

# Impedance of black shale from Münsterland 1 borehole: an anomalously good conductor?

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## SUMMARY

Black shale containing about 5 per cent organic matter has very low electrical resistivity in comparison to shale which contains no organic matter. The low resistivity of the black shale is attributed to carbon, produced by pyrolysis reactions associated with diagenesis, located at grain boundaries in the black shale. Some conductivity anomalies in the Earth's crust and upper mantle may be caused by carbon produced in this manner.

**Key words:** black shale, carbon, conductivity, anomalies, electrical resistivity

## INTRODUCTION

The major rock-forming minerals are highly insulating. Quartz, probably the most common mineral in the crust, has an electrical resistivity that varies from more than  $10^{12} \Omega \text{ m}$  at the surface of the earth to as low as  $10^4 \Omega \text{ m}$  (Kronenberg & Kirby 1987) at the base of the crust, if we assume a temperature of around  $1000^\circ\text{C}$ . Similarly, for olivine and pyroxene, the major phases in the mantle, the resistivity measured at oxygen fugacities within the respective stability fields at  $1000^\circ\text{C}$  is only about  $10^3 \Omega \text{ m}$  (Duba *et al.* 1974; Huebner *et al.* 1979; Cemic *et al.* 1980). These high values for the resistivity of the major mineral constituents of Earth's crust and mantle require that the conductivity anomalies observed by field methods in the crust and upper mantle (Shankland & Ander 1983; Haak & Hutton 1986) must be caused by low-resistivity material at grain boundaries and in pore spaces. Low resistivity in the crust can be caused by a combination of temperature and a pore-fluid or grain-boundary phase composed of water and ions in solution (Olhoeft 1981). Similarly, low resistivity in the mantle can be produced by partial melt at grain boundaries (Shankland *et al.* 1981).

Based on arguments related to the low resistivity of oil shales resulting from grain-boundary carbon produced during pyrolysis, Duba & Shankland (1982) have suggested that some low-resistivity anomalies shallower than 150 km within the Earth could be attributed to a thin film of interconnected carbon at grain boundaries. In this paper we report the results of an investigation of the effects of carbon

at grain boundaries on the complex impedance, measured at frequencies between 17 and  $10^5 \text{ Hz}$ , of a black shale from a drill core at 5425 m depth. We also report measurements of electrical resistivity of this shale to temperatures slightly greater than  $400^\circ\text{C}$ .

## RESULTS

### Experimental

The rock selected for this study is a black shale from the Münsterland 1 borehole near Münster, West Germany. The borehole was completed to almost 6000 m in 1962 (Richwien *et al.* 1963). Our sample was from a depth of 5425 m, part of a rock sequence of lowermost Upper Carboniferous and Lower Carboniferous age, which is characterized by abundant black shales. The well logs show resistivities of 2–3  $\Omega \text{ m}$  in the interval where this sequence occurs (Wolburg 1963). This black shale sequence outcrops about 80 km SE of Münster and can be located in this region by self-potential measurements, geoelectrical surveys and other geophysical techniques that are sensitive to conductivity anomalies (Jödicke 1984).

These shales can be easily distinguished by their extremely black colour which is due to an organic carbon content of 5–8 per cent (Paproth 1986). No graphite was detected by X-ray studies of the samples we measured. Microscopic investigation of thin sections and polished sections under oil immersion revealed clumps of amorphous carbon together with finely dispersed carbonaceous material throughout the matrix.

The major portion of the organic matter in these shales originates from microscopic plankton, which were preserved

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in the sediment under anaerobic conditions during deposition and diagenesis. Only a portion of this material is visible as maceral 'bituminite'; the rest is sub-microscopic and either is absorbed at the surfaces of clay minerals or fills the interstices between grains (Clausen *et al.* 1982). Increasing diagenesis and metamorphism result in the coalification process, e.g. the prograde loss of hydrocarbons and, consequently, an increasing percentage of free carbon in the sediment. Optical reflectance of vitrinite particles indicates the meta-anthracite stage (about 300 °C) has been reached in the black shale at 5425 m depth in the Münsterland 1 borehole (Teichmüller *et al.* 1979). This study shows that the organic component of the shale consists of about 95 per cent carbon, 1.5 per cent hydrogen and 2 per cent volatiles. The bulk of the rock consists of ultra-fine-grained (cryptocrystalline) illite, with occasional thin silty or calcareous layers. Up to 11 per cent of the rock is pyrite which occurs as globular or framboidal pyrite (Love & Amstutz 1966; Schallreuter 1984) interspersed in the bedding planes and also forming small veinlets (Jödicke 1986).

