *Report RME-3157,* U. S. Atomic Energy Commission, Washington, D. C. 115 pp.

McEUEN, R. B., J.W. BERG, Jr., and K. L. COOK, 1959. Electrical properties of synthetic metalliferous ore, *Geophysics,* No. 3, Vol. 24, 510

MOTT, N. F. and R. W. GURNEY, 1950. *Electronic processes in ionic crystals,* Clarendon Press, Oxford, 274 pp.

SCOTT, W. J. and G. f. WEST, 1969. Induced polarization of synthetic high-resistivity rocks containing disseminated sulphides, *Geophysics,* No. 1, Vol. 34, 87.

SHAUB, Yu. B., 1965. Use of the non-linear conductivity effect in rocks for electrical prospecting, *Izve. Phys. Solid Earth,* English ed., No. 6, 409.

SHAUB, Yu. B., 1969. On the uses of the effects of non-linear electrical conductivity in the detection of disseminated sulfide ores, *Izv. Phys. Solid Earth,* English ed., No. 1, 53.

SHAUB, Yu. B. and V. A. IVANOV, 1971. Experimental discrimination of sulfide ores and graphites by the use of the effects non-linear electrical conductivity, *Izv. Phys. Solid Earth,* English ed., No. 3, 222.

SIMMONS, J. G., 1971. DC *conduction in thin films,* Mills and Boom, London, 69 pp.