In order to compare the complex resistivity of this black shale with that of a shale similar in composition except for carbon content, we selected a shale from 68 m depth in the Konzen drillhole, about 25 km SE of Aachen, West Germany. The sample is a silt-banded pelite with microscopic magnetite and about 3 vol. per cent pyrite visible on joints and foliation planes.

Complex resistivity measurements were made on right circular cylindrical samples 30 mm in diameter and 10 mm long in a simple parallel plate device at room temperature and at an electrode clamping pressure of about 1 MPa (10 bar). The samples were enclosed in shrink-fit tubes so that measurements could be performed in an evacuated and saturated state without disturbing the electrode-sample interface. Distilled water and 0.001 M KCl were used as the saturants.

Resistivity measurements to temperatures of about 420 °C were performed using the furnace and experimental assembly described in detail by Huenges & Will (1987). A brief description is given here. The sample, with cylindrical faces coated with a graphite paste, is held between platinum electrodes in a gas-tight tube through which an experimental atmosphere of a chosen gas or mixture of gases can flow.

Temperatures were measured with chromel–alumel thermocouples on both sides of the sample with an accuracy of about 3 °C. Resistivity was calculated from resistance measured with an accuracy of 1 per cent during heating and cooling cycles by an impedance bridge operating at a frequency of 1.6 kHz. At room temperatures in both experimental arrangements, the complex electrical impedance was measured, also with an accuracy of 1 per cent using a lock-in analyser and a potentiometer in a computer-controlled system. Data were collected over the frequency range 17–10<sup>5</sup> Hz. The system is equipped with the capability to go to frequencies as low as 10<sup>-5</sup> Hz using a Fast Fourier Transform method. After seeing that there was no significant change in either phase or resistance in the black shale measured at a vacuum of 1 kPa at frequencies between 17 and 10<sup>-4</sup> Hz, we decided not to spend the relatively long time required to collect data at frequencies below 17 Hz.

## RESULTS

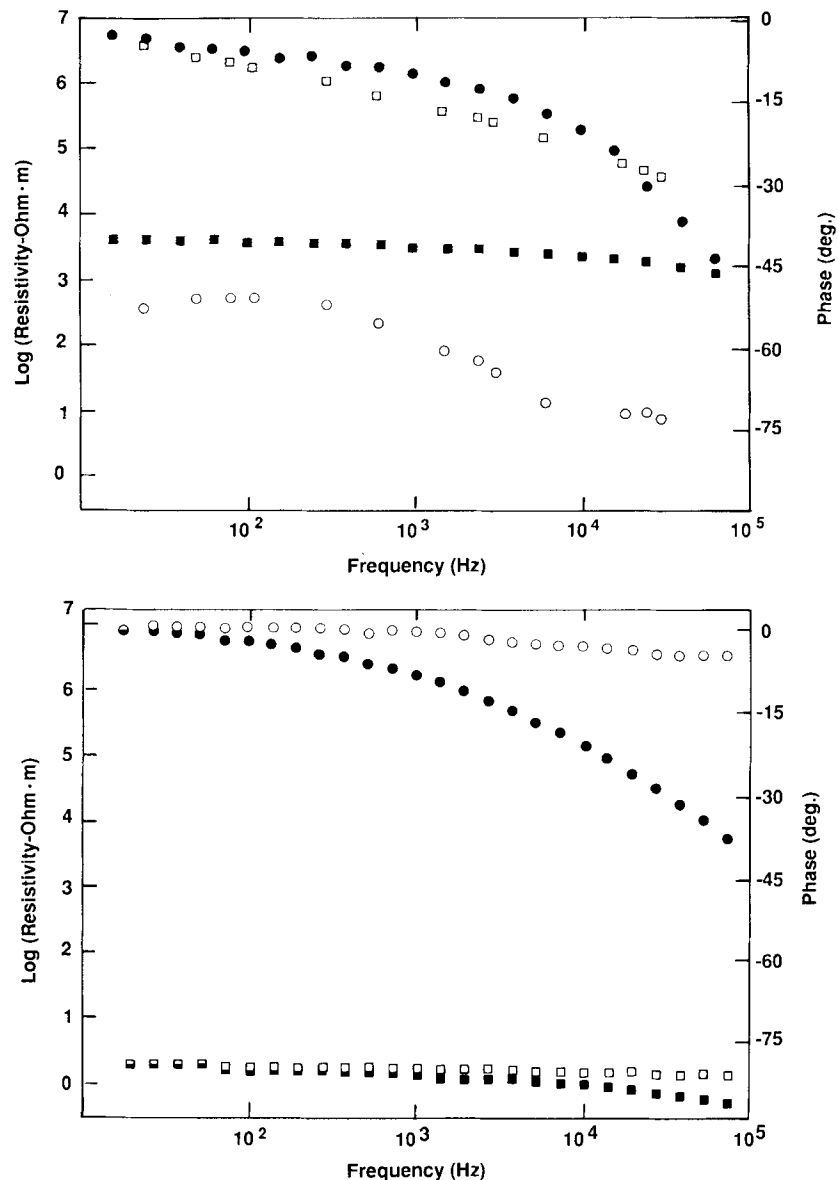
Figure 1(a) is a Bode plot of the complex resistivity of the Konzen shale from 68 m depth measured in a vacuum of 1 kPa and in distilled water. Saturation with distilled water decreases the resistivity by more than three orders of magnitude at 17 Hz. Also, the phase angle is dramatically decreased with water saturation of this shale. This behaviour in evacuated and saturated conditions is similar to that observed in other rocks at similar conditions (Olhoeft 1985; Duba *et al.* 1978).

Figure 1(b) is a Bode plot of the complex resistivity measured perpendicular to the bedding, of the black shale from 5425 m depth in the Münsterland 1 borehole. The scales for Figs 1(a) and (b) were chosen to allow easy comparison so that the dramatic difference in the properties of the two shales would be readily apparent. The resistivity of the 'dry' black shale is very low compared with 'dry' ordinary shale. Saturation with water has a very small effect on resistivity of this black shale, in contrast to that of normal shale. Also, the phase-shift increases when the black shale is saturated with water, whereas in normal shales the phase-shift decreases when they become saturated with water. The phase-shift at higher frequencies in water-saturated black shale is similar to that observed for the water-saturated Konzen shale, because the dielectric properties of water dominate at frequencies above a few kHz.

Figure 2 shows the resistivity of the Münsterland black shales measured parallel to the bedding in a vacuum of 1 kPa and saturated with distilled water. The resistivity and phase variation with frequency are similar to those measured perpendicular to the bedding as is shown in Fig 1(b). Fig. 3 shows the temperature-dependence of the resistivity of the sample measured at a frequency of 1.6 kHz in air at a heating rate of 0.1 °C min<sup>-1</sup>, except for the first heating cycle to 150 °C, which was at a heating rate of 1 °C min<sup>-1</sup>, and a cooling rate that varied from about 4 °C min<sup>-1</sup> at 400 °C to about 1 °C min<sup>-1</sup> at 200 °C. Using the temperature dependence of resistivity and assuming a Boltzmann relationship, we have calculated activation energies for each line segment in Fig. 3 and tabulated them in Table 1.

Data for the heating cycles to 150 °C and 250 °C are shown in the insert to Fig. 3 at a much enlarged resistivity scale so that the low activation energies may be appreciated. During the first heating to 150 °C, the resistivity decreased about 0.06 log units after 3 hr at 150 °C. It returned to the original value at 60 °C upon resaturation with air at about 50 per cent relative humidity. The sample was then heated to 250 °C and, upon cooling from this temperature, the resistivity measured at 60 °C had decreased by about 0.1 log units.

Upon heating to temperatures of 320 °C, the sample experienced an increase in resistivity of almost an order of magnitude. As Table 1 shows, the activation energy calculated for all these heating and cooling cycles, up to and including the 320 °C cycle, varies between 0.01 and 0.04 eV. The final heating cycle was to a temperature of 417 °C, in which the temperature was held constant for 24 hr. At temperatures greater than about 280 °C, the resistivity values are slightly greater than those measured on the



**Figure 1.** (a) Resistivity and phase as a function of frequency for Konzen shale measured perpendicular to bedding. (b) Resistivity and phase as a function of frequency for Münsterland black shale measured perpendicular to bedding:  $\square$ , resistivity scale;  $\circ$ , phase scale; open symbols, measurements in a vacuum of 1 kPa; closed symbols, measurements in distilled water.

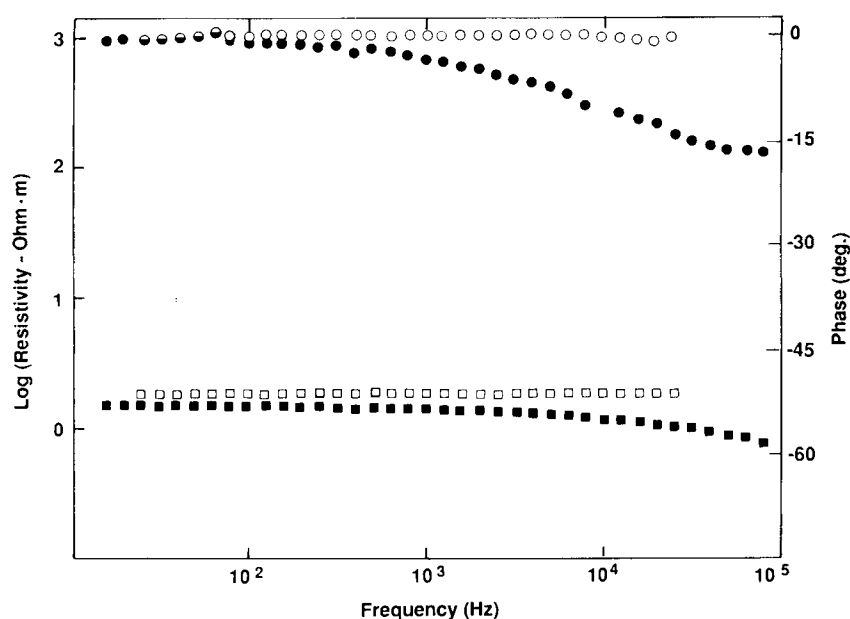
previous cooling cycle. At higher temperatures, this increase in resistivity is even more apparent. The resistivity increased more than three orders magnitude in 24 hr while temperature was maintained constant at 417°C. Following this time period, the sample was cooled to room temperature. From these data, measured upon cooling, activation energies of 0.65, 0.46, and 0.31 eV are calculated.

Figure 4 is a Bode plot of the complex electrical resistivity of the black shale after it has been heated to 417°C. Measurements were made on the sample in a vacuum of 1 kPa, saturated with distilled water, and saturated with 0.001 M KCl. Measured in the vacuum, the laboratory-metamorphosed black shale is slightly less resistive than the shale from the 68 m interval of the Konzen borehole at low frequencies (see Fig. 1a). At higher frequencies, however, the difference increases and the laboratory-metamorphosed

sample is almost two orders lower in resistivity at  $10^5$  Hz than the normal shale. More astounding, however, are the results when the laboratory-metamorphosed black shale is saturated with distilled water. Its resistivity is about two orders of magnitude lower at any frequency than a normal shale saturated with distilled water, and is only five times more resistive than black shale, when saturated with distilled water, prior to the high-temperature event. The sample was a rose-pink after heating. Upon breaking it in half, we observed that the rose-pink colour persisted to a depth of between 2 and 3 mm, then the sample was black throughout.

## DISCUSSION AND CONCLUSIONS

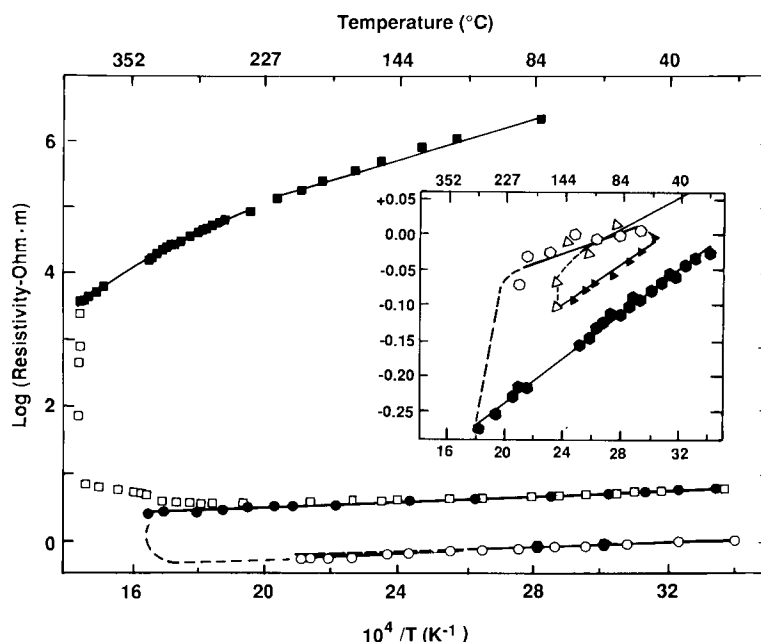
Figures 1(a) and (b) indicate that the black shale is a much better conductor than the shale from Konzen. Except for



**Figure 2.** Resistivity and phase as a function of frequency for Münsterland black shale measured parallel to bedding:  $\square$ , resistivity scale;  $\circ$ , phase scale; open symbols, measurements in a vacuum of 1 kPa; closed symbols, measurements in distilled water.

pyrite and carbon contents, both shales have similar compositions. Unlike normal shales, the resistivity of the black shale is affected very little by water saturation. However, when both shales are saturated, the phase-shift with frequency is similar—an indication that the slight frequency-dependence of the resistivity of black shale is due to water.

The very small frequency-dependence of resistivity of the black shale, either in the evacuated or water-saturated condition, with respect to that of a normal shale measured in our laboratory under the same conditions and in the same apparatus (Fig. 1), is an indication that conduction in the black shale is controlled by an interconnected phase whose conduction is practically frequency-independent. Both



**Figure 3.** Temperature-dependence of resistivity of Münsterland black shale at 1.6 kHz. Open symbols are data from heating cycles; closed symbols are data from cooling cycles. Solid lines are fits to the data and were used to calculate the activation energies given in Table 1. The inset is an enlarged-scale plot of the resistivity measurements made on initial heating to 150 and 250 °C. Cooling from 250 °C (bottom line of inset) is coincident with heating to 320 °C (bottom line of main figure). Symbols refer to measurements made to maximum temperatures in the following order:  $\Delta$ , 150 °C;  $\circ$ , 250 °C;  $\diamond$ , 320 °C;  $\square$ , 417 °C.

**Table 1.** Activation energies determined for Münsterland black shale. Numbers in parentheses denote standard deviations of fits to the data

Heating		Cooling	
Temperature range (°C)	Activation energy (eV)	Temperature range (°C)	Activation energy (eV)
25–150	0.02 (1)	150–60	0.03 (2)
60–200	0.01 (2)	250–25	0.03 (2)
25–250	0.04 (1)	320–25	0.04 (1)
25–250	0.03 (1)	417–313	0.65 (7)
		313–327	0.46 (9)
		237–84	0.31 (4)

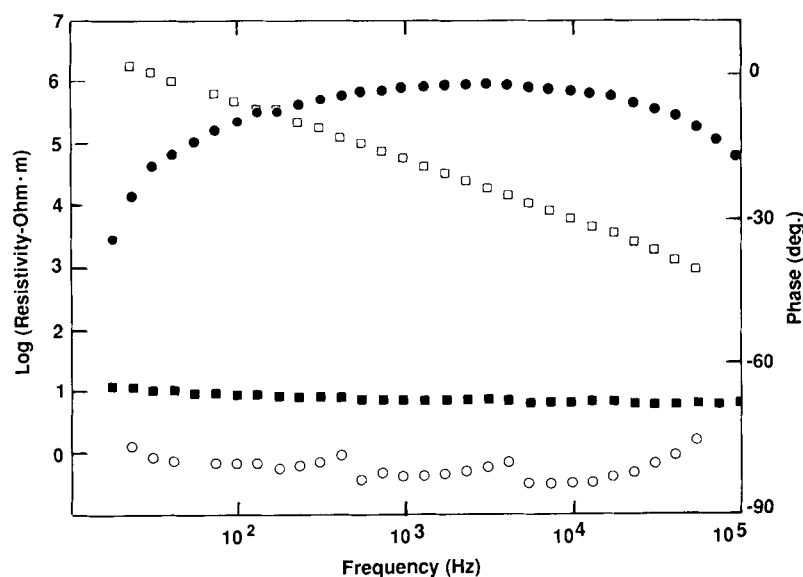
carbon and pyrite can serve as such a phase. Olhoeft (1985), for example, reports similar low resistivities (no more than an order of magnitude greater than that of the black shale of Fig. 1b) and low-frequency variation of phase and resistivity in this frequency range for a saturated sandstone containing carbonaceous matter and another containing pyrite. Rocks whose conductivity is controlled by pyrite have a maximum in phase angle at about 100 Hz (Mahan *et al.* 1986; Pelton *et al.* 1978), whereas those whose conductivity is controlled by carbon have a minimum in phase angle at  $\sim 100$  Hz (Pelton *et al.* 1978). Figs 1(b) and 2 show no detectable variation in phase near 100 Hz. Therefore the heating of the black shale sample in air, as shown in Fig. 3, was designed to measure activation energy to compare with values for carbon and pyrite in the literature. The activation energies obtained in Table 1 for the sample when heated to final temperatures of less than or equal to 320 °C are 0.04 eV or less. Such low activation energies are associated with carbon at grain boundaries (Devenyi *et al.* 1971; Duba & Shankland 1982) and are two to ten times lower than those measured for pyrite (Krivoshein *et al.* 1980).

Another clue to the phase responsible for the low resistivity is the order-of-magnitude increase in resistivity observed after almost 12 hr at 320 °C, as shown in Fig. 3. This increase is not caused by a phase change in pyrite

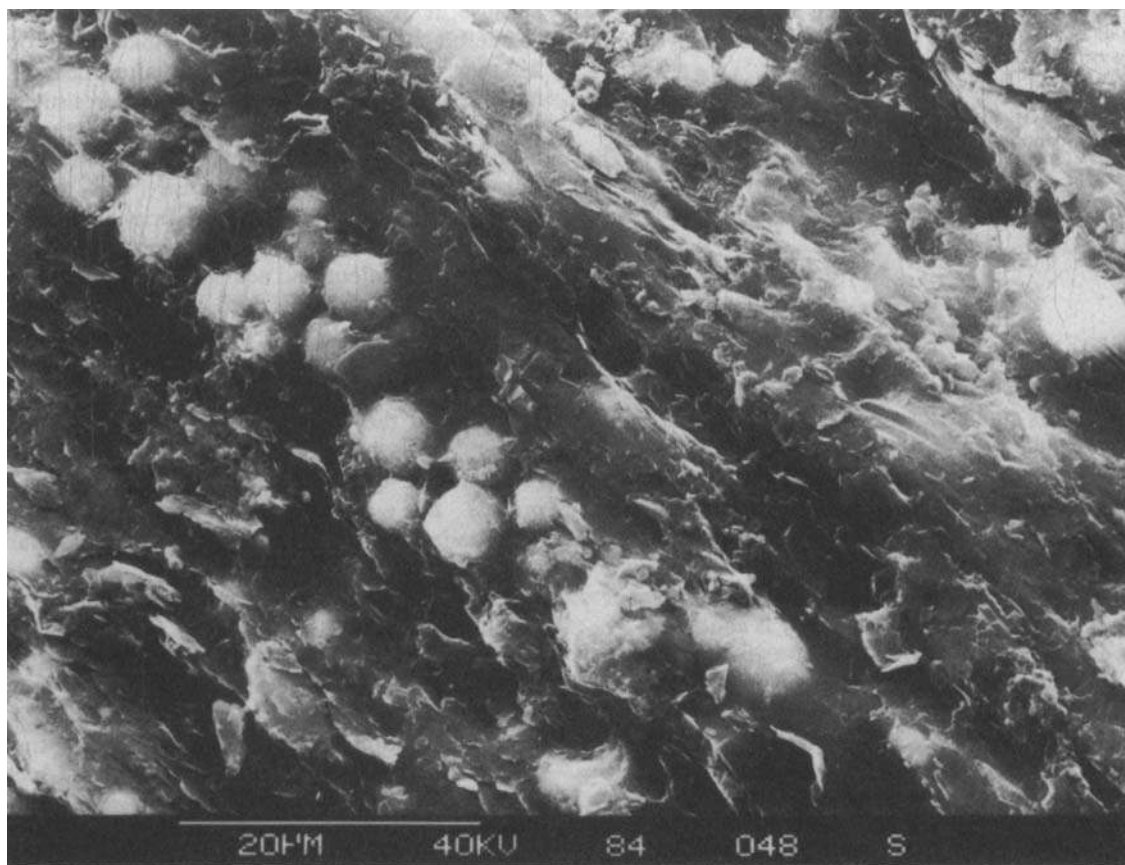
because it is stable to 743 °C at atmospheric pressure (Kullerud & Yoder 1959). The pink colour of the outer 2–3 mm of the sample observed after heating to 417 °C indicates that the observed increase in resistivity is due to oxidation of the carbon. X-ray studies of the sample after heating to 417 °C indicate that the pyrite content is not substantially changed. Because of the frequency-independent nature of the resistivity, the low activation energies, the decrease in conductivity with time at 320 °C, the change in colour and activation energy after heating to a temperature of 417 °C, and the petrography discussed below, we conclude that the low resistivity of this black shale is caused by carbon at grain boundaries, as first proposed by Jödicke (1984). We believe the low electrical resistivity of the black shale is the result of carbonaceous matter that has reached the meta-anthracite stage (Teichmüller & Teichmüller 1981). The same ordering process that causes optical reflectance anisotropy is hypothesized to decrease the resistivity of the carbonaceous matter, in general accordance with the dependence of resistivity on the carbon content of coals (Parkhomenko 1967).

Although the thin films of carbonaceous matter on the grain boundaries are not accessible to view in either optical or electron microscopes because of their small thickness after coalification, our results indicate that they form an efficient electrical network throughout the rock. Jödicke (1985) has suggested that the order of graphitoid complexes is higher in thin carbonaceous films along grain boundaries than it is in large carbon particles in the matrix because the former have been subjected to relatively greater shear stresses during lithification.

Such a process would also contribute to lower resistivity in these rocks. However, pyrite, which is also a good conductor with a resistivity as low as  $5 \times 10^{-5} \Omega \text{ m}$  (Parasnis 1956), does not contribute to the low resistivity directly because there is no continuous contact between the spheres (Fig. 5). Furthermore, because of the layered formation of



**Figure 4.** Resistivity and phase as a function of frequency for the Münsterland black shale after heating in air to 417 °C:  $\square$ , resistivity scale;  $\circ$ , phase scale; open symbols, measurements in a vacuum of 1 kPa; closed symbols, measurements in distilled water.



**Figure 5.** Electron micrograph of the Münsterland 1 black shale. Spheres are framboidal pyrite.

the framboidal pyrite, a strong anisotropy of resistivity should occur. That, however, was not the case, as shown by a comparison of the resistivity of the black shale measured parallel to bedding (Fig. 1b) and that measured perpendicular to bedding (Fig. 2). X-ray studies, after a chemical analysis using acid solution techniques, indicated that pyrite persisted in the organic matter, which is resistant to solution. Because pyrite should have dissolved in the acid mixture of 3 vol per cent HCl and 1 vol per cent HNO<sub>3</sub> used in this process, we assume it has a protective organic coating which serves to link these highly conducting spheres together. However, as electrical conductivity measurements on oil shale (Duba 1983) and carbonaceous chondrite meteorites (Duba & Boland 1984) indicate, grain-boundary carbon is sufficient to cause high conductivity. Pyrite crystals in the matrix enhance the overall conductivity of the black shale because the carbon serves to connect them together.

The high conductivity of this shale has implications for Earth's crust and upper mantle. Field measurements have characterized many zones in the crust and mantle as having low resistivity. Many places exist where the presence of carbon-bearing sediments is known or is possible. We believe that many such sediments will probably end up becoming good conductors as a result of pyrolysis reactions during diagenesis. The major requirement to drive such reactions is temperature, since there are geological situations where the pressure varies from a few bars, in the case of contact metamorphism of a carbonaceous body (Teichmüller *et al.* 1979), to as much as 200 mPa, for the

Münsterland black shale. Because light hydrocarbons are driven off in this process, the discovery of high-conductivity anomalies in the crust is a reason to consider further geophysical investigations of the shallower crust to determine whether the light hydrocarbons lost during diagenesis of the sediments have been trapped in overlying strata. In addition, diagenetic and metamorphic process that proceed deeper in the crust and mantle probably could also produce good conductors from carbonaceous material. The suggestion that some upper-mantle conductivity anomalies could be the result of carbon at grain boundaries (Duba & Shankland 1982) seems more probable in view of the measurements reported in this study.

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